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Quenching of MgTPP and ZnTPP fluorescence by molecular oxygen

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Abstract

The rate constants for the quenching by oxygen of the lowest excited singlet states of two model metalloporphyrins, MgTPP and ZnTPP, have been measured in acetonitrile, ethanol and toluene and the data used to determine the quenching mechanism. The quenching rates are close to, but significantly slower than, diffusion-limited and do not scale with the solvent viscosity. Quenching via charge transfer in the encounter complex is a minor process even in polar solvents. The major quenching process involves spin-allowed S_1–T_2 radiationless relaxation of the metalloporphyrin in the $^3(M\cdots O_2)$ encounter complex, a process that has a small apparent potential energy barrier.

Keywords: Fluorescence quenching; Metalloporphyrins; Oxygen; Excited singlet states

1. Introduction

Molecular oxygen is routinely excluded when measuring the UV–visible spectroscopic and photon-induced dynamic properties of porphyrins, metalloporphyrins and related compounds because it is known to quench the triplet states of these compounds [1,2] and to be involved in a series of reactions that result in their ultimate photodegradation [3]. Although much is also known about oxygen quenching of the fluorescence of electronically excited singlet states [1,2,4–6], little quantitative information is known about its quenching of the fluorescence of metalloporphyrins and important related molecules other than chlorophyll [7].

This is surprising because metalloporphyrins and related compounds are routinely employed in photodynamic therapy, sometimes under hyperbaric conditions, in which the interaction of their excited electronic states with molecular oxygen is central to the mechanism of the therapeutic process. The data on triplet quenching by oxygen are legion, but a quantitative, mechanistic investigation of the quenching of porphyrin excited singlets appears to have been overlooked. We have therefore measured the rate constants for the quenching of the lowest singlet excited states (S_1, 1 ^1E_u in D_{4h} symmetry) of two model meso-substituted tetraphenylmetalloporphyrins, MTPP (M = Mg, Zn), by molecular oxygen in several solvents and have used the data to elucidate the fluorescence quenching mechanism.

2. Experimental

2.1. Materials

MgTPP and ZnTPP were obtained from Frontier Scientific and were used as received. Acetonitrile, ethanol and toluene were obtained from Sigma–Aldrich, Commercial Alcohols Inc. and Fluka, respectively, and were kept dry by the addition of molecular sieves and air-free handling operations. Samples were degassed by repeated freeze–pump–thaw cycles on a clean vacuum line. Samples were saturated with oxygen (Praxair, 99.999%) by passing the gas through a drying column and then bubbling it through pre-prepared solutions for at least 30 min. Solution concentrations were kept sufficiently low to avoid complications due to solute aggregation.

2.2. Instrumentation

Absorption spectra were taken on a Varian-Cary 500 spectrometer and fluorescence spectra were taken on a Jobin-Yvon Spex Fluorolog instrument. Care was taken to calibrate the spectrometers accurately and to operate them in their regions of linear response. Fluorescence spectra were corrected for variations in

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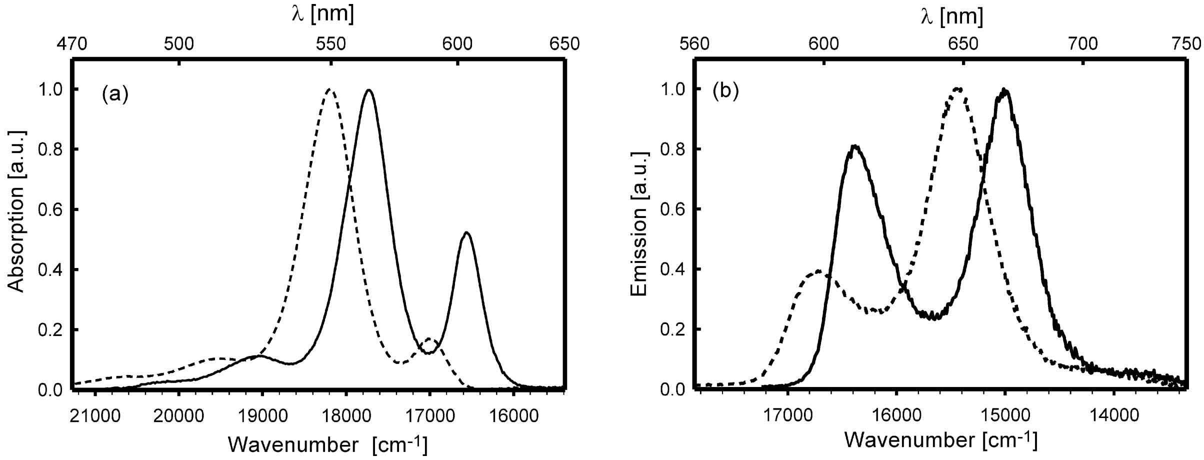


