ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 102 (1996) 47–49

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Volume changes on triplet production and quenching: time-resolved optoacoustic studies [1]

Silvia E. Braslavsky

Max-Planck-Institut für Strahlenchemie, Postfach 10 13 65, D-45413 Mülheim an der Ruhr, Germany

Abstract

The volume changes accompanying triplet state formation, decay and quenching in aqueous solution were followed by temperature-dependent, laser-induced, optoacoustic spectroscopy (LIOAS) measurements. The origin of these volume changes mainly involves specific solvent–solute interactions, which are different in the triplet state than in the parent ground state.

Keywords: Charge transfer; Photoacoustics; Triplets; Volume changes

1. Introduction

Photothermal methods are based on the monitoring of changes in the medium produced after light absorption and due to radiationless deactivation [1]. In liquid media, the heat pulse produced by the deactivation processes is transformed into a volume change, which may be monitored by following either the pressure changes with pressure transducers, e.g., piezoelectric elements, or refractive index changes. The former method, called laser-induced optoacoustic spectroscopy (LIOAS) permits the monitoring of deactivation processes between approximately 15 ns and 10 μs [2].

In 1972, Callis et al. [3] reported that, in photoacoustic experiments (i.e., amplitude-modulated excitation and phase-sensitive detection), part of the pressure pulse could be due to the photoinduced structural volume changes arising from light-induced rearrangements in the systems studied. Since the thermal contribution depends on the thermoelastic parameters of the solution, while the structural contribution to the pressure pulse can be considered to be temperature independent in the small temperature range studied, it was proposed that both contributions could be separated in aqueous solutions by performing temperature-dependent photoacoustic measurements. This proposal takes advantage of the strong temperature dependence of the thermal expansion coefficient β of water.

The Parson group applied the method to several types of photoinduced reaction (in general, with biological supramolecular systems; see, for example, Refs. [4] and [5] for a complete account) and determined the photoinduced structural volume changes, as well as the stepwise enthalpy changes, taking place in the microsecond to millisecond time range in these systems.

In more recent times, Peters and coworkers have used temperature-dependent, laser-induced, calorimetric measurements with piezoelectric detection to determine the enthalpy and volume changes photoinduced in haem proteins in aqueous solutions [6] (see also Ref. [5]). Simpler photochemical reactions, as well as more complex systems, have been studied using similar approaches by other groups (see Refs. [2] and [5] for more complete referencing).

In order to understand chromophore–protein interactions in biological photoreceptors more clearly, we have used temperature-dependent LIOAS for the study of several biological supramolecular systems [5], in particular bacteriorhodopsin [7] and photosynthetic units [8,9]. In D1–D2–cyt *b*-559 reaction centre complexes containing no quinone, the formation of the triplet state ^{3}[P680 Pheo] by recombination of the triplet radical pair ^{3}[P680$^+$Pheo$^-$] is accompanied by an expansion of 4.4 ± 1.0 ml mol^{-1} [9].

Since the origin of the structural volume changes (ΔV_R) when triplet states are photoproduced is not completely clear, we performed a series of temperature-dependent LIOAS measurements on systems involving the production and quenching of triplet states. The lecture delivered on the occasion of the London International Conference in Photochemistry reviewed the results of these studies.

---

[1] Invited lecture presented at the XVII International Conference on Photochemistry, London, 1995.

1010-6030/96/$15.00
PII S1010-6030(96)04373-0

2. Experimental section

The experimental details of the system used have been described previously [2,7–9]. Essentially, nanosecond laser pulses were used for excitation, while the pressure pulse was detected with either a Pb–Zr–Ti piezoelectric transducer or with a polyvinylidene fluoride film. The heat integration time, determined by the laser beam cross-section, was between 150 and 600 ns in the various systems studied. Pinholes and slits (the latter permit measurements at lower photon densities) were used to shape the laser beam. The LIOAS signals were amplified, time resolved with a transient digitizer and averaged in order to increase the S/N ratio. A solution of a calorimetric reference was measured under the same conditions as the sample solution [2]. The signal handling has also been described previously [2,7–9]. When transient species with relatively short lifetimes (e.g. triplet states) were produced, reconvolution programs were used [10,11]. In order to exclude multiphoton excitation processes, the linearity of the signals with the laser fluence was always controlled. The temperature was varied between approximately 4 and 25 °C, depending on the system studied.

