# Shielding of Electron Acceptors Coordinated to Rhenium(I) by Carboxylato Groups. Intraligand and Charge-Transfer Excited-State Properties of *fac*-('Anthraquinone-2-carboxylato')(2,2′-bipyridine)tricarbonylrhenium (*fac*-[$\mathrm{Re^I(aq\text{-}2\text{-}CO_2)(2,2'\text{-}bipy)(CO)_3}$])

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The photophysical and photochemical properties of (*OC*-6-33)-(2,2′-bipyridine-$\kappa N^1,\kappa N^{1'}$)tricarbonyl(9,10-dihydro-9,10-dioxoanthracene-2-carboxylato-$\kappa$O)rhenium (*fac*-[$\mathrm{Re^I(aq\text{-}2\text{-}CO_2)(2,2'\text{-}bipy)(CO)_3}$]) were investigated and compared to those of the free ligand 9,10-dihydro-9,10-dioxoanthracene-2-carboxylate (=anthraquinone-2-carboxylate) and other carboxylato complexes containing the (2,2′-bipyridine)tricarbonylrhenium ([$\mathrm{Re(2,2'\text{-}bipy)(CO)_3}$]) moiety. Flash and steady-state irradiations of the anthraquinone-derived ligand ($\lambda_{\mathrm{exc}}$ 337 or 351 nm) and of its complex reveal that the photophysics of the latter is dominated by processes initiated in the Re-to-(2,2′-bipyridine) charge-transfer excited state and 2,2′-bipyridine- and (anthraquinone-2-carboxylato)-centered intraligand excited states. In the reductive quenching by *N*,*N*-diethylethanamine (TEA) or 2,2′,2″-nitrilotris[ethanol] TEOA, the reactive states are the 2,2′-bipyridine-centered and/or the charge-transfer excited states. The species with a reduced anthraquinone moiety is formed by the following intramolecular electron transfer, after the redox quenching of the excited state:

$$[\mathrm{Re^I(aq-2-CO_2)(2,2'\text{-}bipy^{\bullet})(CO)_3}]^- \rightleftharpoons [\mathrm{Re^I(aq-2-CO_2{}^{\bullet})(2,2'\text{-}bipy)(CO)_3}]^-$$

The photophysics, particularly the absence of a $\mathrm{Re^I}$-to-anthraquinone charge-transfer excited state photochemistry, is discussed in terms of the electrochemical and photochemical results.

**Introduction.** – The substitution of a halide ligand X by the spectator ligand $\mathrm{L_S}$ in [$\mathrm{Re^IXL_A(CO)_3}$], where $\mathrm{L_A}$ is a bis(monodentated azine) or a bidentate azine[1]), has provided useful procedures for the preparation of related [$\mathrm{Re^IL_SL_A(CO)_3}$] complexes [1–7]. Interest in the properties that $\mathrm{L_S}$ imposes on the $-\mathrm{Re^IL_A(CO)_3}$ moiety is brought about by possible applications of the Re complexes to biochemical processes [8–11] and to $\mathrm{CO_2}$ reduction [12]. Also, the derivatization of polymers with chromophores, *e.g.*, with pendant $-\mathrm{Re^IL_A(CO)_3}$ groups [13] has prompted investigation of the role of $\mathrm{L_S}$ in the reactivity of some $\mathrm{Re^I}$ monomers [14]. Literature reports show, for example, that the function of $\mathrm{L_S}$ is to exert small perturbations that alter the electronic structure of the chromophore and modify its photophysics [6]. In the other extreme of a strong electronic interaction between $\mathrm{L_S}$ and the $\mathrm{Re^I}$ chromophore, the spectator ligand can participate in redox processes similar to those of $\mathrm{L_A}$. Indeed, competitive electron transfer to $\mathrm{L_A}$ and $\mathrm{L_S}$ has been observed in the ground and excited

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[1]) Abbreviations used in this work: 2,2′-bipyridine, 2,2′-bipy; 2,2′-biquinoline, 2,2′-biq; pyrazine, pz; 2,2′,2″-nitrilotris[ethanol], TEOA; *N*,*N*-diethylethanamine (=triethylamine), TEA; 4-nitrobenzoato, $\mathrm{NO_2Bz}$; pyrazine-2-carboxylato, pz-2-$\mathrm{CO_2}$; 9,10-dihydro-9,10-dioxoanthracene-2-carboxylato (=anthraquinone-2-carboxylato), aq-2-$\mathrm{CO_2}$; Re-to-X charge-transfer excited state, $\mathrm{MLCT_{X\leftarrow Re}}$; intraligand excited state, IL.

states of $[Re^I(4\text{-nitrobenzoato})L_A(CO)_3]$ ($L_A$ = 1,10-phenanthroline, 2,2′-bipyridine, and (4-phenylpyridine)$_2$). For example, the reduction of the complexes by $^{\bullet}CH_2OH$ radicals [7] is followed by an equilibration between species of $Re^I$ with coordinated ligand-radicals, (*Eqns. 1* and *2*).

$$[Re^I(4\text{-}O_2N-C_6H_4-CO_2)L_A(CO)_3] + {}^{\bullet}CH_2OH \rightarrow$$
$$[Re^I(4\text{-}O_2N-C_6H_4-CO_2{}^{\bullet})L_A(CO)_3]^- + CH_2O + H^+ \quad (1)$$

$$[Re^I(4\text{-}O_2N-C_6H_4-CO_2{}^{\bullet})L_A(CO)_3]^- \rightleftharpoons [Re^I(4\text{-}O_2N-C_6H_4-CO_2)(L_A{}^{\bullet})(CO)_3]^- \quad (2)$$

In contrast to the ground-state reactions, a $Re^I$-to-(4-nitrobenzoato) ($NO_2Bz$) charge-transfer excited state, $MLCT_{NO_2Bz\leftarrow Re}$, is produced by a complex photochemical mechanism (*Eqns. 3–5*): photogeneration of a Re-to-(azine ligand) charge-transfer excited state, $MLCT_{azine\leftarrow Re}$, and its equilibration with an intraligand excited state, IL, precedes the formation of the $MLCT_{NO_2Bz\leftarrow Re}$.

$$[Re^I(4\text{-}O_2N-C_6H_4-CO_2)(azine)(CO)_3] + h\nu \rightarrow MLCT_{azine\leftarrow Re} \quad (3)$$

$$MLCT_{azine\leftarrow Re} \rightleftarrows IL \quad (4)$$

$$IL \rightarrow MLCT_{NO_2Bz\leftarrow 1\ Re} \quad (5)$$

The photophysical and photochemical properties of $[Re^I(NO_2Bz)L_A(CO)_3]$ [7] and $[Re^I(pz\text{-}2\text{-}CO_2)(2,2'\text{-bipy})(CO)_3]$ ((2,2-bipyridine)tricarbonyl(pyrazine-2-carboxylato)rhenium) [14] have strongly suggested that the carboxylato group electronically insulates the $Re^I$ chromophore from the pendant 4-nitrophenyl and pyrazine moieties. In this work, we have studied the photophysics and redox reactivity of the 9,10-dihydro-9,10-dioxoanthracene-2-carboxylate x(=anthraquinone-2-carboxylate; aq-2-$CO_2$) and its complex $[Re^I(aq\text{-}2\text{-}CO_2)(2,2'\text{-bipy})(CO)_3]$, to learn how such insulation by the carboxylato group of the ligand affects photoreactions initiated in $Re^I$-to-$L_A$ and $Re^I$-to-$L_S$ charge-transfer excited states MLCT and intraligand excited states IL.