Fig. 1. Normalized absorption (a) and emission (b) spectra of MgTPP (–––) and ZnTPP (- - -) in toluene at room temperature. Spectral bandwidth = 0.9 nm; emission spectra excited at 400 nm for ZnTPP and at 417 nm for MgTPP.

the detector response with emission wavelength and for reabsorption in regions of overlap of the absorption and emission spectra. Fluorescence lifetimes were measured using a coherent mode-locked picosecond Ti:Sapphire laser with pulse picker as an excitation source and a time-correlated single-photon counting detection system, as previously described [8].

2.3. Methods

In a typical fluorescence decay experiment the frequency-doubled output of the laser at 415 or 420 nm was pulse-picked at 4.75 MHz, and the emission in a monochromator-selected bandpass was monitored at the magic polarization angle to avoid rotational diffusion artifacts. Count rates were selected to be always less than 0.1% of the excitation rate to avoid pulse pile-up distortions. Fluorescence lifetimes were obtained by minimizing the differences between the measured temporal fluorescence profile and computed profiles obtained by iterative convolution of trial fluorescence decay functions with the instrument response function (FWHM ca. 80 ps). Reduced Chi-squared (χ^2) values and the distribution of weighted residuals were used as “goodness-of-fit” criteria. Single exponential fluorescence decay functions always provided the best fits at solution concentrations that were sufficiently dilute to avoid solute aggregation. Fluorescence lifetimes were measured in triplicate and no evidence of demetallation, such as that reported by Azenha et al. [6], was found in any of the solutions.

All experiments were conducted at a room temperature of 22 ± 1 °C.

3. Results

The absorption and fluorescence spectra of MgTPP and ZnTPP in degassed toluene are shown in Fig. 1. The spectra are similar in acetonitrile and ethanol, except for small solvatochromic shifts. These spectra are similar to those obtained previously [9] and require no further comment, except to note that the S_1 fluorescence intensities are diminished slightly in air- and oxygen-saturated solutions, whereas the S_2 fluorescence intensities are independent of the concentration of oxygen up to $P_{O_2} = 1$ bar. Prolonged exposure of air- or oxygen-saturated solutions of both metalloporphyrins to light results in photodegradation of the samples and the growth of new absorption bands due to the photoproducts, as previously observed [3]. The spectroscopic data obtained from these spectra are given in Table 1, together with additional data required for further analysis of the quenching results.

Although the decrease of S_1–S_0 fluorescence intensity with increasing oxygen concentration was easily observed using steady-state fluorescence spectroscopy, an accurate, quantitative measure of the quenching effect in dilute solutions could only be obtained by measuring the S_1 fluorescence lifetimes using time-correlated single photon counting. Typical Stern–Volmer plots for the quenching of the S_1 fluorescence of dilute solutions of MgTPP and ZnTPP by molecular oxygen are given in Fig. 2, and the data derived from these experiments are summarized in Table 2. The values of the measured rate constants, k_{Q,O_2}, represent the sum of the rate constants for all parallel

