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Time-Resolved Photoacoustics Study of the Ruthenium(II) Bis(2,2′-bipyridine)(4,4′-dicarboxy-2,2′-bipyridine) Complex

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The formation and the decay of the triplet metal to ligand charge transfer state (^{3}MLCT) of ruthenium(II) bis(2,2′-bipyridine)(4,4′-dicarboxy-2,2′-bipyridine) ($Ru(bpy)_2(dcbpy)$) were characterized using photoacoustic calorimetry. At pH 6 and 2, the ^{3}MLCT state formation leads to a volume change of –8 mL mol^{-1} and enthalpy changes of 17 kcal mol^{-1} and 13 kcal mol^{-1}, respectively. We attribute the volume contraction to structural changes and to solvent electrostriction. At pH 4, the photoexcitation of the complex leads to an expansion of 14 mL mol^{-1} and an enthalpy change of $\sim$119 kcal mol^{-1} due to protonation of the carboxyl group in the excited state.

Introduction

The photochemistry and photophysics of ruthenium polypyridyl complexes have been widely studied mainly due to the potential use of these complexes as photosensitizers in solar energy conversion[1−3] and as luminescent probes for characterizing microheterogeneous environments.[4] Photoexcitation of ruthenium polypyridyl complexes has been shown to generate a single metal to ligand charge transfer state (^{1}MLCT) that undergoes a rapid (<1 ps), highly efficient intersystem crossing ($\Phi \approx 1$) to a manifold of closely spaced triplet states (^{3}MLCTs).[5] The solution triplet states of ruthenium complexes have a relatively long-lived emission ($\tau \approx 600$ ns) and decay to the ground state, largely through a nonradiative deactivation channel.[6]

An interesting group of ruthenium complexes contains ligands with a protonatable group that undergoes a proton transfer reaction in the excited state. Ruthenium(II) bis(2,2′-bipyridine)(4,4′-dicarboxy-2,2′-bipyridine) ($Ru(bpy)_2(dcbpy)$) was the first transition metal complex in which a proton transfer was observed in the excited state.[2] This complex resembles the parent $Ru(bpy)_3$ complex in that it exhibits a long-lived emitting ^{3}MLCT excited state. Transient resonance Raman and IR studies suggest that the ^{3}MLCT excited state of ruthenium complexes is composed of a Ru(III) ion and an electron delocalized over one of the polypyridyl ligands on a time scale ranging from hundreds of picoseconds to a few nanoseconds after excitation.[7] In mixed ligand complexes, the electron is located on the ligand with the largest reduction potential.[8] In complexes with protonatable ligands such as 4,4′-dicarboxybipyridine or 2,2′-bipyrimidine, formation of the ^{3}MLCT state causes significant changes in the acid/base equilibrium of the complex. For example, the $Ru(bpy)_2(dcbpy)$ complex becomes more basic in the excited state than in the ground state, exhibiting a pK_a shift of roughly two pH units.[9,10]

Volume and enthalpy changes coupled to the formation and the decay of the ^{3}MLCT state of several ruthenium complexes have been determined using photoacoustic calorimetry (PAC).[11,12] It has been shown that the excitation of $Ru(bpy)_3$ leads to a volume contraction of $\sim$3.5 mL mol^{-1}, and the observed volume decrease was attributed to a shortening of the Ru−bpy bond in the excited state.[12] For the $Ru(bpy)(CN)^{4-}$ and $Ru(bpy)(CN)_3(CNCH_3)^-$ complexes, positive volume changes of 15 and 10 mL mol^{-1}, respectively, have been reported for the formation of the ^{3}MLCT state.[11] The observed volume increase was interpreted as

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photoinduced changes in the hydrogen bond strength between the cyano ligands and the solvent water molecules.