**Experimental.** – *Flash-Photochemical Procedures.* Optical-density changes occurring on a time scale longer than 10 ns were investigated with a flash-photolysis apparatus (FP) by procedures described elsewhere [14][15]. In these experiments, 10-ns flashes of 351-nm light were generated with a *Lambda-Physik SLL-200* excimer laser, or 1-ns flashes of 355-nm light were generated with a *Continuum-Powerlite* Nd-YAG laser [14–16]. The energy of the laser flash was attenuated to values equal to or less than 20 mJ/pulse by absorbing some of the laser light in solns. of $Ni(ClO_4)_2$ with appropriate optical densities. Time-resolved fluorescence experiments (FF) were carried out with a *PTI* flash-fluorescence instrument. The excitation light was provided by a $N_2$ laser with a 0.2 ns pulse width and *ca.* 2 mJ/pulse. Solns. for the photochemical work were deaerated with streams of ultrahigh-purity $N_2$ before and during the irradiations. Concentrations of the photolytes were adjusted to provide homogeneous concentrations of photogenerated intermediates within the volume of irradiated soln.

*Steady-State Irradiations.* The luminescence of the $Re^I$ complexes was investigated in an *SLM-Aminco 8100* interfaced to a *Dell 333P* microcomputer [6]. The spectra were corrected for differences in instrumental response and light scattering. Solns. were deaerated with $O_2$-free $N_2$ in a gas-tight apparatus before recording the spectra.

*Electrochemical Procedures.* The apparatus and procedures used in electrochemical experiments have been described elsewhere [14]. In addition, ac voltammograms were recorded with an exciting amplitude of 1.6 $mV_{rms}$/11 Hz and a sweep rate of 3 $mV\,s^{-1}$. The dc voltammograms were obtained with a conventional computerized set-up. MeCN for spectroscopy (*Merck Uvasol*) was dried over activated alumina for several days. The procedure was found to be suitable for electrochemistry in the $-2.0/+1.0$ V (*vs.* SCE) potential range. $(Bu_4N)PF_6$ was dried at 110° for at least 24 h. Pt and Au discs (*ca.* 6 mm i.d.) were used as working electrodes. The surfaces of the disks were polished to a mirror finish. Potentials were measured against the Ag/AgCl electrode ($-60$ mV *vs.* SCE). The accuracy of the measurement was verified in some experiments with the $Fc/Fc^+$ couple as an internal reference. A Pt mesh, separated from the main compartment by a porous disc, was used as a counter electrode. In the working electrode, a fresh surface was generated before each experiment by polishing it to a mirror finish with alumina (particle size equal to or less than 0.05 μm). It was then rinsed with *Millipore Milli-Q* water, sonicated, and dried before placing the electrode in the soln. The quality of the surface and the electrode performance were tested by briefly cycling the working electrode in a soln. of the supporting electrolyte. Solns. were prepared with anal.-grade reagents. Solns. were deaerated for 30 min with streams of dry $N_2$.

*Spectroelectrochemical Measurements.* Differential spectra were obtained *in situ* at an angle of incidence of 45° with a VIS reflectance spectrometer that makes use of potential modulation [17][18]. In the technique, a low-stray-light spectrometer focusses the light into the electrode at an angle of 45°. The electrode and the light were modulated at 11 Hz. The ensuing changes in the reflected intensity, an ac signal $\Delta R$, were sensed with a photomultiplier. The output was rectified by a lock-in amplifier. The recorded spectrum is, unless stated otherwise, the normalized difference between the optical response at a given potential against that at a potential taken as reference, $R_{ref}$, *i.e.*, $\Delta R/R_{ref} = (R - R_{ref})/R_{ref}$ *vs.* wavelength. The technique has been described in detail elsewhere [18].

*Materials. Silver 9,10-Dihydro-9,10-dioxoanthracene-2-carboxylate* ($Ag(C_{15}H_7O_4)$). An aq. soln. of 9,10-dihydro-9,10-dioxoanthracene-2-carboxylic acid was neutralized by addition of $KHCO_3$. The silver salt was precipitated from the previous soln. by the addition of a stoichiometric amount of $AgNO_3$ dissolved in a minimum amount of $H_2O$.

*(*OC*-6-33)-(2,2′-Bipyridine-κ*N*¹,κ*N*¹′)tricarbonyl(9,10-dihydro-9,10-dioxoanthracene-2-carboxylato-κ*O*)-rhenium* (*fac*-$[Re^I(aq\text{-}2\text{-}CO_2)(2,2'\text{-bipy})(CO)_3]$) was prepared by a modification of literature procedures [1–6][19][20]. $[ReBr(2,2'\text{-bipy})(CO)_3]$ and $Ag(C_{15}H_7O_4)$ were dissolved in a 1:1 molar relation in $CH_2Cl_2$ (100 ml), and the soln. was refluxed overnight. This soln. and a solid containing the $Re^I$ product and AgBr were placed in a *Soxhlet* extraction apparatus, and the $Re^I$ product was separated by this procedure from the solid AgBr. Several recrystallizations were performed by slow addition of isooctane to a conc. soln. of the complex in $CH_2Cl_2$. Two or three of these recrystallizations were repeated until the extinction coefficient remained constant. Anal calc. for $C_{18}H_{11}N_4O_5Re$: C 49.55, H 2.23, N 4.13; found: C 49.33, H 2.22, N 4.19.

The starting material $[ReBr(2,2'\text{-bipy})(CO)_3]$ was available from previous work [2][5][7]. Other materials were reagent grade and used without further purification.

**Results and Discussion.** – Chemical properties of $[Re^I(aq\text{-}2\text{-}CO_2)(2,2'\text{-bipy})(CO)_3]$ were investigated to rationalize the various roles of the ligand-centered and charge-transfer excited states that can be simultaneously activated in the photochemistry and photophysics of $[Re^IX(2,2'\text{-bipy})(CO)_3]$.

*Electrochemical Measurements.* The ac voltammogram of $2.0 \cdot 10^{-4}$ M $[Re^I(aq\text{-}2\text{-}CO_2)(2,2'\text{-bipy})(CO)_3]$ in deaerated MeCN exhibited peaks at $-0.79$, $-1.21$, and $-1.33$ V *vs.* AgCl/Ag corresponding to the successive and reversible addition of three electrons. An additional peak was observed at 1.42 V *vs.* AgCl/Ag, and it was assigned to the $Re^{II}/Re^I$ couple by comparison to the potential of the same couple in related $Re^I$ complexes [2][14]. Under similar conditions, $2.0 \cdot 10^{-4}$ M $[Re^IBr(2,2'\text{-bipy})(CO)_3]$ exhibited two reduction peaks at $-1.26$ and $-1.46$ V *vs.* AgCl/Ag that correlate with two of those seen in the ac voltammogram of $[Re^I(aq\text{-}2\text{-}CO_2)(2,2'\text{-bipy})(CO)_3]$. These peaks can be assigned to the reduction of coordinated 2,2′-bipy. Two peaks, $-0.93$ and $-1.39$ V *vs.* AgCl/Ag, in the ac voltammogram of $1.0 \cdot 10^{-4}$ M free ligand aq-2-$CO_2H$ in

MeCN corresponded to the successive addition of two electrons. Cyclic voltammetry of the aq-2-$CO_2H$ solution showed two reversible waves, each of them corresponding to a one-electron reduction, at the same potentials found in the ac voltammogram. The results of the electrochemical measurements and those of relevant species are shown in *Table 1.*