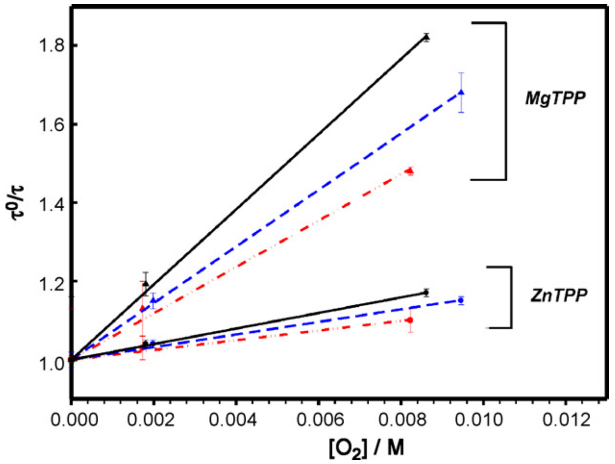


Fig. 2. Stern–Volmer plots for the quenching of the fluorescence of MgTPP (▲) and ZnTPP (●) by molecular oxygen in acetonitrile (—), ethanol (- - -) and toluene (— ● ● —) solutions at room temperature. Linear regressions from (1,0) have slopes and standard deviations given in Table 2.

Table 1
Spectroscopic, electrochemical and related data for MgTPP and ZnTPP in acetonitrile (A), ethanol (E) and toluene (T)

Compound/solvent	Viscosity (cP)	$E(S_1)$[a] (cm^{-1})	E_{ox} (V vs. SCE)	$\Delta G_{S,CT}$ ($kJ\ mol^{-1}$)	$k_{S,CT}$[b] ($\times 10^9\ dm^3\ mol^{-1}\ s^{-1}$)
MgTPP					
A	0.345	16500	0.69[c]	−55.5	4.0
E	1.10	16510	–	–	–
T	0.558	16480	–	–	–
ZnTPP					
A	0.345	16690	0.77[c]	−50.1	3.0
E	1.10	16700	–	–	–
T	0.558	16890	–	–	–
O_2/A	0.345	7880	−0.78[d]		

[a] Wavenumber of overlap of the 0–0 absorption and normalized 0–0 emission bands.

[b] Based on the data of refs. [4,5]. See text.

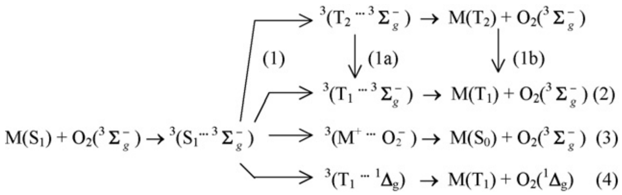
[c] In CH_2Cl_2 (refs. [20,21]). For ZnTPP the values of E_{ox} in CH_2Cl_2 and acetonitrile differ by only 10 mV.

[d] E_{red}: Ref. [5].

processes by which the fluorescence of the metalloporphyrins is quenched by ground state molecular oxygen. The S_1 lifetimes of the metalloporphyrins in degassed solutions are similar to, but more accurate than, those reported previously. The values of τ° in Table 2 should be compared with 9.2 ns (in methylcyclohexane [10]), 8.9 ns (in toluene [9]), 7.6 ns (in benzene [6]) and 5.0 ns (in *o*-chlorobenzene [11]) for MgTPP and 2.7 ns (in methylcyclohexane [10]), 2.8 ns (in toluene [12]), 2.0 ns (in toluene [9]), 2.0 ns (in benzene [6]) for ZnTPP. The solubility data of refs. [13a,b] were used to establish the concentrations of oxygen in the three solvents at room temperature. Excitation of more concentrated solutions ($c > 3 \times 10^{-6}$ M) resulted in progressively shorter measured fluorescence lifetimes, likely due to the effects of aggregation and fluorescence reabsorption artifacts. Only data taken on freshly prepared very dilute solutions ($c < 3 \times 10^{-7}$ M for MgTPP and $c < 3 \times 10^{-6}$ M for ZnTPP) are reported here.

