J. Phys. Chem. A **2006,** *110,* 10185−10190

Photoinduced Electron Transfer from Tetrasulfonated Porphyrin to Benzoquinone Revisited. The Structural Volume-Normalized Entropy Change Correlates with Marcus Reorganization Energy[†]

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Received: April 27, 2006; In Final Form: July 5, 2006

Time-resolved laser-induced optoacoustic spectroscopy was used for the determination of the enthalpy, $\Delta_T H$, and structural volume changes, $\Delta_T V$, concomitant with triplet state formation upon excitation of *meso*-tetrakis-(4-sulfonatophenyl)porphyrin, $TSPP^{4-}$, as well as with the triplet state electron-transfer (ET) quenching by benzoquinone, BQ ($\Delta_R H$ and $\Delta_R V$). The values of $\Delta_T H$ and $\Delta_T V$ for $^3TSPP^{4-}$ formation in the presence of different cations (Li^+, Na^+, K^+, NH_4^+, and Cs^+) correlated with each other and afforded a value of $\Delta_T G = 140 \pm 20$ kJ mol^{-1}, equal to the value of E_T at 77 K, but much larger than the $\Delta_T H$ values in solution at room temperature, due to the large entropic factor in solution. The influence of the cations on $\Delta_T H$ and $\Delta_T V$ (a contraction ranging from 5.4 to 3.8 cm^3 mol^{-1}) is attributed to changing chromophore−water interactions in the ground and triplet states. Upon quenching of $^3TSPP^{4-}$ by BQ, the quantum yield of free radical formation, $\Phi_R = 0.66 \pm 0.04$, is the same in the solutions of the five cations. The values of $\Delta_R H$ and $\Delta_R V$ are small and have a large error. The energy level of the free radicals formed is thus very similar to that of $^3TSPP^{4-}$. $T\Delta_R S$ and $X = T\Delta_R S/\Delta_R V$, i.e., the structural volume change-normalized entropy change for free radicals formation, were derived using average values of $\Delta_R H$ and $\Delta_R V$ together with the calculated $\Delta_R G°$. The measured Marcus reorganization energy, λ, and X fall into the λ vs X linear dependence we previously found for the radical formation upon ET quenching of triplet flavins (^{3}FMN and ^{3}FAD) by amines and amino acids. Thus, $X = T\Delta_R S/\Delta_R V$ in aqueous solutions is a property of the particular donor−acceptor pair linearly correlated to the corresponding Marcus reorganization energy. The value of X is much larger than the predicted value applying the electrostriction concepts in view of the noncontinuum nature of the aqueous solutions.

Introduction

Photosynthesis is the most important clean energy source in the world and the interest in mimicking it has induced many researchers to study both the basic principles and the more technological aspects underlying an efficient energy conversion.[1−3]

The study of model electron-transfer systems using porphyrins as chromophores was recognized already many years ago as a prerequisite for the understanding of the molecular processes in photosynthetic units.[4] An interesting system from the technological point of view involves coupling of the photoexcitation of the water-soluble *meso*-tetrakis(4-sulfonatophenyl)porphyrin ($ZnTSPP^{4-}$)/methyl viologen system with hydrogenase in micelles acting as vectorial nanoreactors, to produce hydrogen.[5]

It is widely known that the photosynthesis process begins with sunlight absorption, which initiates a chain of electron-transfer (ET) events. The theory developed by Marcus[6] explains basic concepts of the diabatic ET and shows that the ET rate constant depends on the reorganization energy. This energy is associated with changes in both the internal structure of the moiety involved and the organization of the surrounding medium.

Taking into account that laser-induced optoacoustics spectroscopy (LIOAS) is an appropriate technique for the monitoring of structural volume and enthalpy changes upon photoinduced reactions in solution,[7,8] we have analyzed the possible correlation between the structural volume changes associated with ET reactions and the corresponding Marcus reorganization energy.

The LIOAS technique has been applied to various systems in which photoinduced ET (PET) takes place.[9−13] In systems in which the chromophore−solvent interactions determine the values of the enthalpy and the entropy changes (as is often the case in aqueous solutions), the compensation of the structural volume and the enthalpy changes during ET upon changes in the nature of the medium can be interpreted as an entropy−enthalpy compensation. This compensation leads to the determination of the entropy changes for the particular step analyzed, in general with a decay time of hundreds of nanoseconds.[9−13] This information is not attainable from any other technique.