Table 1. *Electrochemical Potentials* vs. *the NHE for Re$^I$ Complexes and Relevant Ligands*

| | $E^0$/V *vs.* NHE | | | |
|---|---|---|---|---|
| | + 3e | + 2e | + 1e | − 1e |
| [ReBr(2,2′-bipy)$(CO)_3$][a]) | | − 1.388 | − 1.105 | |
| [Re(2,2′-biq)$(CO)_3$pz]$^{+}$[b]) [14] | − 0.98 | − 0.64 | − 0.49 | + 1.70 |
| [Re(4,4′-bipy)(2,2′-biq)$(CO)_3$]$^{+}$[b]) | − 0.99 | − 0.67 | − 0.50 | + 1.44 |
| [Re(pz-2-$CO_2$)(2,2′-bipy)$(CO)_3$][b]) | − 1.96 | − 1.66 | − 1.09 | + 1.57 |
| [Re(aq-2-$O_2C$)(2,2′-bipy)$(CO)_3$][a]) | − 1.174 | − 1.051 | − 0.636 | + 1.612 |
| 2,2′-biq[b]) [1] | | | − 0.70 | |
| 4,4′-bipy[b]) [21] | | | − 0.49 | |
| pz[b])[c]) [27] | | | $-0.01 \geq E^0 \geq -0.645$ | |
| 2,2′-bipy[b])[d]) [21] | | | − 0.50 | |
| aq-2-$CO_2H$[a]) | | − 1.213 | − 0.757 | |

[a]) Experimental values recorded *vs.* a AgCl/Ag reference electrode. [b]) Experimental values recorded *vs.* a SCE reference electrode. [c]) Potentials reported in aqueous solutions for various acid concentrations, $0 \leq pH \leq 6.8$. [d]) Diprotonated cation. The reduction of the monoprotonated cation is estimated to be displaced between − 0.5 and − 1.0 V from the diprotonated cation.

Spectroelectrochemical experiments were designed for a study of the species generated in the respective one-electron reductions of aq-2-$CO_2H$ and [Re$^I$Br(2,2′-bipy)$(CO)_3$]. The *in situ* differential reflectance spectrum of *Fig. 1,a*, was recorded with a $5.6 \cdot 10^{-4}$ M aq-2-$CO_2H$ solution in 0.1M $(Bu_4N)PF_6$. A potential modulation between $E_{ref} = -0.66$ V and $E = -1.16$ V corresponds to $\Delta OD \approx \Delta R/R = [R_{-1.16} - R_{-0.66}]/R_{-0.66}$. The reflectance spectrum of *Fig. 1,b*, was recorded with $3.6 \cdot 10^{-4}$ M [Re$^I$Br(2,2′-bipy)$(CO)_3$] in 0.1M $(Bu_4N)PF_6$. In this experiment, potential modulation was between $E = -1.86$ V and $E_{ref} = -1.16$ V, *i.e.*, $\Delta OD \approx \Delta R/R = [R_{-1.86}\text{-}R_{-1.16}]/R_{-1.16}$. The spectrum in *Fig. 1,a*, was assigned to the spectrum of the semiquinone radical, aq-2-$CO_2H^{\bullet -}$. In *Fig. 1,b*, the spectrum recorded at a potential where the first electron adds to [Re$^I$Br(2,2′-bipy)$(CO)_3$] (*Table 1*) can be assigned to [Re$^I$Br$(CO)_3$(2,2′-bpy$^\bullet$)]$^-$. These assignments agree well with results of photochemical experiments discussed below and can be used as the basis to credit the reduction of [Re$^I$(aq-2-$CO_2$)(2,2′-bipy)$(CO)_3$] at − 1.050 V *vs.* NHE (*Table 1*) to reduction of the aq-2-$CO_2^-$ligand.

*Absorption and Emission Spectra of [Re$^I$(aq-2-$CO_2$)(2,2′-bipy)$(CO)_3$]*. The absorption spectrum of [Re$^I$(aq-2-$CO_2$)(2,2′-bipy)$(CO)_3$] in various solvents (*Fig. 2, a*) was similar to the spectrum of complexes with the [Re$^I$(2,2′-bipy)$(CO)_3$]$^+$ chromophore moiety [6][7][13][14]. The first absorption band, $\lambda \approx 400$ nm, can be assigned to a Re$^I$-to-(2,2′-bipy) charge-transfer transition, and the next feature at shorter wavelength to a 2,2′-bipy-centered electronic transition. An absorption band from a Re$^I$-to-(aq-2-$CO_2$) charge-transfer transition was expected at longer wavelengths than the previous transitions, *i.e.*, at $\lambda \approx 500$ nm. Its absence from the spectrum is remarkable,

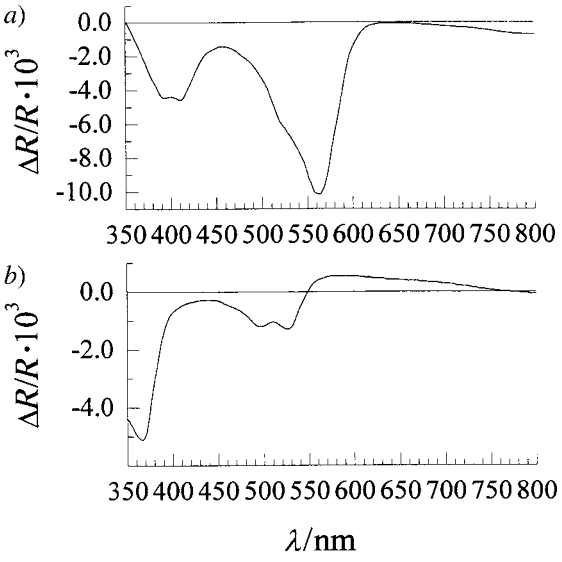

Fig. 1. *Spectra recorded in spectroelectrochemical experiments with deaerated solutions of* a) *$5.6 \cdot 10^{-4}$* M *aq-2-$CO_2H$ and* b) *$3.6 \cdot 10^{-4}$* M *[$Re^IBr(2,2'$-bipy$)(CO)_3$]*. A 45° incidence angle of the light and a frequency of 11 Hz were used in the experiments. Other conditions are indicated elsewhere in this work.

since these charge-transfer transitions usually result in intense absorptions. The reason for the low probability of the transition will be discussed under *Conclusions*.

The solvent- and excitation-wavelength-dependent emission spectrum of [$Re^I$(aq-2-$CO_2$)(2,2′-bipy)$(CO)_3$] (*Fig. 2,b*) strongly resembles the emission spectrum of [$Re^I$(pz-2-$CO_2$)(2,2′-bipy)$(CO)_3$] [14]. On this basis, the main features in the spectrum can be associated with overlapping emissions from ligand-centered and $MLCT_{bipy \leftarrow Re}$ excited states. No feature in the emission spectrum could be associated with a radiative decay of the $MLCT_{aq\text{-}2\text{-}CO_2 \leftarrow Re}$ excited state.