Here, we report the volume and enthalpy changes coupled to the formation of the ^{3}MLCT state of Ru(bpy)$_2$(dcbpy). The excitation of Ru(bpy)$_2$(dcbpy) leads to a contraction of ~ -8 mL mol^{-1} at pH 6 and 2. The observed volume contraction is larger than the volume change determined for Ru(bpy)$_3$. We attribute the additional volume decrease relative to the parent Ru(bpy)$_3$ complex to electrostriction arising from increased electron delocalization on the 4,4′-dicarboxybipyridine ligand in the ^{3}MLCT state. In contrast, at pH 4, a volume expansion of $\sim$14 mL mol^{-1} and an enthalpy change of $\sim$110 kcal mol^{-1} are observed, consistent with protonation of the excited state. The magnitude of the observed volume change corresponds to the volume changes measured previously for the protonation/deprotonation of the excited state of other protonatable compounds such as naphthols[13] and pyranine[14] in water.

Materials and Methods

Ru(bpy)$_3$ was purchased from Sigma-Aldrich. Ru(bpy)$_2$(dcbpy) was synthesized according to a previously published method.[15] The samples were prepared by dissolving solid compounds in deionized water, and the pH was adjusted by adding small amounts of 1 M HCl or 1 M NaOH. Each sample was then placed in a 1 × 1 cm^2 quartz cuvette, sealed with a rubber septum cap, and purged with Ar for 30 min. The absorbance was determined using a dual beam Shimadzu UV-2401 spectrophotometer. Fe(III)(4-sulfonatophenyl)-porphyrin (Fe(III)4SP) was used as a reference compound for the PAC measurements. Its absorbance matched the absorbance of the sample at the excitation wavelength, $A_{355\mathrm{nm}} \sim 0.3$. The emission lifetime measurements were performed as described previously.[16] Our PAC instrumentation has been described in detail elsewhere.[17,18] Typically, $\sim$40 laser pulses were averaged per trace in the temperature range from 16 to 35 °C. Excitation was provided by a frequency-doubled or -tripled Nd:YAG laser (355 or 532 nm, 7 ns, <100 μJ/pulse, 1 Hz repetition rate).

Results and Discussion

We have used PAC to determine the volume and enthalpy changes coupled to the formation and the decay of the ^{3}MLCT state of Ru(bpy)$_2$(dcbpy) at pH 6, 4, and 2 and compared these values to the volume and enthalpy changes associated with the ^{3}MLCT state of the parent Ru(bpy)$_3$ complex at pH 6 and 2. Figure 1 shows an overlay of acoustic traces of Ru(bpy)$_2$(dcbpy) and of the reference compound, Fe(III)4SP, at pH 6. The phase shift of the sample acoustic wave with respect to the reference trace indicates the presence of kinetic processes occurring between 50 ns and $\sim$10 μs. A similar phase shift between the sample wave and the reference wave is observed at pH 2 and 4 as well for the Ru(bpy)$_3$ complex (data not shown). Deconvolution of the experimental data (described in detail previously[17−19]) reveals two kinetic processes after photoexcitation. The first process is found to occur faster than the resolution of the acoustic detector ($\tau < 50$ ns) and is attributed to the formation of the ^{3}MLCT state, since, upon excitation, the ^{3}MLCT state appears within 1 ps.[20] The second process has a lifetime between 200 and 600 ns and reflects the thermal de-excitation of the triplet state. The observed lifetimes are listed in Table 1 together with the fluorescence lifetimes. The lifetimes determined by PAC are consistent with the lifetimes determined by the time-resolved fluorescence measurements and are also in agreement with the values previously reported, $\tau = 570$ ns for Ru(bpy)$_3$ and $\tau = 434$ ns for Ru(bpy)$_2$(dcbpy).[5,6,21] De-excitation of the protonated form of Ru(bpy)$_2$(dcbpy) occurs with a 2-fold shorter lifetime than that of the deprotonated form. A similar pH dependence of the Ru(bpy)$_2$(dcbpy) lifetime was reported by Cherry and Henderson.[21]

From the temperature dependence of the acoustic amplitudes (ϕ_i) for the individual processes, the corresponding