LIOAS studies have shown that the photoinduced formation of the triplet state of $ZnTSPP^{4-}$ ($^3ZnTSPP^{4-}$) is accompanied by a contraction of 1.6 cm^3 mol^{-1}, attributed to bond-length changes without a strong contribution of the solvent shell.[14] A small contraction of ca. 2.4 cm^3 mol^{-1} was also observed upon triplet formation of uroporphyrin in aqueous medium that, however, was suggested to arise from solvent contraction.[15] The much larger contraction of 7 cm^3 mol^{-1} found in the case of $^3TSPP^{4-}$ formation was attributed to a large extent (ca. 70%) to a contraction of the solvent shell around the center of the macrocycle upon formation of the triple state.[16]

In view of the importance of the water structure in determining the magnitude of the volume changes,[9−13] and the possible correlation of these changes with the Marcus reorganization

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[†] Abbreviations: BQ, 1,4-benzoquinone; ET, electron transfer; LIOAS, laser-induced optoacoustic spectroscopy; λ, Marcus reorganization energy; PET, photoinduced electron transfer; ST, several temperature; $TSPP^{4-}$, *meso*-tetrakis(4-sulfonatophenyl)porphyrin.

10.1021/jp062579e CCC: $33.50

energy,[6] we decided to study the ET form $^3TSPP^{4-}$ to benzoquinone (BQ) in water and analyze the effect of addition of structure-organizing (e.g., Li^+) and -perturbing (e.g., Cs^+) monovalent cations. We report in this paper the enthalpy and structural volume changes for $^3TSPP^{4-}$ formation ($\Delta_T H$ and $\Delta_T V$, respectively) and for the ET quenching step affording free radicals ($\Delta_R H$ and $\Delta_R V$) in the presence of BQ, in various cations phosphate salts solutions and analyze their possible correlation with the Marcus reorganization energy (λ).

Experimental Section

Materials. *meso*-Tetrakis(4-sulfonatophenyl)porphyrin, $TSPP^{4-}$ (Porphyrin Products), 1,4-benzoquinone, BQ (Aldrich, 98%), lithium dihydrogen phosphate, LiH_2PO_4 (Aldrich, 99%), lithium hydroxide, LiOH (Sigma, 99%), sodium dihydrogen phosphate, NaH_2PO_4 (Merck, 99%), disodium hydrogen phosphate, Na_2HPO_4 (Fluka, 99%), potassium dihydrogen phosphate, KH_2PO_4 (Merck, 99%), dipotassium hydrogen phosphate, K_2HPO_4 (Merck, 99%), cesium dihydrogen phosphate/dicesium hydrogen phosphate, CsH_2PO_4/Cs_2HPO_4 (Aldrich, 99%), ammonium dihydrogen phosphate, $NH_4H_2PO_4$ (Fluka, 99%), diammonium hydrogen phosphate, $(NH_4)_2HPO_4$ (Fluka, 99%), and the calorimetric reference Bromocresol Purple, BCP (Fluka, standard grade) was used as received. Water was deionized and purified by a Millipore-Milli-Q System apparatus.

Solutions. The buffer solutions of the various cations (Na^+, NH_4^+, K^+, Cs^+) were prepared by dissolving the respective monohydrogen phosphate (HPO_4^{2-}) and dihydrogen phosphate ($H_2PO_4^-$), to give a final concentration of 25×10^{-3} M of each. When Li^+ was used, the solution was prepared by dissolving the appropriate amount of LiH_2PO_4 and LiOH to give a solution 50×10^{-3} and 25×10^{-3} M, respectively.

$TSPP^{4-}$ (1.2×10^{-3} M) and BQ (32×10^{-3} M) solutions were prepared by dissolving the necessary amount of $TSPP^{4-}$ and BQ in the different buffer solutions. Solutions were diluted with the buffers to a final concentration of $[TSPP^{4-}] = 20 \times 10^{-6}$ M and $[BQ] = 0.256 \times 10^{-3}$ M. The solutions were purged with argon during 40 min before spectroscopic measurements.

UV–Visible Spectra. The spectra were recorded using a Shimadzu UV-2401 PC spectrophotometer. The absorption spectra of all solutions were the same before and after the LIOAS and flash photolysis experiments.

Transient Absorbance. The nanosecond-flash photolysis equipment used for the transient absorbance experiments has already been described[17] and was used as a simplified single beam equipment. Excitation by the 11 ns pulses at 532 nm was from a Nd:YAG laser (SL802, Spectron Laser System) using the second harmonic of the laser. The analyzing beam from a pulsed 150 W Xe arc was focused into the 1 cm optical path length sample cuvette, perpendicular to the excitation, after passing through a monochromator, focused again into a second monochromator slit and detected by a Hamamatsu R3896 photomultiplier wired with a five dynode chain for rapid detection. The output of the photomultiplier was fed through a 50 Ω load resistor into a TDS 520A Tektronix transient recorder. The signals were taken by and elaborated with a homemade program in a Compaq Tru64 Unix workstation. A total of 49 signals were averaged for each decay. A personal computer with Origin program was used for further treatment of the averaged transient absorbance data.