*Photolysis of aq-2-$CO_2H$.* The spectrum generated in 351-nm flash irradiations of aq-2-$CO_2H$ is solvent dependent (*Fig. 3*). Such a dependence on the solvent is similar to those communicated for the triplets of other anthraquinone derivatives [22–24]. In deaerated MeCN, 351-nm flash irradiations of $1.0 \cdot 10^{-4}$ M aq-2-$CO_2H$ produced a transient spectrum (*Fig. 3,a*). Traces from the decay of the spectrum between the wavelengths 370 and 700 nm were well-fitted to a single exponential with a lifetime of 3.5 μs. In flash fluorescence experiments with similar solutions, traces from the luminescence decay, $\lambda_{exc}$ 337 nm and $\lambda_{ob}$ 460 nm, were well-fitted to a single exponential with a lifetime $\tau$ of $(7.5 \pm 0.8)$ μs. In contrast to the experiments in MeCN, a biexponential function with lifetimes $\tau_1 = (932 \pm 5)$ ns and $\tau_2 = (5.1 \pm 0.3)$ μs provided the best fit for the traces showing the decay of the transient absorption spectrum in MeOH. The short-lived and long-lived components of the decay correlated, in terms of the spectrum and solvent dependence, with the triplet of the anthraquinone, and they will be respectively named $^T$aq-2-$CO_2H$ and $^T$aq-2-$CO_2H'$ (*Eqns. 6–8*).

$$\text{aq-2-CO}_2\text{H} + h\nu \rightarrow {}^T\text{aq-2-CO}_2\text{H} + {}^T\text{aq-2-COH}'_2 \qquad (6)$$

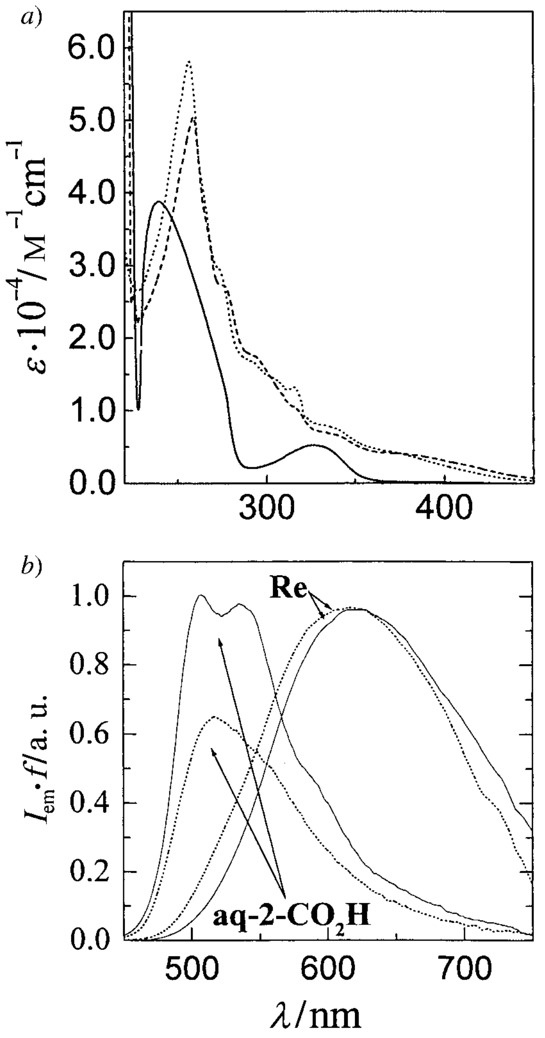

Fig. 2. a) *Absorption spectra of [Re$^I$(aq-2-CO$_2$)(2,2′-bipy)(CO)$_3$] in CH$_2$Cl$_2$ (...) and MeCN (- - -) and of aq-2-CO$_2$H in MeCN (_).* b) *Emission spectra of the Re complex in deaerated MeCN at the excitation wavelengths $\lambda_{exc}$ = 350 nm (_) and $\lambda_{exc}$ = 400 nm (...) and emission spectra of aq-2-CO$_2$H at $\lambda_{exc}$ = 350 nm in deaerated CH$_2$Cl$_2$ (...) and MeCN (_).* The factor *f* normalizes the intensity to the maximum emission observed with each compound.

$$^{T}\text{aq-2-CO}_2\text{H} \rightarrow \text{aq-2-CO}_2\text{H} + h\nu'; \ \tau_1 = 932 \text{ ns} \tag{7}$$

$$^{T}\text{aq-2-CO}_2\text{H}' \rightarrow \text{aq-2-CO}_2\text{H} + h\nu''; \ \tau_2 = 5.0 \ \mu\text{s} \tag{8}$$

The species $^{T}$aq-2-CO$_2$H and $^{T}$aq-2-CO$_2$H′ in *Eqns. 7–8* can be the same solvated species that have been observed in the photophysical processes of various anthraquinones [22]. This proposal provides also a good rationale for the photophysics of aq-2-$CO_2H$ in $CH_2Cl_2$. Indeed, a very short-lived luminescence with a lifetime of *ca.* 10 ns was detected in 337-nm flash-fluorescence experiments with solutions of aq-2-$CO_2H$ in deaerated $CH_2Cl_2$. Either a reaction between the aq-2-$CO_2H$ triplets and the solvent or a solvent-assisted decay of the luminescence could be the cause of the short lifetime of the luminescence in $CH_2Cl_2$. A comparison of the luminescence quantum yields in $CH_2Cl_2$ ($\phi = (6.7 \pm 0.7) \cdot 10^{-3}$) and MeCN ($\phi = (1.6 \pm 0.2) \cdot 10^{-2}$) and the corresponding lifetime favors the latter proposition. The low solubility of aq-2-$CO_2H$ in $CH_2Cl_2$ impeded the application of time-resolved spectroscopy to the study of the aq-2-$CO_2H$ excited states in this solvent.

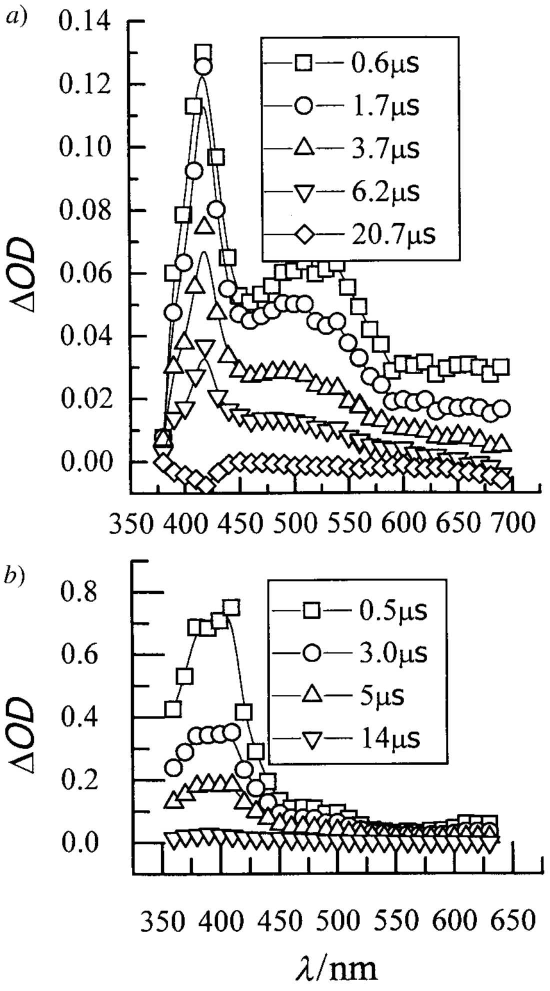

Fig. 3. *Transient spectrum generated in 351-nm flash irradiations of deaerated 1.0 · $10^{-4}$* M *aq-2-$CO_2H$ solutions* a) *in MeCN and* b) *in MeOH*