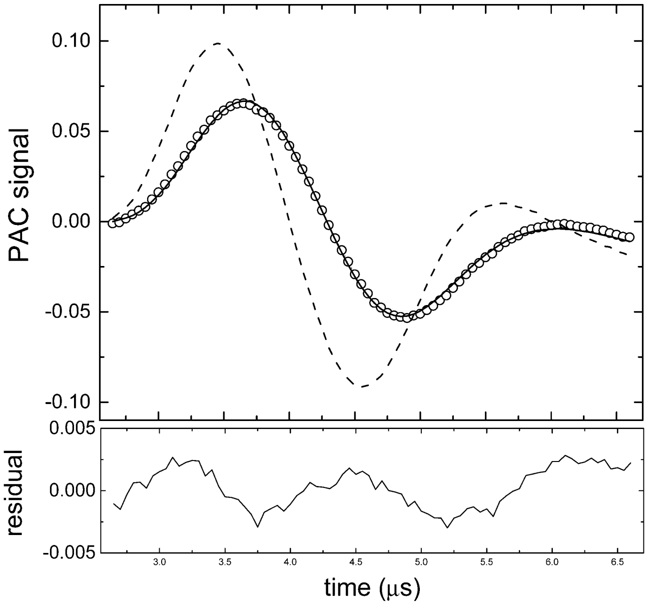

Figure 1. Overlay of a photoacoustic wave of Ru(bpy)$_2$(dcbpy) (open circles) and of the reference (dashed line) at pH 6 and 16 °C. The absorbances of the sample and the reference matched at the excitation wavelength. The traces represent an accumulation of 40 laser shots. A solid line shows the fit.

Table 1. Lifetimes of the ^{3}MLCT State of Ru(bpy)$_3$ and Ru(bpy)$_2$(dcbpy) Obtained from Time-Resolved Fluorescence and PAC Measurements

complex	pH	τ_{em} (ns)	τ (ns)
Ru(bpy)$_3$	6	590	570
	2	566	625
Ru(bpy)$_2$(dcbpy)	6	500	504
	4	330	320
	2	270	300

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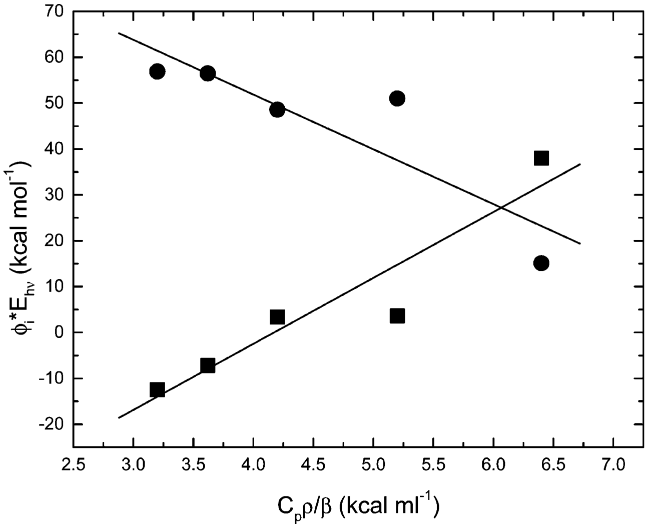

Figure 2. Plot of $\phi_i{}^*E_{h\nu}$ vs ($C_p\rho/\beta$) for Ru(bpy)$_2$(dcbpy) at pH 4. The $\phi_i{}^*E_{h\nu}$ values associated with the formation of the ^{3}MLCT state are shown as squares, and the $\phi_i{}^*E_{h\nu}$ values associated with the subsequent decay are shown as circles. The excitation wavelength was 532 nm.