The efficiency of radical formation upon ET after $TSPP^{4-}$ excitation in 75×10^{-3} M of Li^+, NH_4^+, and K^+ phosphate buffer with 0.256×10^{-3} M BQ, Φ_R, was determined by the comparative method with eq 1.[18]

$$\Phi_R = \Phi_T \frac{\Delta_R A}{\Delta_T A} \frac{\epsilon_T}{\epsilon_R} \qquad (1)$$

The initial triplet absorption, $\Delta_T A$, was used as internal reference ($\Phi_T = 0.78$).[19,20] It was obtained by extrapolation to 0 time of the monoexponential fitting of the transient absorption decay at 460 nm (Figure 1). The molar absorption coefficient of $^3TSPP^{4-}$, and of the $TSPP^{3-\bullet}$ radical at 460 nm, were $\epsilon_T = 65\,000$ M^{-1} cm^{-1} and $\epsilon_R = 21\,000$ M^{-1} cm^{-1}, respectively.[21] The transient absorbance remaining after 4 μs upon quenching of $^3TSPP^{4-}$ (Figure 1), due to the absorption by $TSPP^{3-\bullet}$, $\Delta_R A$, and measured at 6 μs, was used for the determination of Φ_R.

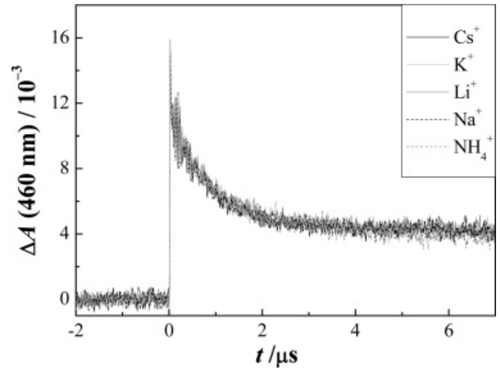


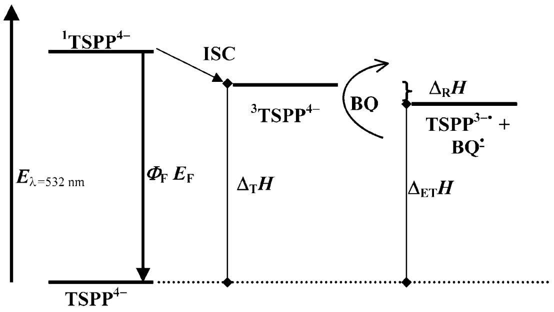
Figure 1. Transient absorption decays observed at 460 nm and at 20 °C upon excitation of $TSPP^{4-}$ solutions in the presence of BQ in 50×10^{-3} M phosphate buffer (25×10^{-3} M $H_2PO_4^-$ and 25×10^{-3} M HPO_4^{2-}) for several cation (Cs^+, K^+, NH_4^+, Na^+, Li^+), with a 15 ns laser pulse at 532 nm [$A(532) = 0.10$]. The absorbance remaining at $t > 3$ μs is due to the absorption of the porphyrin radical anion $TSPP^{3-\bullet}$.

LIOAS. The setup has been already described in several papers.[7,22,23] Excitation at 532 nm was performed with the laser described above. Incident laser energies were varied with a neutral density wedge and measured with a pyroelectric energy meter (RJP732 head connected to a Rm-6600A Universal Radiometer, Laser Probe Inc.). The measurements were performed in the linear regime of amplitude vs laser radiant energy, up to 200 μJ/pulse. The cuvette was in a temperature-controlled (±0.02 °C) cuvette holder FLASH 100 (Quantum Northwest, Spokame, WA) equipped with a V103-RM ultrasonic transducer. The signal was fed into a 5662 preamplifier (Panametrics Inc., Waltham, MA). A total of 100 acoustics waves were averaged for the sample and calorimetric reference each time under the same conditions. Absorbance at λ_{exc} for the calorimetric reference and the samples were matched within 2% and were ca. 0.10 (the exact value depending on the sample). The laser beam was shaped by a 0.5 mm width slit in front of the cuvette.