4. Discussion

The possible mechanisms by which molecular oxygen can quench excited singlet states of organic compounds in dilute fluid solution are well-established and are summarized in Scheme 1, using the notation of refs. [4,5].



Scheme 1.

In Scheme 1, process (1) followed by either (1a) or (1b) – electron spin-allowed radiationless transitions either within the encounter complex or following its dissociation – produce the same net result as process (2). The two processes are identified separately here because $T_2({}^3E_u)$ lies below S_1 in MgTPP and ZnTPP and is expected to be formed in preference to T_1 (also ${}^3E_u$) because of the closer S_1–T_2 electronic energy match and resulting more favorable electronic spin–orbit coupling and Franck–Condon factors [14]. Process (4) is allowed on spin conservation grounds but will not occur at a competitive rate because the S_1–T_1 energy spacings in MgTPP and ZnTPP are substantially smaller than the $O_2({}^3\sum_g^-)$ to $O_2({}^1\Delta_g)$ excitation energy of 94 $kJ\ mol^{-1}$. Direct quenching of S_1 to the ground state without intervention of a charge-transfer intermediate is not competitive because of the large electronic energy mismatch between the initial and final product states [14]. This leaves two electron

Table 2
Fluorescence lifetime data, Stern–Volmer constants and bimolecular quenching constants for MgTPP and ZnTPP in acetonitrile, ethanol and toluene at 295 K

	Solvent					
	Acetonitrile		Ethanol		Toluene	
	MgTPP[a]	ZnTPP[a]	MgTPP[a]	ZnTPP[a]	MgTPP[a]	ZnTPP[a]
τ_{av}^0 [ns][b]	8.23 ± 0.16	2.02 ± 0.01	8.11 ± 0.01	2.07 ± 0.02	8.78 ± 0.13	2.13 ± 0.02
$\tau_{av}^{1/5}$ [ns][b]	6.90 ± 0.03	1.94 ± 0.01	7.05 ± 0.02	2.00 ± 0.01	7.77 ± 0.07	2.06 ± 0.03
$\tau_{av}^{1.0}$ [ns][b]	4.58 ± 0.08	1.73 ± 0.01	4.92 ± 0.05	1.80 ± 0.01	5.95 ± 0.01	1.93 ± 0.03
$K_{SV,av}$ [$dm^3\ mol^{-1}$]	93.6 ± 3.3	19.4 ± 0.7	72.0 ± 1.0	16.0 ± 1.2	59.0 ± 4.7	12.4 ± 1.4
k_{Q,O_2} [$\times 10^9\ dm^3\ mol^{-1}\ s^{-1}$]	11.6 ± 0.4	9.81 ± 0.35	8.88 ± 0.12	7.75 ± 0.58	6.72 ± 0.53	5.81 ± 0.65

[a] Compound.

[b] Average fluorescence lifetimes taken under vacuum, at laboratory air pressure and under pure oxygen at laboratory atmospheric pressure. Averages are usually based on three independent determinations.

Table 3
Quenching of S_1 fluorescence of MgTPP and ZnTPP by oxygen in acetonitrile (A), ethanol (E) and toluene (T) at room temperature

Compound/solvent	Viscosity (cP)	k_{Q,O_2} ($\times 10^9$ dm^3 mol^{-1} s^{-1})	k_{diff} ($\times 10^9$ dm^3 mol^{-1} s^{-1})	R_1[a]	R_2[b]
MgTPP					
A	0.345	11.6 ± 0.4	40	0.34	0.29
E	1.10	8.88 ± 0.12	13	–	0.68
T	0.558	6.72 ± 0.53	25	–	0.27
ZnTPP					
A	0.345	9.81 ± 0.35	37	0.31	0.27
E	1.10	7.75 ± 0.58	12	–	0.65
T	0.558	5.81 ± 0.65	23	–	0.25

[a] $R_1 = k_{S,CT}/k_{Q,O_2}$ (see text).
[b] $R_2 = k_{Q,O_2}/k_{\text{diff}}$.

spin-allowed processes to consider in establishing the mechanism of oxygen quenching of the two model metalloporphyrins examined here; radiationless relaxation in the encounter complex, process (2) (preceeded by processes (1) + (1a) or (1b)), and direct quenching to the ground state of the metalloporphyrin via charge transfer (CT) in the encounter complex, process (3).