volume and enthalpy changes accompanying the formation (ΔV_{form} and ΔH_{form}) and the decay ($\Delta V_{\mathrm{decay}}$ and $\Delta H_{\mathrm{decay}}$) of the ^{3}MLCT state were determined using

$$\phi_i E_{h\nu} = (Q + \Delta V/(\beta/C_p\rho))\Phi \tag{1}$$

where β is the coefficient of thermal expansion of the solvent, C_p is the heat capacity, ρ is the density, Q is the heat released to the solvent, ΔV is the volume change, $E_{h\nu}$ is the energy of an absorbed photon, and Φ is the quantum yield. The enthalpy change for the fast process is then calculated from

$$\Delta H_{\mathrm{form}} = E_{h\nu} - Q \tag{2}$$

while the enthalpy of the decay of the excited state is

$$\Delta H_{\mathrm{decay}} = -Q \tag{3}$$

A plot of $\phi_i{}^*E_{h\nu}$ versus ($C_p\rho/\beta$) is shown in Figure 2 for Ru(bpy)$_2$(dcbpy) at pH 4 and in Figure 3 at pH 2 and 6. The corresponding plot for Ru(bpy)$_3$ at pH 6 and 2 is shown in Figure 4. The values obtained with 355 nm excitation were the same as those obtained using 532 nm excitation. The extracted volume and enthalpy changes are listed in Table 2. Taking into account that the quantum yields for the nonradiative decay of the ^{3}MLTC states are close to unity (0.96 and 0.97 for Ru(bpy)$_3$ and Ru(bpy)$_2$(dcbpy), respectively[22]), we found that all excited molecules return back to the ground state giving $\Delta V_{\mathrm{form}} = -\Delta V_{\mathrm{decay}}$ as well as $\Delta H_{\mathrm{form}} = -\Delta H_{\mathrm{decay}}$.

Table 3 shows the reactions describing the formation of ^{3}MLCT state at each pH value together with the corresponding values of ΔV_{form} and ΔH_{form}. At pH 6 and 2, the formation of the ^{3}MLCT state of Ru(bpy)$_3$ and the subsequent decay are accompanied by a volume decrease of -3.5 ± 0.5 mL mol^{-1} and a volume expansion of 3.2 ± 0.6 mL mol^{-1}, respectively. A volume contraction for the formation of the triplet state has been reported by the Braslavsky group ($\Delta V_{\mathrm{form}} = -3$ mL mol^{-1})[11] and by Goodman and Herman ($\Delta V_{\mathrm{form}} = -3.5$ mL mol^{-1}).[12] The observed enthalpy change for the formation of the ^{3}MLCT state at pH 6 ($\Delta H_{\mathrm{form}} = 43.9 \pm 2.2$ kcal mol^{-1}) and for the decay ($\Delta H_{\mathrm{decay}} = 49.8 \pm 3.4$ kcal mol^{-1}) corresponds to the energy of the ^{3}MLCT

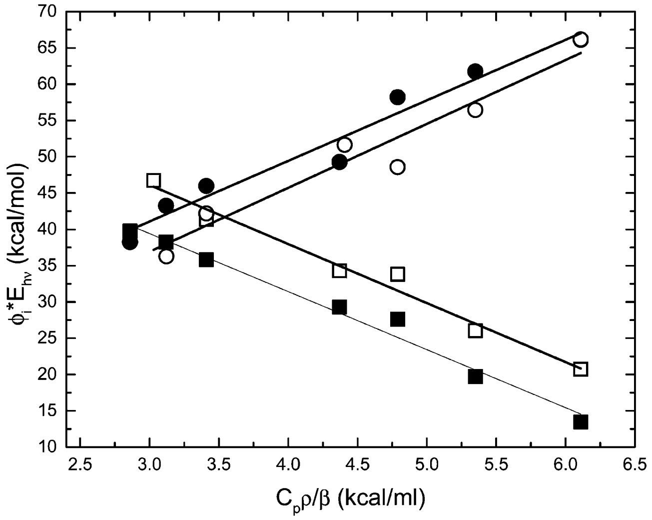

Figure 3. Plot of $\phi_i{}^*E_{h\nu}$ for Ru(bpy)$_2$(dcbpy) at pH 2 (open symbols) and pH 6 (solid symbols). The $\phi_i{}^*E_{h\nu}$ values associated with the formation of the ^{3}MLCT state are shown as squares, and the $\phi_i{}^*E_{h\nu}$ values associated with the subsequent decay are shown as circles. The excitation wavelength was 355 nm.