3. Results and discussion

The values of the structural volume change per photoconverted mole (ΔV_R) associated with intramolecular charge transfer, i.e., the formation of metal-to-ligand charge transfer (MLCT) states (of triplet nature) of Ru(II) bipyridine-cyano complexes in aqueous solution, are attributed mainly to the photoinduced changes in the specific interactions between the complexes and the water molecules in the first solvation shell [11]. In particular, the values determined for the formation of the MLCT state in the homologous series $Ru(bpy)(CN)_4^{2-}$, $Ru(bpy)(CN)_3(CNCH_3)^-$ and $Ru(bpy)(CN)_2(CNCH_3)_2$, which involve expansions for the first two compounds (i.e., $\Delta V_R = 15$, 10 and approximately 0 ml mol^{-1} respectively), directly correlate with the number of cyanide ligands available for donor–acceptor interactions with water. A parallel correlation with the number of cyanide ligands is found for the solvent effect on the MLCT energy of the complexes, as measured from the slope of the plots of the emission energy vs. solvent acceptor number. This correlation confirms that solvent (water in this case) reorganization around a transient species (the MLCT complex) is responsible for the values of ΔV_R observed. For all the Ru cyano complexes analysed, the values of the lifetimes derived from the technique of fitting the LIOAS signal with a reconvoluted signal agree very well with the emission lifetimes, as shown in Table 1.

The values of the enthalpy content obtained from the temperature-dependent LIOAS data (last column in Table 2) are in good agreement with the 0–0 values obtained from the crossing of the absorption and emission curves (value between E_{max} and E_{onset} in Table 1) [11]. This comparison assumes a negligible entropy change.

In the case of intermolecular electron transfer quenching of triplet xanthene dyes (eosin and erythrosin) by metal cyanides in aqueous solution, contractions are observed for the photooxidations, whereas expansions are observed for the photoreductions. These structural volume changes cannot be explained by either intrinsic changes in the molecular parameters, such as the bond lengths or angles, or by electrostriction. Rather, the values of ΔV_R are again largely attributed to water reorganization around the system present after the time window of the experiment (approximately 600 ns in this case [12]). In these cases, the metal cyanides suffer a contraction of the H-bonded water molecules, after the acceptance of the electron from the organic dye triplet state, since there is more electron density on the CN bond in the reduced cyanide. The opposite holds for the organic dye triplet photoreductions.

For electron transfer between $Ru(bpy)_3^{2+}$ and $Fe(H_2O)^{3+}$ in 10 mM H_2SO_4, a contraction of 11 ml mol^{-1} is observed. Smaller values are determined for the above-mentioned photo-oxidations and photoreductions of xanthene dyes [12].

Relatively large contractions are observed for the formation of the triplet states of tetraphenylporphyrin-tetrasulphonate and tetraphenylporphyrin-tetracarboxylate in alkaline solutions. The contraction value (12 ml per photoconverted mole of porphyrin) for the former compound follows a titration curve identical to that of the absorption and fluorescence with $pK_a = 5.0 \pm 0.2$, decreasing by one order of magnitude in acidic medium. This correlation indicates that the values of ΔV_R are associated with changes in the molecular properties of the transient species which induce changes in the aqueous solvation sphere [13].

As indicated in Section 1, an expansion is observed for the formation of the triplet state by recombination of the

Table 1
Emission energies in aqueous solution (kJ mol^{-1}), emission lifetimes τ_{em} and lifetimes measured by LIOAS τ [11]

Compound	E_{max} (77 K)	E_{max} (298 K)	E_{onset} (298 K)	τ_{em} (ns)	τ (ns)
$Ru(bpy)(CN)_4^{2-}$	229.8	196.3	230.2	100	100[a]
$Ru(bpy)(CN)_3(CNCH_3)^-$		215.6	248.2	640	n.d.
$Ru(bpy)(CN)_2(CNCH_3)_2$		232.3	264.6	540	580[b]
$Ru(bpy)(CN)(CNCH_3)_3^+$		244	278	650	630[b]
$Ru(bpy)_2(CN)_2$		194.7	222.3	250	250[b]
$Ru(bpy)_3^{2+}$	200.5	196.3	219.8	670	650[b]

[a] ±20 ns. [b] ±50 ns.

Table 2

Volume change per molecule (ΔV_R) and enthalpy content (ΔH) for the transient species formed on excitation of ruthenium cyano complexes with 355 nm light (unless otherwise stated) [11]. All transients have MLCT character, with the exception of $Ru(bpy)(CN)(CNCH_3)_3^+$

Compound	ΔV_R transient formation (ml mol^{-1})	ΔV_R transient decay (ml mol^{-1})	ΔH (kJ mol^{-1})
$Ru(bpy)(CN)_4^{2-}$	15.3 ± 0.9^a	-16.7 ± 0.9^a	$211 \pm 20^{a,b}$
			$177 \pm 20^{a,c}$
$Ru(bpy)(CN)_3(CNCH_3)^-$	10.3 ± 1.1^d		254 ± 24^d
	8.8^f		239^f
$Ru(bpy)(CN)_2(CNCH_3)_2$	-0.9 ± 0.1^e		$197 \pm 20^{c,f}$
	1.4^f		
$Ru(bpy)(CN)(CNCH_3)_3^+$	-1.0 ± 0.1^e		$261 \pm 20^{c,f}$
	-0.4^f		$274^{b,f}$
$Ru(bpy)_2(CN)_2$	5.1 ± 1.0^a	-6.2 ± 0.9^a	$188 \pm 24^{a,b}$
			$170 \pm 26^{a,c}$
$Ru(bpy)_3^{2+}$	-3.2 ± 0.5^h	$+2.7 \pm 0.5^h$	$192 \pm 20^{c,h}$
	-2.8^f		$210 \pm 20^{b,h,f}$
	-2.1 ± 0.5^g		233 ± 25^g