The spectrum of the semiquinone radical aq-2-$CO_2H^{\bullet-}$ was recorded and used for the characterization of species generated in the photoredox reactions of [$Re^I$(aq-2-$CO_2$)(2,2′-bipy)$(CO)_3$] (see below). To record the spectrum of aq-2-$CO_2H^{\bullet-}$, the aq-2-$CO_2H$ triplets were reduced with the electron donors TEA or TEOA[1]). The 351-nm flash irradiation of $1.0 \cdot 10^{-4}$ M aq-2-$CO_2H$ in deaerated MeCN containing $1.0 \cdot 10^{-3}$ M TEA produced a transient spectrum (*Fig. 4*) that decayed *via* a process with a first-order kinetics with a lifetime $\tau$ of (5.1 ± 0.3) μs. The spectrum can be assigned to the semiquinone radical aq-2-$CO_2H^{\bullet-}$ by comparison to the spectrum generated in spectrochemical experiments and to the literature spectra of related semiquinone radicals [22][25][26]. The experimental observations suggest that the triplets generated *via Eqns. 6–8* undergo electron transfer with TEA and TEOA. The reactions with TEA are illustrated in *Eqns. 9* and *10*.

$$^{T}\text{aq-2-CO}_2\text{H} + \text{TEA} \xrightarrow{k_1} \text{aq-2-CO}_2\text{H}^{\bullet-} + \text{TEA}^{\bullet+} \qquad (9)$$

$$^{T}\text{aq-2-CO}_2\text{H}' + \text{TEA} \xrightarrow{k_2} \text{aq-2-CO}_2\text{H}^{\bullet-} + \text{TEA}^{\bullet+} \qquad (10)$$

A value, $k_Q = k_1 + k_2 = 5 \cdot 10^9$ M$^{-1}$ s$^{-1}$, for the overall quenching rate constant was calculated from the rate of growth of the aq-2-$CO_2H^{\bullet-}$ radical with a lifetime $\tau$ of (210 ± 10) ns (see inset to *Fig. 4*).

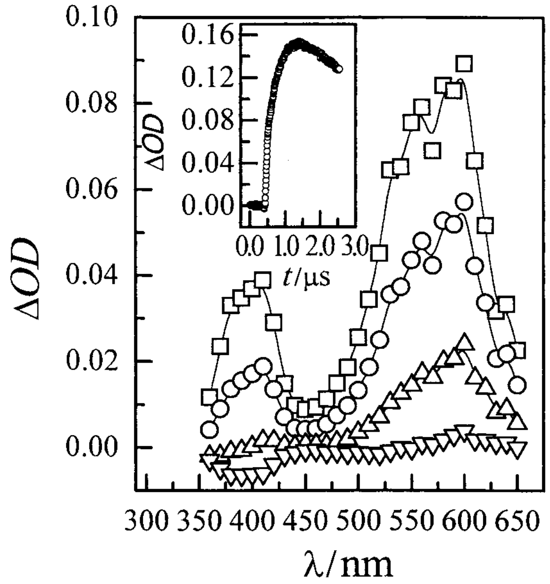

Fig. 4. *Transient spectrum of the semiquinone radical generated in 351-nm flash irradiation of $1.0 \cdot 10^{-4}$* M *aq-2-$CO_2H$ in deaerated MeCN containing $1.0 \cdot 10^{-3}$* M *TEA.* Delays with respect to the laser flash are (□), (○), (△), and (▽). The inset shows the growth of the semiquinone radical at $\lambda_{ob} = 580$ nm.

Time-resolved fluorescence experiments ($\lambda_{exc}$ 337 nm) were carried out with solutions of aq-2-$CO_2H$ in deaerated MeCN containing various TEOA concentrations ($0 \leq [\text{TEOA}] \leq 6 \cdot 10^{-5}$ M). The quenching of the aq-2-$CO_2H$ luminescence by TEOA was similar to the one described for the quenching by TEA in *Eqns. 7–10*. Oscillographic traces showing the decay of the luminescence were fitted to a biexponential function with lifetimes dependent on [TEOA] and independent of the monitoring wavelength. Quenching rate constants $k_1 = (3.4 \pm 0.2) \cdot 10^{10}$ $\text{M}^{-1}$ $\text{s}^{-1}$ and $k_2 = (1.1 \pm 0.2) \cdot 10^{10}$ $\text{M}^{-1}$ $\text{s}^{-1}$ were calculated from plots of the reciprocal of the lifetime *vs.* [TEOA]. In 350-nm steady-state irradiations, a *Stern-Volmer* constant, $K_{SV} = (8.7 \pm 0.5) \cdot 10^4$ $\text{M}^{-1}$, was calculated from the slope of a plot of the reciprocal of the emission intensity. This value is in good agreement with the one calculated with the rate constants from the time-resolved measurements, *i.e.* $K = (8.1 \pm 0.5) \cdot 10^4$ $\text{M}^{-1}$.

*Photolysis of [Re$^I$(aq-2-CO$_2$)(2,2′-bipy)(CO)$_3$].* Flash irradiations at 351-nm of deaerated $2.0 \cdot 10^{-4}$ M [$\text{Re}^\text{I}$(aq-2-$\text{CO}_2$)(2,2′-bipy)$(\text{CO})_3$] in MeCN produced a transient spectrum that was ascribed to the formation of IL, $\text{MLCT}_{\text{bipy}\leftarrow\text{Re}}$, and aq-2-$\text{CO}_2$-centered excited states (*Eqn. 11*).

$$[\text{Re}^\text{I}(\text{aq-2-CO}_2)(2,2'\text{-bipy})(\text{CO})_3] + h\nu \rightarrow \{\text{IL} + \text{MLCT}_{\text{bipy}\leftarrow\text{Re}} + [\text{Re}^\text{I}(^\text{T}\text{aq-2-CO}_2)(2,2'\text{-bipy})(\text{CO})_3]\ [\text{Re}^\text{I}(^\text{T}\text{aq-2-CO}_2^{\prime})(2,2'\text{-bipy})(\text{CO})_3\} \quad (11)$$

The transient spectrum decayed in three steps with exponential dependence, $\exp(-t/\tau_\text{i})$ where $\tau_\text{i}$ with $i = 1,2,3$ are the lifetimes of the three steps. The first two steps were similar to those previously observed in the photophysics of [$\text{Re}^\text{I}$(pz-2-$\text{CO}_2$)(2,2′-bipy)$(\text{CO})_3$] and assigned to the decay of a (2,2′-bipy)-centered intraligand excited state IL and to a $\text{Re}^\text{I}$-to-2,2′-bipy) charge-transfer excited state $\text{MLCT}_{\text{bipy}\rightarrow\text{Re}}$ [14]. In [$\text{Re}^\text{I}$(aq-2-$\text{CO}_2$)(2,2′-bipy)$(\text{CO})_3$], the first step, $\tau_1 \approx (41 \pm 5)$ ns, was assigned to the decay of the IL excited state (*Fig. 5*). A second step in the decay of the transient, lifetime $\tau_2 \approx (460 \pm 50)$ ns, was assigned to the decay of the $\text{MLCT}_{\text{bipy}\rightarrow\text{Re}}$ (*Fig. 5*). The experimental observations suggest that excitations with $\lambda_\text{exc} \leq 350$ nm (*Eqn. 11*) populate IL and $\text{MLCT}_{\text{bipy}\rightarrow\text{Re}}$ excited states which decay *via Eqns. 12* and *13*. A final step in the demise of the transient spectrum with a lifetime $\tau_3$ $(4.9 \pm 0.5)$ μs followed the disappearance of the $\text{MLCT}_{\text{bipy}\rightarrow\text{Re}}$ (*Fig. 5*). By comparison to the photophysics of the free aq-2-$\text{CO}_2$H in MeCN, this final step can be assigned to the decay of the Re-coordinated $^\text{T}$aq-2-$\text{CO}_2^{\prime}$ (*Eqn. 14*).