LIOAS Signal Handling. The procedure to analyze the LIOAS signal has been widely described in many publications and reviewed.[7,11,22,24] The time evolution of the pressure wave was assumed to be a sum of monoexponential functions. The convolution of the decay function and the reference signal yielded the fractional amplitudes (φ_i) and the lifetime (τ_i) of the transient (Sound Analysis 3000, Quantum Northwest Inc., Spokane, WA). The time window was between 40 ns and 3 μs. At a given temperature and for each resolved *i*th step the fractional amplitude φ_i is the sum of the fraction of absorbed energy released as heat (α_i) and a term containing the molar structural volume change ($\Delta_i V$), according to eq 2,[22,25]

$$\varphi_i = \alpha_i + \frac{\Phi_i \Delta_i V}{E_\lambda}\left(\frac{c_p \rho}{\beta}\right)_T \qquad (2)$$

SCHEME 1: PET between TSPP^{4-} *meso*-Tetrakis(4-sulfonatophenyl)porphyrin and Benzoquinone (BQ)



where E_λ is the molar excitation energy, Φ_i is the quantum yield of the respective process, $\alpha_i = q_i/E_\lambda$ (with q_i the heat liberated in step i), $\beta = (\partial V/\partial T)_P/V$ is the volume expansion coefficient, c_p is the specific heat capacity at constant pressure, and ρ is the mass density of the solvent, the last three quantities at temperature T. The temperature at which $\beta = 0$, $T_{\beta=0}$, was smaller in the presence of different cation buffers than in neat water (3.90 °C)[7] and the values recorded were between 3.10 and 3.60 °C. Owing to this observation, the values of $(c_p\rho/\beta)_T$ were determined by comparing the LIOAS signals of a reference in neat water with those in the desired solution at each temperature. A significant change was observed only at temperatures <15 °C. The measurements were performed with BCP following the procedure described by Gensch et al.[7]

Results

The production of ^{3}TSPP^{4-} as well as the ET reaction between ^{3}TSPP^{4-} and BQ were carried out in the presence of 75×10^{-3} M of Li$^+$, Na$^+$, K$^+$, NH$_4^+$ and Cs$^+$ as phosphate salts at pH 6.85 ± 0.05. The absorption spectra of the porphyrin with and without BQ in the presence of the various cations were all identical.

Transient Absorption Data: Quantum Yield of ET and Lifetime Dependence on Temperature. The ^{3}TSPP^{4-} transient absorbance decays at 20 °C in the presence of the five cations and excited with identical laser energies showed no differences (Figure 1). Thus, Φ_T and Φ_R are the same for all cations used, within experimental error. The quantum yield of free radical formation upon ET quenching of ^{3}TSPP^{4-} by BQ (Scheme 1), determined from the transient absorbance at 460 nm, 6 μs after the laser pulse with eq 1, was $\Phi_R = 0.66 \pm 0.04$ for all cation solutions.

The Gibbs activation energies, $\Delta G^\ddagger$, were calculated using the semiclasical Marcus[26] relationship (eq 3). The $\ln(T^{1/2}/\tau)$ was plotted as a function of T^{-1} (Figure 2, Table 1). Within the relatively small temperature range and the experimental error, a small increase in $\Delta G^\ddagger$ with the structure-organizing monovalent cations is observed. With the slope in Figure 2 (eq 3), eq 4, and the calculated $\Delta G°$ (vide infra), the value of the Marcus reorganization energy, λ, was derived (the same for the five cations).

$$\ln\left(\frac{T^{1/2}}{\tau}\right) = \ln A - \frac{\Delta G^\ddagger}{RT} \tag{3}$$

$$\Delta G^\ddagger = \frac{(\Delta G° + \lambda)^2}{4\lambda} \tag{4}$$

LIOAS Results. The several-temperatures method in LIOAS was used for the elaboration of the data upon excitation of TSPP^{4-} with and without BQ. The sample signals were convoluted with those of the reference using a sum of single-exponentials function for the time evolution of the pressure wave in the samples. Only one exponential term was observed for TSPP^{4-} in the absence of BQ (Table 2), whereas two terms were needed for the fitting in the presence of BQ.

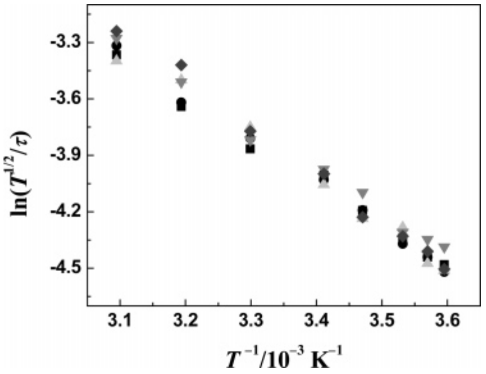


Figure 2. Modified Arrhenius plot (eq 3) for the determination of the Gibbs activation energy, $\Delta G^\ddagger$, for the ET reaction between TSPP^{4-} and BQ. pH = 6.85 ± 0.07, [TSPP^{4-}] = 20×10^{-6} M, [BQ] = 0.256×10^{-3} M, λ_{exc} = 532 nm, λ_{obs} = 460 nm, in 50×10^{-3} M phosphate buffer (25×10^{-3} M H$_2$PO$_4^-$/25×10^{-3} M HPO$_4^{2-}$) of (◆) Li$^+$, (●) Na$^+$, (▲) NH$_4^+$, (▼) K$^+$, and (■) Cs$^+$.