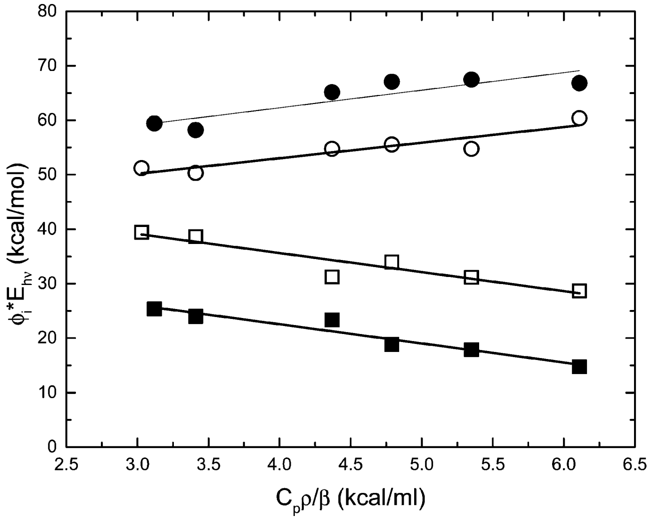

Figure 4. Plot of $\phi_i{}^*E_{h\nu}$ for Ru(bpy)$_3$ at pH 6 (solid symbols) and pH 2 (open symbols). The $\phi_i{}^*E_{h\nu}$ values associated with the formation of the ^{3}MLCT state are shown as squares, and the $\phi_i{}^*E_{h_\nu}$ values associated with the subsequent decay are shown as circles. The excitation wavelength was 355 nm.

Table 2. Values of Volume and Enthalpy Changes upon Excitation and Subsequent Decay of the ^{3}MLCT State for Ru(bpy)$_3$ and Ru(bpy)$_2$(dcbpy)[a]

complex	pH	ΔV_{form} (mL mol^{-1})	ΔH_{form} (kcal mol^{-1})	$\Delta V_{\mathrm{decay}}$ (mL mol^{-1})	$\Delta H_{\mathrm{decay}}$ (kcal mol^{-1})
Ru(bpy)$_3$	6	-3.5 ± 0.5	43.9 ± 2.2	3.2 ± 0.8	-49.4 ± 3.9
	2	-3.5 ± 0.6	31.5 ± 3.1	2.9 ± 0.6	-41.6 ± 2.5
Ru(bpy)$_2$(dcbpy)	6	-7.9 ± 0.4	17.1 ± 2	8.3 ± 0.7	-16.0 ± 3.0
	4	14 ± 3	113 ± 14	-12 ± 4	-99 ± 17
	2	-8.2 ± 0.9	13.7 ± 4.1	7.5 ± 0.8	-12.4 ± 3.3

[a] The errors correspond to the standard deviation of linear fits.

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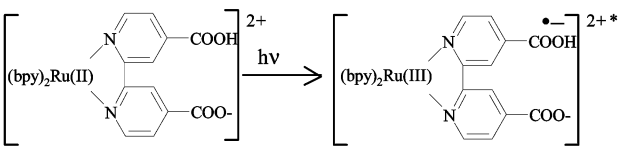
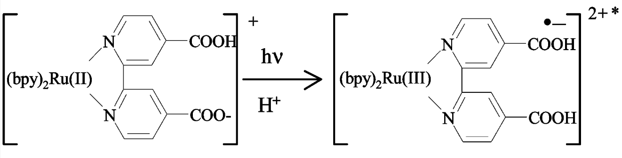
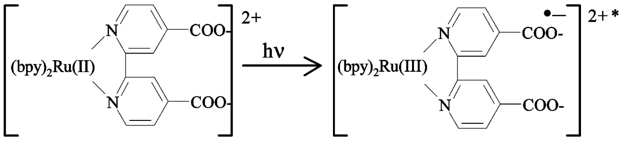
Table 3