$$\text{IL} \rightarrow [\text{Re}^\text{I}(\text{aq-2-CO}_2)(2,2'\text{-bipy})(\text{CO})_3] + h\nu'''; \ \tau_1 = 41 \text{ ns} \quad (12)$$

$$\text{MLCT}_{\text{bipy}\leftarrow\text{Re}} \rightarrow [\text{Re}^\text{I}(\text{aq-2-CO}_2)(2,2'\text{-bipy})(\text{CO})_3] + h\nu'''; \ \tau_2 = 460 \text{ ns} \quad (13)$$

$$[\text{Re}^\text{I}(^\text{T}\text{aq-2-CO}_2^{\prime})(2,2'\text{-bipy})(\text{CO})_3] \rightarrow [\text{Re}^\text{I}(\text{aq-2-CO}_2)(2,2'\text{-bipy})(\text{CO})_3] + h\nu'; \ \tau_3 = 4.9 \ \mu\text{s} \quad (14)$$

Since halocarbon solvents are considerably more reactive than MeCN, the photobehavior of the $\text{Re}^\text{I}$ complex was investigated in $\text{CH}_2\text{Cl}_2$. The transients generated in flash irradiations of deaerated $2.0 \cdot 10^{-4}$ M [$\text{Re}^\text{I}$(aq-2-$\text{CO}_2$)(2,2′-bipy)-$(\text{CO})_3$] in $\text{CH}_2\text{Cl}_2$ at 351 nm were different from those observed in MeCN. A transient

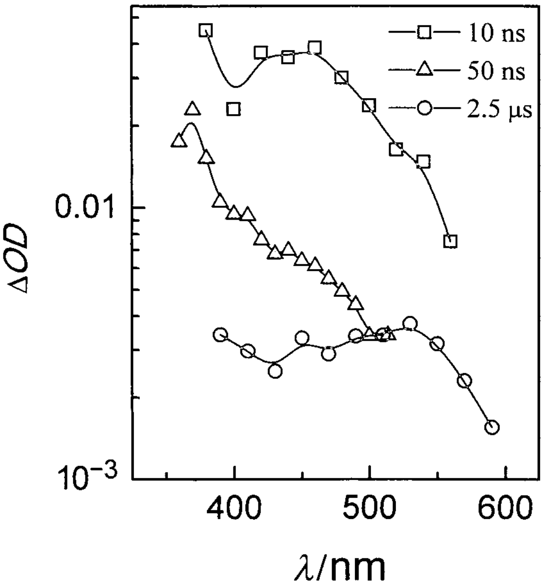

Fig. 5. *Transient spectra recorded with different delays* (2.5 μs, 10 ns, and 50 ns), *after the 351-nm flash irradiation of 1.0 · $10^{-4}$* M *[Re$^I$(aq-2-CO$_2$)(2,2′-bipy)(CO)$_3$] in deaerated MeCN*

spectrum calculated by extrapolation to the beginning of the laser flash is a convolution of two spectra (*Fig. 6*). One component of the transient spectrum was deconvoluted by means of spectra recorded with 20 and 70 ns delays relative to the laser-flash trigger. The deconvoluted spectrum was short-lived and vanished shortly after the 351-nm laser flash had extinguished, *i.e.*, $t \approx 30$ ns. Features of the short-lived spectrum were similar to those found in the spectrum of the aq-2-CO$_2$ triplet seen in flash photolysis of the free ligand (*Fig. 3*) and the complex in MeCN (*Fig. 5*). In this regard, it can be assigned to the combined contributions of the species [Re$^I$($^T$aq-2-CO$_2$)(2,2′-bipy)(CO)$_3$] to the transient spectrum. The long-lived transient spectrum exhibited spectral features previously seen in the MLCT$_{\text{bipy}\to\text{Re}}$ excited-state spectrum of complexes containing a pendant – Re$^I$(2,2′-bipy)(CO)$_3$ chromophore. Comparisons between the decay kinetics of the transient absorption spectrum in flash photolysis and the kinetics of the luminescence in flash fluorescence experiments were made with deaerated MeCN solutions containing *ca.* $10^{-4}$ M [Re$^I$(aq-2-CO$_2$)(2,2′-bipy)(CO)$_3$]. The decay of the luminescence and the transient absorption spectrum were both of a first order and had almost the same lifetimes, *i.e.*, $\tau = (110 \pm 10)$ ns for the decay of the luminescence and $\tau = (116 \pm 20)$ ns for the decay of the transient spectrum. On this experimental basis and a comparison of the results with those of related Re$^I$ complexes, the slow decaying component of the transient spectrum was assigned to the decay of the luminescent MLCT$_{\text{bipy}\to\text{Re}}$ excited state of [Re$^I$(aq-2-CO$_2$)(2,2′-bipy)(CO)$_3$].

In the flash photochemical experiments in CH$_2$Cl$_2$, the decay of the MLCT$_{\text{bipy}\to\text{Re}}$ spectrum did not return the optical density to the baseline. The optical density decayed to the base line *via* a slower process that was first order kinetically. A lifetime $\tau$ of

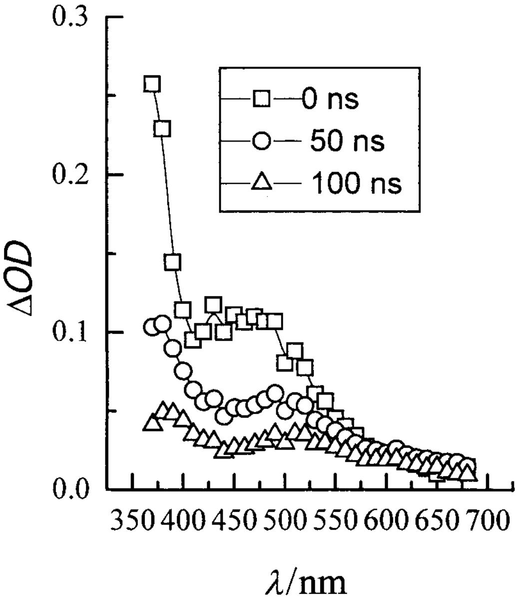

Fig. 6. *Transient spectra with different delays* (0, 50, and 100 ns) *after the 351-nm flash irradiation of 1.0 · $10^{-4}$* M *[$Re^I$(aq-2-$CO_2$)(2,2′-bipy)$(CO)_3$] in deaerated $CH_2Cl_2$*