TABLE 1: Activation Gibbs Energies, $\Delta G^\ddagger$, for the ET Reaction between ^{3}TSPP^{4-} and BQ at Several Temperatures and in Various 50×10^{-3} M Ion Phosphate Salts[a]

ion	$\Delta G^\ddagger$/ kJ mol^{-1}	λ/ kJ mol^{-1} [b]
Li$^+$	21.3 ± 0.6	155
Na$^+$	19.3 ± 0.5	147
NH$_4^+$	18.5 ± 0.9	143
K$^+$	18.4 ± 0.7	143
Cs$^+$	18.0 ± 0.7	14

[a] Results obtained with eq 3 with data in Table S2; pH = 6.85 ± 0.07, [TSPP^{4-}] = 20×10^{-6} M, [BQ] = 0.256×10^{-3} M, λ_{exc} = 532 nm, λ_{obs} = 460 nm, with correlation $r^2 > 0.99$. [b] λ calculated with $\Delta G^\ddagger = (\Delta G° + \lambda)^2/4\lambda$, $\Delta G° = -40.3$ kJ mol^{-1}.

TABLE 2: Fraction of Heat Released, α_1, and Structural Volume Change, $\Delta_T V$, for ^{3}TSPP^{4-} Formation[a]

	α_1	q_1/ kJ mol^{-1}	$\Delta_T V$/ cm^3 mol^{-1} [b]	$\Delta_T H$/ kJ mol^{-1} [b]
Li$^+$	0.76	171 ± 9	−5.4 ± 0.1	56 ± 9
Na$^+$	0.71	161 ± 5	−4.9 ± 0.1	69 ± 5
NH$_4^+$	0.68	154 ± 7	−4.6 ± 0.1	78 ± 7
K$^+$	0.69	155 ± 5	−3.96 ± 0.09	77 ± 5
Cs$^+$	0.66	148 ± 4	−3.81 ± 0.08	86 ± 4

[a] λ_{exc} = 532 nm, pH = 6.85 ± 0.07, [TSPP^{4-}] = 20×10^{-6} M, [BQ] = 0.256×10^{-3} M. [b] The errors are standard deviations of the data from several measurements.

Of the four parameters necessary for the fitting of the LIOAS signals in the presence of BQ, i.e., the two lifetimes τ_1 and τ_2 and the two preexponential factors φ_1 and φ_2, τ_2 was fixed to the value obtained in the flash photolysis experiments, inasmuch as this lifetime corresponds to the formation of the free radicals, whereas τ_1 corresponds to the fast ^{3}TSPP^{4-} formation. The values derived are in Table 3.

On the basis of simple energy balance considerations, the fraction of heat released during the production of ^{3}TSPP^{4-} in the absence of BQ, α_1, is related to the triplet enthalpy content, $\Delta_T H$, and the fluorescence quantum yield, Φ_F, by eq 5,

$$\Delta_T H = \frac{E_\lambda - \alpha_1 E_\lambda - E_F \Phi_F}{\Phi_T} \tag{5}$$

TABLE 3: Parameters Determined upon Excitation of ^{3}TSPP^{4-} in the Presence of BQ[a]

	α_1	q_1/ kJ mol^{-1}	$\Delta_T V \pm 0.1$/ cm^3 mol^{-1}	$\Delta_T H \pm 10$/ kJ mol^{-1}	α_2	q_2/ kJ mol^{-1}	$\Delta_R V$/ cm^3 mol^{-1}
Li^+	0.78	175 ± 10	−4.8	51	0.05	10 ± 3	2.27 ± 0.06
Na^+	0.73	164 ± 4	−4.8	65	0.06	13 ± 4	2.55 ± 0.09
NH_4^+	0.73	165 ± 8	−4.6	64	0.05	11 ± 5	2.4 ± 0.1
K^+	0.70	158 ± 5	−4.0	72	0.06	14 ± 2	2.05 ± 0.05
Cs^+	0.73	167 ± 3	−4.1	61	0.11	24 ± 4	2.09 ± 0.09

[a] Fraction of heat released for the first and second step as determined by LIOAS, α_1 and α_2, and structural volume change for the formation of ^{3}TSPP^{4-} and for the ET process, $\Delta_T V$ and $\Delta_{ET} V$, respectively, from convolution of a biexponential function and reference signal, $\lambda_{exc} = 532$ nm, pH = 6.85 ± 0.07, [TSPP^{4-}] = 20×10^{-6} M, [BQ] = 0.256×10^{-3} M.