pH	reaction	$\Delta V_{form}/\Delta H_{form}$
2		-8.2 ml mol^{-1}/ 13.7 kcal mol^{-1}
4		14 ml mol^{-1}/ 113 kcal mol^{-1}
6		-7.9 ml mol^{-1}/ 17.1 kcal mol^{-1}

state from its emission maxima (48 kcal mol^{-1}).[21] In contrast to the solvent independent behavior of Ru(bpy)$_3$, the volume and enthalpy changes coupled to the formation of the ^{3}MLCT state of Ru(bpy)$_2$(dcbpy) exhibit a strong pH dependence. We have observed a contraction of ~ -8 mL mol^{-1} accompanying the formation of the excited state at pH 6 and 2 and a volume expansion of $\sim$14 mL mol^{-1} at pH 4. From previous spectrophotometric titrations, two pK_a values for the ground state of Ru(bpy)$_2$(dcbpy) have been reported, pK_{a1} = 1.75 and pK_{a2} = 2.8−2.9.[9,10,22] Several values have been reported for the pK_a* value of the ^{3}MLCT state. Nazeeruddin and Kalyanasundaram have observed a single pK_a* value of 4.25 from measurements of the pH dependence of the fluorescence emission intensities.[10] On the contrary, Lay and Sasse[22] have determined two pK_a* values for the excited state, pK_{a1}* = 3.4 and pK_{a2}* = 4.5.

At pH 6, the ground state and the excited state are both expected to be deprotonated, and the observed volume change should reflect the formation of the excited state without a concomitant proton transfer reaction. In general, the reaction volume change can be considered as the sum of an intrinsic and solvation component:

$$\Delta V = \Delta V_{\text{stuct}} + \Delta V_{\text{solv}} \tag{4}$$

where ΔV_{struct} describes the structural volume due to changes in bond length and bond angle during the formation of the product. Volume changes associated with changes in polarity, electrostriction, and dipole moment during the reaction are represented by ΔV_{solv}. For the ^{3}MLCT excited state of ruthenium complexes, there is an ambiguity in describing the excited state. The excited electron can be either localized, [Ru(III)(bpy$^{\bullet-}$)(bpy)]$^{2+}$*, or delocalized, [Ru(III)(bpy$^{1/3\bullet-}$)$_3$]$^{2+}$*, on the bipyridine ligands. From transient resonance Raman and IR measurements, there is direct evidence for localization in the equilibrated excited state.[7] Although the lowest MLCT state is localized, the excited electron undergoes a rapid subnanosecond ligand-to-ligand electron transfer, as shown by time-resolved polarization measurement.[23] However, on the PAC time scale, the excited state electron undergoes rapid exchange between all ligands, leading to an average excited state dipole moment of close to zero. Since the ground state also has a dipole moment of zero (due to the spherical symmetry of the complex), there would be minimal contribution to the volume changes due to electrostriction, and the observed volume change should correspond to ΔV_{struct}. In previous studies, the volume contraction measured for the excitation of Ru(bpy)$_3$ has been attributed to the shortening of the Ru−bpy bond upon excited state formation.[11,12]

For the Ru(bpy)$_2$(dcbpy) complex, the presence of a carboxylic group on one of the bipyridine ligands may cause more pronounced localization of the excited electron on the substituted ligand in the ^{3}MLCT state and thus minimize fast ligand-to-ligand electron exchange, leading to a change of the dipole moment in the excited state. For such a case, the observed volume change would include the structural contribution as well as a contribution due to electrostriction. Considering the same structural changes for the ^{3}MLCT state of Ru(bpy)$_2$(dcbpy) as for its parent complex ($\Delta V = -3.5$ mL mol^{-1}), we found that the volume change due to electrostriction is ~ -4.5 mL mol^{-1}. Previously, Feitelson and Mauzerall reported a similar volume change of -2.4 mL mol^{-1} for the charge separation between triplet zinc uroporphyrin and naphthoquinone-2-sulfonate in water.[24]