(3.7 ± 0.4) μs was measured for the exponential decay of this spectrum. While the spectrum exhibited features different from those seen in the spectrum of the aq-2-$CO_2H^{\bullet-}$ radical, it closely resembled the spectrum of the coordinated bipy$^{\bullet-}$ radical produced in the reductive quenching of the excited state by electron donors. A decay of the transient spectrum to the baseline suggested a minor photodecomposition of the Re complex and that the redox process has a quantum yield smaller than $10^{-4}$. The possible photodecomposition of [$Re^I$(aq-2-$CO_2$)(2,2′-bipy)$(CO)_3$] was also investigated in steady-state photolyses of the complex. Irradiations of 3.0 · $10^{-4}$ M [$Re^I$(aq-2-$CO_2$)(2,2′-bipy)$(CO)_3$] in deaerated $CH_2Cl_2$ at 350 nm, $I_0 = 6.5 \cdot 10^{-4}$ Einstein $l^{-1}$ $min^{-1}$, were carried out for periods equal to or less than 60 min. In accordance with flash photolysis observations, the steady-state photolysis produced no permanent UV/VIS spectral changes in the spectrum of the solutions. Since no $Cl^-$ from any reductive decomposition of the solvent was detected at the end of the irradiations, the detection limit of the $Cl^-$ analysis suggests that the quantum yield of the reductive decomposition of $CH_2Cl_2$ must be equal to or smaller than $10^{-3}$. The photoinduced oxidation of $CH_2Cl_2$ by the highly reactive excited states to produce a coordinated bipy$^{\bullet-}$ radical was investigated by means of the luminescence of the complex in $CH_2Cl_2$ and MeCN. The quantum yield of the luminescence had a larger value in $CH_2Cl_2$ than in MeCN (*Table 2*). The quantum yield and lifetime of the luminescence in these solvents suggest a small difference between the values of the rate constant for the radiative and radiationless relaxations of the $MLCT_{bipy \leftarrow Re}$ in these solvents. Such differences must be large enough to overcome contributions from any reaction of the excited state with the solvent. The experimental information also suggests little if any involvement of the coordinated aq-2-$CO_2$ triplets and the $MLCT_{aq\text{-}2\text{-}CO_2 \leftarrow Re}$ in the oxidation of $CH_2Cl_2$.

Table 2. *Quantum Yield of Luminescence $\phi_{ems}$, as a Function of Solvent and Excitation Wavelength*

| Photolyte | $\lambda_{exc}$ nm | Solvent | $\phi_{ems}$ |
|---|---|---|---|
| $[Re^I(aq\text{-}2\text{-}CO_2)(2,2'\text{-}bipy)(CO)_3]$ | 350 | MeCN | $(1.3 \pm 0.1) \cdot 10^{-3}$ |
| | | $CH_2Cl_2$ | $(3.7 \pm 0.4) \cdot 10^{-3}$ |
| | 400 | MeCN | $(1.4 \pm 0.1) \cdot 10^{-3}$ |
| | | $CH_2Cl_2$ | $(4.1 \pm 0.4) \cdot 10^{-3}$ |
| aq-2-$CO_2H$ | 337 | MeCN | $(6.7 \pm 0.7) \cdot 10^{-3}$ |
| | | $CH_2Cl_2$ | $(1.6 \pm 0.2) \cdot 10^{-2}$ |

Indeed, the spectrum of the coordinated aq-2-$CO_2^{\bullet 2-}$ radical would have been observed in flash photolysis in the case of an efficient oxidation of $CH_2Cl_2$ by these excited states.

More information about the excited-state redox reactivity was obtained by using TEA as an electron donor. The 351-nm flash photolysis of *ca.* $10^{-4}$ M $[Re^I(aq\text{-}2\text{-}CO_2)(2,2'\text{-}bipy)(CO)_3]$ in deaerated $CH_2Cl_2$ containing $10^{-3}$ M TEA removed the spectrum of the excited states within the time scale of the flash, *i.e.*, *ca.* 10 ns. A spectrum with $\lambda_{max} \approx 520$ nm assigned to the product of the reaction of the electronically excited Re complex with TEA remained after the flash irradiation. The spectrum of this product is red-shifted and featureless by comparison to those of the semiquinone radicals of various anthraquinone derivatives and the spectrum of aq-2-$CO_2^{\bullet 2-}$. It compares well with the spectrum of the coordinated bipy$^{\bullet -}$ radical [14]. The experimental observation suggests that the oxidation of TEOA by the $MLCT_{bipy \leftarrow Re}$ and/or IL excited states (*Eqns. 15* and *16*) is more efficient than the oxidation by triplets of the coordinated aq-2-$CO_2$ (*Eqn. 17*).

$$IL + TEOA \rightarrow [Re^I(aq\text{-}2\text{-}CO_2)(2,2'bipy^{\bullet})(CO)_3]^- + TEOA^{\bullet +} \tag{15}$$

$$MLCT_{bipy \leftarrow Re} + TEOA \rightarrow [Re^I(aq\text{-}2\text{-}CO_2)(2,2'\text{-}bipy^{\bullet})(CO)_3]^- + TEOA^{\bullet +} \tag{16}$$

$$\begin{aligned} &\{[Re^I({}^Taq\text{-}2\text{-}CO_2)(2,2'\text{-}bipy)(CO)_3] + [Re^I({}^Taq\text{-}2\text{-}CO_2')(2,2'\text{-}bipy)(CO)_3]\} \\ &\qquad + TEOA \rightarrow [Re^I(aq\text{-}2\text{-}CO_2)(2,2'\text{-}bipy^{\bullet})(CO)_3]^- + TEOA^{\bullet +} \end{aligned} \tag{17}$$

The diminished redox reactivity of the coordinated aq-2-$CO_2$ triplets may be attributed to the small redox potential of the (${}^Taq\text{-}2\text{-}CO_2^-$ and ${}^Taq\text{-}2\text{-}CO_2^{-\prime}$)/aq-2-$CO_2^{\bullet 2-}$ couples by comparison to those of the $Re^{II}/Re^I$ and the IL/bipy$^{\bullet -}$ in the respective $MLCT_{bipy \leftarrow Re}$ and IL excited states. Some spectral changes, observed 500 ns after the laser irradiation, show the formation of the aq-2-$CO_2^{\bullet 2-}$ radical (*Fig. 7*). Given the differences in the standard potentials of the bipy/bipy$^{\bullet -}$ and aq-2-$CO_2^-$)/aq-2-$CO_2^{\bullet 2-}$ couples, the spectral changes could be attributed to a relaxation of the equilibrium between the coordinated bipy$^{\bullet -}$ and aq-2-$CO_2^{\bullet 2-}$ radicals (*Eqn. 18*). The decay of these species with a lifetime $\tau$ of $(3.5 \pm 0.4)$ μs was slower than their equilibration.

$$[Re^I(aq\text{-}2\text{-}CO_2)(2,2'\text{-}bipy^{\bullet})(CO)_3]^- \rightleftharpoons [Re^I(aq\text{-}2\text{-}CO_2^{\bullet})(CO)_3(2,2'\text{-}bipy)(CO)_3]^- \tag{18}$$

**Conclusions.** – The photophysical an photochemical properties of $[Re^I(aq\text{-}2\text{-}CO_2)(2,2'\text{-}bipy)(CO)_3]$ can now be related to the actual excited-state properties. A

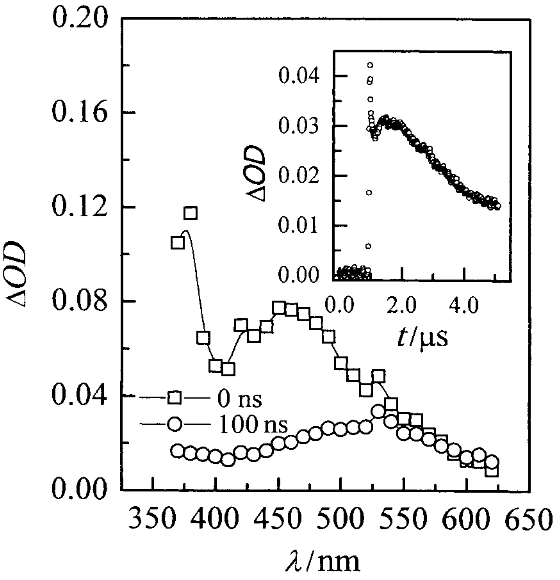

Fig. 7. *Spectral changes observed after the 351-nm flash irradiation of* $1.0 \cdot 10^{-4}$ M *[$Re^I$(aq-2-$CO_2$)(2,2′-bipy)$(CO)_3$ in deaerated MeCN containing* $1.0 \cdot 10^{-3}$ M *TEA*. Delays with respect to the laser flash: 0 ns (□) and 100 ns (○). Inset: a trace, $\lambda_{ob} = 530$ nm, shows a growth of the optical density assigned elsewhere to an equilibration between [$Re^I$(aq-2-$CO_2$)(2,2′-bipy$^•$)$(CO)_3$]$^-$ and [$Re^I$(aq-2-$CO_2^•$)(2,2′-bipy)$(CO)_3$]$^-$.