TABLE 4: Enthalpy Change for ^{3}TSPP^{4-} Formation, $\Delta_T H$, and for the Free Radicals formation, $\Delta_{ET} H$, from the Ground State, as Well as Enthalpy Change from ^{3}TSPP^{4-} + BQ to the Free Radicals, $\Delta_R H$ (see Scheme)[a]

phosphate	$\Delta_T H$/ kJ mol^{-1} [b]	$\Delta_{ET} H \pm 30$/ kJ mol^{-1}	$\Delta_R H \pm 40$/ kJ mol^{-1} [c]
Li^+	56 ± 9	51	−5
Na^+	69 ± 5	62	−7
NH_4^+	78 ± 7	75	−3
K^+	77 ± 5	69	−7
Cs^+	86 ± 4	65	−20

[a] $\lambda_{exc} = 532$ nm, pH = 6.85 ± 0.07, [TSPP^{4-}] = 20×10^{-6} M, [BQ] = 0.256×10^{-3} M. [b] The enthalpy changes are from the LIOAS determination with TSPP^{4-} without BQ. [c] Average value −8 kJ mol^{-1}.

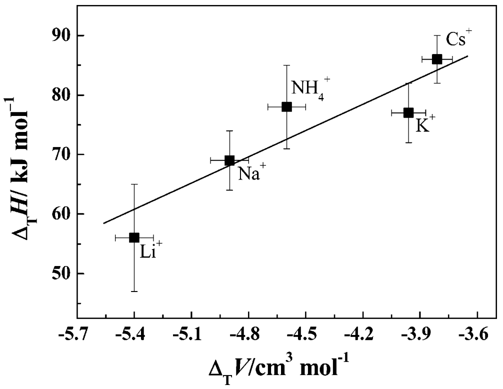


Figure 3. Relationship between the enthalpy change, $\Delta_T H$, and the structural volume change $\Delta_T V$, for ^{3}TSPP^{4-} formation, as derived from LIOAS data. The slope of the linear fitting is 15 ± 4 kJ cm^{-3} and the ordinate 140 ± 19 kJ mol^{-1}.

where the average energy of the fluorescence emission is $E_F = 174$ kJ mol^{-1},[16] $\Phi_F = 0.058$,[16] $\Phi_T = 0.78$,[19,20,21] and $E_\lambda = 224.9$ kJ mol^{-1} is the laser molar energy.

The enthalpy change for the free radicals formation from ^{3}TSPP^{4-} upon electron transfer, $\Delta_R H$ (see Scheme 1), is calculated with eq 6 and α_2 (longer-lifetime process) (Table 4). The other symbols are as above.

$$\Delta_R H = \Delta_T H\left(\frac{\Phi_T - \Phi_R}{\Phi_R}\right) - \frac{\alpha_2 E_\lambda}{\Phi_R} \qquad (6)$$

Discussion

A good linear correlation was observed between the enthalpy change for ^{3}TSPP^{4-} formation, $\Delta_T H$, and the structural volume change associated with this process, $\Delta_T V$ (Figure 3), with a slope 15 ± 4 kJ cm^{-3}. The values of $\Delta_T H$ (Table 2) are at least 40% smaller than previously reported from phosphorescence experiments at low temperature, 140 kJ mol^{-1}.[20] However, the ordinate of 140 ± 20 kJ mol^{-1}, i.e., the value of the heat released at a zero structural volume change, is in good agreement with the value derived from phosphorescence determinations at 77 K (140 kJ mol^{-1}).[20] At 77 K the entropic terms is thus negligible and $\Delta_T H = \Delta_T G$. This is a very interesting result indicating that in fluid media at room temperature the entropic factor constitutes a large contribution to the Gibbs energy for the triplet formation. This entropic factor depends on the degree of organization of the water structure.

This type of compensation between ΔH and ΔV, which can be readily seen as an enthalpy−entropy compensation, has been described previously for photoinduced intra-[9,10] and intermolecular[13,27] ET reactions in aqueous solutions in the presence of various monovalent salts, and also in the decay of the photoisomerized red-shifted transient of sensory rhodopsin II where the solvent properties were widely changed.[28] The compensation reflects the fact that the interaction between the chromophore and the solvent strongly dominates both enthalpy and entropy changes of the process.[29]

Despite the fact that the effect is often too small to be detected, enthalpy−entropy compensations have been observed in several occasions in a wide range of reactions.[29,30] It is important to remark that the LIOAS technique is very sensitive to small changes in the water structure, and therefore, it is a very powerful tool to evaluate these changes. We also note that the values in the extremes in Figure 3 (i.e., for Li$^+$ and Cs$^+$) differ much more than their mutual errors would allow. Thus, application of the statistical criteria proposed by Liu and Guo[30] to all systems analyzed in this paper as well as in our previous studies, has convinced ourselves of the validity of the compensation effect. On the other hand, the value of $\Delta_T H$ for ^{3}TSPP^{4-} formation measured in the presence of BQ (Table 3) shows differences much smaller than those in its absence (Table 2). This is most likely due to the fact that there are too many parameters to fit with the LIOAS signal convoluted using a double exponential function and, therefore, it is not possible to distinguish between the small fractions of heat released. However, an important change is observed in $\Delta_T V$.