At pH 4, a volume change of 14 mL mol^{-1} and an enthalpy change of 113 kcal mol^{-1} upon ^{3}MLCT state formation is observed. In addition to the oxidation of the metal center and localization of the excited electron on the dicarboxybipyridine ligand, the protonation of one carboxylic acid group due to the formation of the excited state is expected on the basis of the reported pK_a values for the ground and excited states. The observed volume change thus represents the sum of the volume change due to the protonation of the carboxylic

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group (ΔV_{prot}) and the volume change due the metal ligand change transfer (ΔV_{MLCT}). Using $\Delta V_{\mathrm{MLCT}} = -8$ mL mol^{-1} and the observed value $\Delta V = 14$ mL mol^{-1}, ΔV_{prot} is estimated to be ~22 mL mol^{-1}. Previously, a volume expansion of 11 mL mol^{-1} was reported for the protonation of aliphatic carboxylic acids.[25] It has been shown that the solvation of a proton leads to a volume change of ~ −5 mL mol^{-1}. Hence, for the protonation of a carboxylic group, a volume change of ~16 mL mol^{-1} is expected and is in agreement with the observed value. Losi and Viappiani have shown that the deprotonation of the excited state of naphthols results in a volume contraction between −11 and −16 mL mol^{-1}.[13] These values are in the range of the observed value for the protonation of Ru(bpy)$_2$(dcbpy).

At pH 2, we observe a volume decrease of −8 mL mol^{-1} for the formation of the ^{3}MLCT state. This value is the same as the volume change observed at pH 6, indicating the absence of the protonation/deprotonation reaction at pH 2. According to the pK_a values reported for the ground state, the Ru(II)(bpy)$_2$(dcbpy) complex is monoprotonated at this pH.[9,10,22] This indicates that the complex is also expected to be monoprotonated in the excited state, since no volume change due to protonation was observed. Hence, the reported pK_{a1}* value of 3.1 appears to be too high, and we propose that the pK_{a1}* value is <2. In fact, Shimidzu et al. have proposed from emission measurements that, at pH 1.5, the Ru(bpy)$_2$(dcbpy) complex is monoprotonated in the excited state.[26]

The enthalpy changes for the formation and the decay of the ^{3}MLCT state determined at pH 6 and 2 are ~17 kcal mol^{-1} and 13 kcal mol^{-1}, respectively. These values indicate the stabilization of the ^{3}MLCT state in the Ru(bpy)$_2$(dcbpy) complex as compared to the Ru(bpy)$_3$ complex. On the other hand, the values obtained by PAC are considerably lower than the values obtained from the fluorescence measurements. On the basis of the emission maxima, the energy of the triplet state was found to be 43 and 41 kcal mol^{-1} for the deprotonated Ru(bpy)$_2$(dcbpy) complex and for the protonated complex, respectively.[21] The enthalpy change measured using PAC may not match the energy of the ^{3}MLCT state determined by fluorescence emission due to the fact that optical methods do not include the enthalpy change of the solute as well as of the surrounding solvent. Borsarelli and Braslavsky[11] have proposed that such contributions may be significant in the case of solutes forming strong hydrogen bonds with solvent molecules.

Summary

Formation of the ^{3}MLCT state of Ru(bpy)$_2$(dcbpy) is accompanied by a volume change of ~ −8 mL mol^{-1}. The observed volume contraction for this complex is larger than that observed for Ru(bpy)$_3$, in agreement with more significant localization of the excited electron on the substituted ligand. The additional contraction is attributed to electrostriction in the excited state due to a change in the excited state dipole moment. At pH 4, a positive volume change of 14 mL mol^{-1} was observed, consistent with the protonation of the excited state at that pH value. No proton transfer reaction was observed at pH 2, and the measured volume change corresponds to that measured at pH 6, indicating that the Ru(bpy)$_2$(dcbpy) complex is monoprotonated at pH 2.

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