*Jablonski* diagram (*Fig. 8*) shows the relative positions of the excited states involved in the photophysics and photochemistry of [$Re^I$(aq-2-$CO_2$)(2,2′-bipy)$(CO)_3$] when it is excited with photonic energies $E_{h\nu} < 29.6 \cdot 10^3$ cm$^{-1}$ mol$^{-1}$. Redox potentials of the $Re^{II}$/$Re^I$, bipy/bipy$^{•-}$ and aq-2-$CO_2^-$/aq-2-$CO_2^{•2-}$ couples in *Table 1* were used for the calculation of the 0-0 point energies $E_{0-0}$ of the $MLCT_{bipy \leftarrow Re}$ and $MLCT_{aq\text{-}2\text{-}CO_2 \leftarrow Re}$. A value of the 0-0 point energy, $E_{0-0} \approx 23.5 \cdot 10^3$ cm$^{-1}$ mol$^{-1}$, was assigned to the IL based on the luminescence of the protonated 2,2′-bipyridine. The value $E_{0-0} \approx 21.3 \cdot 10^3$ cm$^{-1}$ mol$^{-1}$ for the aq-2-$CO_2$ triplets was calculated from the emission spectra and compared well with published values of $E_{0-0}$ [22–24]. These calculations placed the IL, $MLCT_{bipy \leftarrow Re}$, and $^T$aq-2-$CO_2$ in close proximity and the $MLCT_{aq\text{-}2\text{-}CO_2 \leftarrow Re}$ at a lower energy. The *Jablonski* diagram suggests that the poor reactivity of the $MLCT_{aq\text{-}2\text{-}CO_2 \leftarrow Re}$ toward the oxidation of $CH_2Cl_2$ or TEA could be a consequence of its low energy. However, other factors may affect the reactivity of MLCT excited states. For example, it appears to be a significant difference between the nuclear equilibrium configurations of the $MLCT_{bipy \leftarrow Re}$ excited state and the ground state. The separation between the maximum of the absorption spectrum for the transition to the $MLCT_{bipy \leftarrow Re}$, $\nu \approx 25 \cdot 10^3$ cm$^{-1}$, and the $E_{0-0}$ energy in the emission spectrum of [$Re^I$(aq-2-$CO_2$)(2,2′-bipy)$(CO)_3$] correspond to a reorganization energy $\lambda_{org} \approx 4 \cdot 10^3$ cm$^{-1}$. This value is in agreement with $\lambda_{org} \approx 3 \cdot 10^3$ cm$^{-1}$, calculated²) with the mean

---

²) A bond-reorganization energy was calculated with $\lambda_{org} \approx 3/2 \times f \times (\Delta d)^2$ [27] where $f$ = mean of the breathing force constants and $\Delta d$ = the difference of the metal-ligand distance in the oxidized and reduced complexes. Literature values of the parameters were used for the calculation.

IR frequencies of the $Re^I$-azine and $Re^{II}$-azine stretching modes and the difference between the corresponding bond lengths [3][14][28][29]. The effect of the reorganization energy and displacement of the potential surfaces is shown in the inset to *Fig. 8*. A reorganization energy of a similar magnitude can be expected for the $MLCT_{aq\text{-}2\text{-}CO_2 \leftarrow Re}$. However, the optical transition to this excited state is expected to be in the VIS region, *i.e.*, $\lambda \approx 550$ nm, on the exclusive basis of the calculated $E_{0-0}$ and $\lambda_{org}$ energies. The absence of intense spectral features attributable to such an optical transition in the spectrum of $[Re^I(aq\text{-}2\text{-}CO_2)(2,2'\text{-}bipy)(CO)_3]$ and similar transitions in other $Re^I$ complexes with related carboxylato spectators [14] suggests a rather low transition probability. It is possible that a nonadiabatic photoinduced transfer of charge from the $Re^I$ donor to the anthraquinone acceptor is responsible for the low transition probability. It is possible that the nonadiabatic transfer results from the carboxylato-induced decoupling of the donor and acceptor wavefunctions. A similar reason justifies that upper excited states IL, $MLCT_{bipy \leftarrow Re}$, and $^Taq\text{-}2\text{-}CO_2$ fail to convert to the $MLCT_{aq\text{-}2\text{-}CO_2 \leftarrow Re}$. Indeed, efficient conversions of the higher-energy excited states to the low lying $MLCT_{aq\text{-}2\text{-}CO_2Re}$ will result in a fast relaxation to the ground state, a condition previously observed with $Re^I$ complexes with low-lying MLCT states [5]. In this regard, the carboxylato-induced isolation of the $MLCT_{aq\text{-}2\text{-}CO_2 \leftarrow Re}$ provides an efficient reaction path (*Eqns. 15–18*) for the indirect reduction of the spectator ligand, *i.e.*, one that avoids the wasteful relaxation to the ground state. This indirect reaction path provides a way to profit from the redox chemistry of the reduced spectator ligand.

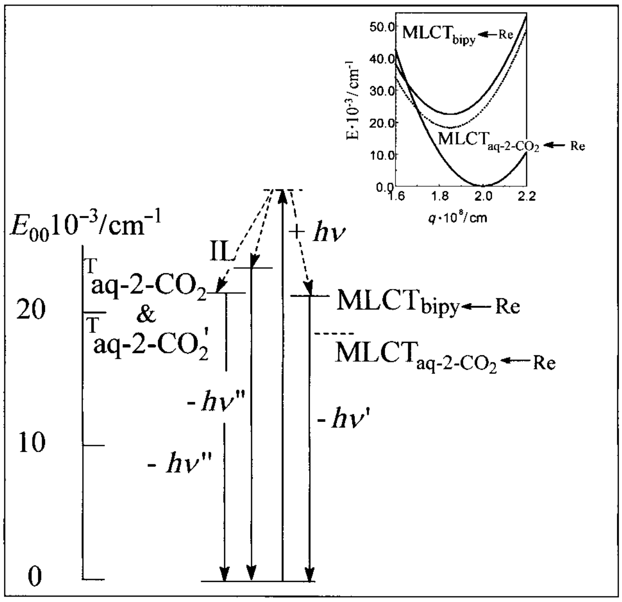

Fig. 8. Jablonski *diagram showing the zero-point energies* $E_{0-0}$ *of the electronic levels relevant to the 351-nm photolysis of* $[Re^I(aq\text{-}2\text{-}CO_2)(2,2'\text{-}bipy)(CO)_3]$. The inset shows the displacement between potential curves, calculated under the harmonic approximation, for the ground-state (_), the $MLCT_{bipy \leftarrow Re}$(_), and $MLCT_{aq\text{-}2\text{-}CO_2 \leftarrow Re}$, (- - -). Other details of the calculation are given elsewhere in this work.

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