The diffusion-limited rate constant, k_{diff}, can be calculated using Eq. (1),

$$k_{\text{diff}} = 4\pi N_A(D_M + D_{O_2})(r_M + r_{O_2}) \quad (1)$$

where N_A is the Avogadro's constant, D_M and D_{O_2} are the diffusion coefficients of the metalloporphyrin and oxygen, respectively, and r_M and r_{O_2} are the corresponding mean diffusional radii [15]. The values of D_{O_2} and r_{O_2} in acetonitrile are well-established; $7.12 \pm 0.64 \times 10^{-5}$ cm^2 s^{-1} and 0.2 nm, respectively [4,5]. The values of D_M for MgTPP and ZnTPP in ACN in Table 3 were obtained from previous reports [16,17] of direct measurements of their diffusion coefficients in similar low-viscosity solvents (e.g. dimethylformamide), and then scaling these values by the inverse ratio of the bulk solvent viscosities at 298 K. For MgTPP and ZnTPP in acetonitrile, we therefore use $D_M = 0.75 \pm 0.12 \times 10^{-5}$ and $0.99 \pm 0.12 \times 10^{-5}$ cm^2 s^{-1}, respectively. Obtaining meaningful values of r_M for the metalloporphyrins is more problematic because the bare molecules are disc-like objects rather than spheres. However, in coordinating solvents such as acetonitrile, the two positions along the C_4 axis perpendicular to the plane of the macrocycle will be occupied by non-covalently bound solvent molecules, so that the diffusing species is more spherical. Using the known crystal structure of ZnTPP with bis-coordinated tetrahydrofuran as a model [18], the molecule has maximum dimensions of $r_M = 0.48$ nm along the Zn–meso-phenyl group axis and $r_M = 0.47$ nm along the Zn–solvent axis. The value of r_M is therefore taken to be 0.48 nm for both MgTPP and ZnTPP in acetonitrile. This compares with an average value of $r_M = 0.38$ nm used by Wilkinson and Worrall [4,5] to calculate k_{diff} for a large number of polynuclear aromatic hydrocarbons in acetonitrile. The values of k_{diff} for the quenching of the S_1 states of MgTPP and ZnTPP by O_2 in acetonitrile at 298 K are thus calculated to be 4.0×10^{10} and 3.7×10^{10} dm^3 mol^{-1} s^{-1}, respectively. These values should be compared with $k_{\text{diff}} = 4.5 \times 10^{10}$ dm^3 mol^{-1} s^{-1} used by Wilkinson and Worrall [4,5] in their studies of the oxygen quenching of excited polynuclear aromatic hydrocarbons in the same solvent and $k_{\text{diff}} = 1.8 \times 10^{10}$ dm^3 mol^{-1} s^{-1} calculated using the Stokes–Einstein relationship in the slip limit [15]. The remaining values of k_{diff} in Table 3 were obtained by scaling the values obtained in acetonitrile by the inverse ratios of the solvent viscosities.

The rate constant for quenching by the CT process, $k_{S,CT}$—process (3), can be estimated from the correlations obtained by Wilkinson and Worrall [4,5] for the quenching of the singlet states of polynuclear aromatic hydrocarbons in solution if the value of the Gibbs free energy change for the one-electron reduction of O_2 by the excited metalloporphyrin can be found. (This assumes that CT accounts for all of the fluorescence quenching other than process (2), as is the case with the Wilkinson and Worrall correlations [4,5].) Eqs. (2) and (3) give the appropriate relationships and the required data are given in Table 1.