[a] 0.5 mm slit, calculated by convolution at several temperatures. [b] Calculated from the slow heat. [c] Calculated from the prompt heat, i.e. delivered within the observation window. [d] 0.3 mm pinhole, calculated using amplitudes and several temperatures. [e] 0.3 mm pinhole, calculated using amplitudes and two temperatures. [f] 0.2 mm slit and convolution at two temperatures. [g] 0.2 mm slit, convolution, several temperatures and $\lambda_{exc} = 500$ nm. [h] 0.3 mm pinhole, calculated by convolution at several temperatures.

triplet radical pair on laser excitation of a fully active, quinone-depleted and antenna-depleted photosynthetic reaction centre. This expansion should be attributed to reorganization of the protein either around the radical pair formed on laser pulse excitation, or around the triplet state formed by charge recombination. The measurements afford a triplet formation quantum yield of 0.5 or more, independent of the optical properties of this species [9].

4. Conclusions

In conclusion, the structural volume changes determined in aqueous media by photothermal methods (e.g., LIOAS) serve to indicate the reorganization of the medium around the species resulting from light absorption and, in the case of LIOAS, with lifetimes longer than or (by using deconvolution techniques) of the order of the heat integration time of the experiment. This means lifetimes in the nanosecond to microsecond time range, i.e., the lifetime range of triplet species.

With the systems studied so far in aqueous solution, the values of the structural volume changes observed should be explained by specific solute–solvent interactions which are different for the parent compound than for the transient species present in the time window analysed. Due to the structured nature of water, this effect is particularly notorious for water solutions. The influence of other effects, such as electrostriction [14], may become more important in other, less organized, solvents.

Acknowledgements

The data and conclusions presented here are the result of joint efforts with coworkers and collaborators (authors of the referenced papers). The author greatly acknowledges the able technical assistance of E. Hüttel, D. Lenk, S. Pörting and G. Wojciechowski, and is indebted to Professor Kurt Schaffner for his support and interest in the projects involving photothermal measurements. The financial support by the EU (Project ERBCHBGCT 930313) is acknowledged.

References

[1] A.C. Tam, *Rev. Mod. Phys., 58* (1986) 381–432.

[2] S.E. Braslavsky and G.E. Heibel, *Chem. Rev., 92* (1992) 1381–1410, and references cited therein.

[3] J.B. Callis, W.W. Parson and M. Gouterman, *Biochim. Biophys. Acta, 267* (1972) 348–362.

[4] H. Arata and W.W. Parson, *Biochim. Biophys. Acta, 636* (1981) 70–81.

[5] P.J. Schulenberg and S.E. Braslavsky, in A. Mandelis and P. Hess (eds.), *Progress in Photothermal and Photoacoustic Science and Technology*, Vol III: Life and Earth Sciences, SPIE, 1996, in press.

[6] K.S. Peters, *Angew. Chem. Int. Ed. Engl., 33* (1994) 294–302.

[7] P.J. Schulenberg, M. Rohr, W. Gärtner and S.E. Braslavsky, *Biophys. J., 66* (1994) 838–843.

[8] S. Malkin, M.S. Churio, S. Shochat and S.E. Braslavsky, *J. Photochem. Photobiol. B: Biol., 23* (1994) 79–85.

[9] I. Yruela, M.S. Churio, T. Gensch, S.E. Braslavsky and A.R. Holzwarth, *J. Phys. Chem., 98* (1994) 12 789–12 795.

[10] J. Rudzki Small, L.J. Libertini and E.W. Small, *Biophys. Chem., 42* (1992) 29–48.

[11] J.-L. Habib Jiwan, B. Wegewijs, M.T. Indelli, F. Scandola and S.E. Braslavsky, *Rec. Trav. Chim. Pays-Bas, 114* (1995) 542–548; also *Poster presented at the XVII ICP Conference, London, 1995*.

[12] J.-L. Habib Jiwan, A.K. Chibisov and S.E. Braslavsky, *J. Phys. Chem., 99* (1995) 10 246–10 250.

[13] (a) T. Gensch, C. Viappiani and S.E. Braslavsky, *Poster presented at the XVII ICP Conference, London, 1995*; (b) T. Gensch and S.E. Braslavsky, *J. Phys. Chem.*, in press.

[14] D. Mauzerall, J. Feitelson and R. Prince, *J. Phys. Chem., 99* (1995) 1090–1093.