The above observations support the concept that the enthalpy and structural volume changes for ^{3}TSPP^{4-} formation contain a large solvent contribution probably because the macrocycle is more strongly hydrogen-bonded with the surrounding water molecules in the triplet state than in the ground state.[16]

On the other hand, the volume change produced upon formation of the radicals varies with the water structure, as supported by the correlation observed between the $\Delta_R V$ values and the tabulated organizing entropies of the cations, $\Delta S°$(cat.) (note that the cations are listed according to the decreasing organizing ability from Li$^+$ to Cs$^+$).[31] However, no correlation, within the large error, between $\Delta_R H$ and $\Delta_R V$ is observed. This is due to the very small $\Delta_R H$ values compared to the PET system previously studied,[9,10,13,27] where good correlations were observed (see values of α_2 in Table 3). This already indicates that the energy content of the free radicals formed is very similar to that of ^{3}TSPP^{4-}.

With the values of the redox potentials for the donor porphyrin from the triplet state, $E(^3\text{TSPP}^{4-}/\text{TSPP}^{3-\bullet}) = 0.34$ V[20] and for the acceptor BQ, $E(\text{BQ}/\text{BQ}^{-\bullet}) = 0.078$ V,[32] and neglecting the Coulombic term, the standard Gibbs energy is calculated for the ET reaction from the triplet state as $\Delta_R G° = -40.3$ kJ mol^{-1}. Taking into account the average value of $\Delta_R H = -8$ kJ mol^{-1} (Table 4), the average $T\,\Delta_R S = 32.3$ kJ mol^{-1} is obtained in the temperature range 7−25 °C, which shows

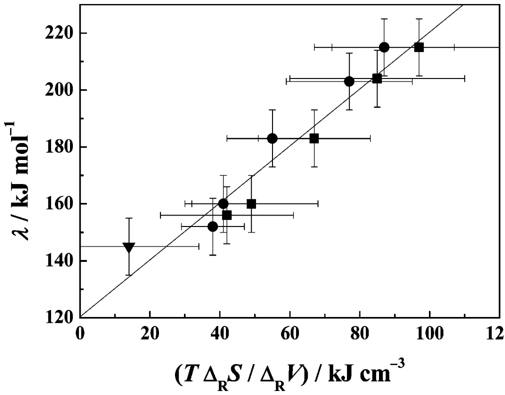


Figure 4. Relationship between $X = T\Delta_RS/\Delta_{ET}V$ and the Marcus reorganization energy, λ, for different ET reactions: (▼) ^{3}TSPP^{4-}; BQ. ET reactions from tryptophan, tyrosine, histidine, triethanolamine, and EDTA to (●) FMN and (■) FAD as acceptors.[12,28] Slope = 1.01 ± 0.09 cm^3 mol^{-1}, $\lambda_{X=0} = 120 \pm 6$ kJ mol^{-1}. Without the data for the system presented in this paper (▼), the parameters for the line are the same within the experimental error, i.e., slope = 1.13 ± 0.9 cm^3 mol^{-1}, $\lambda_{X=0} = 111 \pm 6$ kJ mol^{-1}.

that the entropic change is the driving force for the separation of the free ions and cannot be neglected. This entropic term must come from the solvent reorganization energy (vide infra).

Following our argumentation line in previous papers,[13,27] we calculated $X = T\,\Delta_RS/\Delta_RV = 14 \pm 20$ kJ cm^{-3}, using an average value of Δ_RV.[33] This corresponds to a reorganization energy $\lambda = 145 \pm 10$ kJ mol^{-1}.[34] These values fit well in line with those obtained for the free radical formation upon ET quenching of ^{3}FMN (flavine monucleotide) and ^{3}FAD (flavin adenine dinucleotide) by tryptophan, tyrosine, histidine, triethanolamine, and EDTA (ethylenediaminetetraacetic acid) (Figure 4).[27]

The values represented in Figure 4 empirically afford eq 7, with $\lambda_{X=0} = 120 \pm 6$ kJ mol^{-1} and a slope $B = 1.01 \pm 0.09$ cm^3 mol^{-1}.

$$\lambda = \lambda_{X=0} + BX = \lambda_{X=0} + B\frac{T\Delta_RS}{\Delta_RV} \tag{7}$$