$$E_{CT} = F(E_M^{Ox} - E_{O_2}^{Red}) + C \quad (2)$$

$$\Delta G_S^{CT} = E_{CT} - E_{S_1} \quad (3)$$

Here, the values of ΔG_S^{CT} for the metalloporphyrins were calculated only for acetonitrile because electrochemical data are not available for the other solvents and because the value of C, which depends on Coulombic interactions and solvation energies of the CT species, is inversely proportional to the solvent's dielectric constant and will therefore be smallest in acetonitrile. A value of $C = 0$ was adopted here, as is common practice, so that $k_{S,CT}$ would be calculated on the same basis as that adopted by Wilkinson and Worrall [4,5] for acetonitrile solutions. The calculated values of ΔG_S^{CT} are given in Table 1.

Note that the observed quenching constants, k_{Q,O_2}, all approach, but are significantly smaller than the diffusion limit and do not scale with solvent viscosity (cf. R_2 in Table 3). Thus, quenching does not occur at a fixed fraction of the diffusion-limited rate as would be expected of a barrierless but spin-statistically limited process. Similar behaviour is found in the oxygen quenching of the fluorescence of chlorophyll *a* [7] and of several substituted anthracene derivatives [19]. Thus, oxygen quenching of the S_1 states of these two model metalloporphyrins would appear to involve at least one process that has a small apparent activation energy.

Process (3), quenching via charge-transfer, is expected to exhibit a small potential energy barrier and should be particularly important in polar solvents where electrostatic interactions would stabilize an encounter complex with dipolar character. However, the rates of the CT processes calculated on the basis of the $k_{\mathrm{S,CT}}$ versus $\Delta G_{\mathrm{S}}^{\mathrm{CT}}$ results of Wilkinson and Worrall [4,5] are smaller (by a factor of about 3 for both MgTPP and ZnTPP in acetonitrile solution) than the observed overall quenching rates (cf. data in Tables 1 and 3). In fact a value of $\Delta G_{\mathrm{S}}^{\mathrm{CT}} < -100\,\mathrm{kJ\,mol^{-1}}$ would be required for process (3) to approach the diffusion-limited value [3,4], whereas the calculated values are about half this magnitude. A worst-case analysis of the errors involved in determining $k_{\mathrm{S,CT}}$ by the method outlined above results in values of R_1 in Table 3 with a maximum of about 0.5; errors in R_1 therefore do not change the general conclusion. Thus, process (2), preceeded by (1) + (1a) or (1b), must represent the major fluorescence quenching mechanism, at least in acetonitrile solution where the data of Wilkinson and Worrall may be used to obtain values of $k_{\mathrm{S,CT}}$ with the least error.

Processes 1 + (1a) or (1b) and 2 are both fully electron spin-allowed, but must nevertheless possess some source of inefficiency because the overall quenching rate is significantly smaller than the diffusion-limited maximum. If the full difference in these rates were assigned to an apparent activation barrier, the barriers would lie between ca. $270\,\mathrm{cm^{-1}}$ in acetonitrile and toluene and ca. $80\,\mathrm{cm^{-1}}$ in ethanol at room temperature. Because this apparent "barrier" is a weak function of the nature of the solvent, it could simply be associated with differences between the energies and dynamics of solvation of the various encounter complexes and their precursors.

5. Conclusions

Molecular oxygen quenches the S_1 states of two model metalloporphyrins, MgTPP and ZnTPP, in solution at rates that are near, but nevertheles significantly smaller than the diffusion limit and do not scale with solvent viscosity. The dominant mechanism involves electron spin-allowed S_1–T_2–T_1 relaxation of the porphyrin in the triplet encounter complex, a process that has a small apparent potential energy barrier. Quenching by a charge transfer mechanism plays at most a minor role.

Oxygen quenching must therefore be taken into account in determining the excited state relaxation dynamics of aerated solutions of those metalloporphyrins with S_1 lifetimes in the ns range even at normal atmospheric pressures. The oxygen quenching of the fluorescence of metalloporphyrins with shorter-lived excited singlet states (e.g. those containing heavy metals) will only be important under hyperbaric conditions.

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