Taking into account that the electrostrictive volume change is the derivative of the relative permittivity with respect to pressure (eq 8), and the electrostrictive entropy change of solvation is given by eq 9,

$$\Delta_{el}V = \frac{\partial\Delta_{el}G}{\partial p} = -\frac{e^2}{2\epsilon_r r}\left(\frac{\partial \ln \epsilon_r}{\partial p}\right)_T \tag{8}$$

$$\Delta_{el}S = \frac{\partial\Delta_{el}G}{\partial T} = \frac{e^2}{2\epsilon_r r}\left(\frac{\partial \ln \epsilon_r}{\partial T}\right)_p \tag{9}$$

it is possible to derive the expected electrostrictive value of $X = T\,\Delta_{el}S/\Delta_{el}V = 2.9$ kJ cm^{-3}, using the tabulated values of $(\partial \ln \epsilon_r/\partial T)_p$ and $(\partial \ln \epsilon_r/\partial P)_T$ in water. X would thus be independent of the nature of the partners and of the radii involved in the ET reaction.[31] The possible changes of $(\partial \ln \epsilon_r/\partial T)_p$ and $(\partial \ln \epsilon_r/\partial P)_T$ in the different phosphate buffers would cancel because all systems presented here (Figure 4) are in the same buffers.

The experimental X values, however, cover a wide range for different systems (Figure 4), although all have been measured in the same solvent. This again shows that electrostriction is not enough to explain the results and specific chromophore−solvent interactions should be considered, e.g., hydrogen bonds, which are different in the various systems and are modified when the various salts are used.[8] The concept of electrostriction was developed for a continuum medium. Water and aqueous solutions are by no means continuum media in view of the strong hydrogen bonds within the water molecules and with the solutes. This should be the major reason for the discrepancies found.

The outer reorganization energy, λ_{out}, i.e., the reorganization energy due to the medium, is approximately calculated using eq 10 (also developed for continuous media),[26]

$$\lambda_{out} = N_Ae^2\left(\frac{1}{2r_a} + \frac{1}{2r_d} - \frac{1}{r_{da}}\right)\left(\frac{1}{n^2} - \frac{1}{\epsilon_r}\right) \tag{10}$$

with N_A Avogadro's constant, e the charge of the electron, ϵ_r the relative permittivity, the radii $r_d = 7$ Å for TPPS,[4−35] $r_a = 2.8$ Å for BQ,[36] and $r_{ad} = r_d + r_a$. The calculation affords the value $\lambda_{out} = 113$ kJ mol^{-1}, which represents a large part of the experimental $\lambda = 145 \pm 10$ kJ mol^{-1} (Figure 2). Thus, despite the limitations of the calculation, it is possible to ascertain that the main part of λ is due to the reorganization of the solvent, in line with the high value of the entropic term (vide supra). Therefore, in the present system the solvent reorganization is the driving force taking the ions from the contact pair into the bulk.

In conclusion, our data indicate that the value of $X = T\,\Delta_RS/\Delta_RV$, with Δ_RV the structural volume change for the production of free radicals upon ET and $T\,\Delta_RS$ the corresponding entropic term, is an intrinsic property of each ET reaction studied, but the widely different X values correlate with the respective observed Marcus reorganization energy, λ, at least in the same aqueous solvent.

Our present data also show that the entropy change due to solvent reorganization is the main driving force for the separation of the free radicals after ET upon quenching of ^{3}TPPS^{4-} by BQ in aqueous solutions and that entropy changes cannot be neglected in aqueous systems.

Finally, we remark that the modification of the noncontinuum water structure by the added ions and the enthalpy−entropy compensation are important concepts helping to understand the factors involved in the ET reaction in this media and could be also an important tool to obtain thermodynamic parameters that are not derived from other techniques. From our data it seems that X is an intrinsic property of each ET reaction studied and it is correlated with the Marcus reorganization energy, at least when the solvent plays an important role in the total reaction driving force.

Acknowledgment. Dedicated to Kurt Schaffner on the occasion of his 75th birthday. G.O.A., V.M., and L.C. are recipients of fellowships from the Alexander von Humboldt Foundation (Germany), DAAD-La Caixa (Barcelona, Spain), and University of Granada (Granada, Spain), respectively. We are indebted to Professor Wolfgang Lubitz for his support and to Heike Deinert, Dagmar Lenk, and Gül Koc-Weier for their able technical assistance.

Supporting Information Available: The ET times for different BQ concentrations as well as for the maximum BQ concentration (0.256 × 10^{-3} M) at various temperatures are listed in two tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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(34) From the two possible λ values as solutions of the semiempirical Marcus equation, $\lambda > -\Delta_R G°$ was chosen because the reaction under study is in the normal activated region of the Marcus equation (note that in our previous paper,[27] the inequality describing this situation was wrongly written).

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