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Evidence against "Dimol-Sensitized Luminescence" in Solutions Containing Singlet Oxygen

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Since Khan and Kasha[1] proposed nearly three decades ago that luminescence may be observed by direct energy transfer to an acceptor M from excited molecular oxygen pairs in energetically favorable situations (*cf.* eq 1), there has, until recently, been no experimental evidence to support this view.

$$^1\Delta_g + {}^1\Delta_g \rightleftharpoons [^1\Delta_g]_2 \xrightarrow{M} {}^1M^* \quad (1)$$

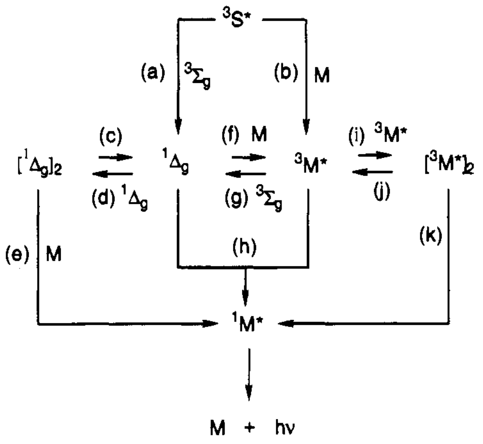
$$M \xrightarrow{^1\Delta_g} {}^3M^* \xrightarrow{^1\Delta_g} {}^1M^* \quad (2)$$

Indeed, Ogryzlo and Pearson[2] and Wilson[3] provided evidence to suggest that, in the cases of the very weak singlet-oxygen ($^1\Delta_g$)-sensitized fluorescence of both violanthrone[2] and rubrene,[3] the process involved sequential excitation of the acceptor according to eq 2. In contrast, 2 decades later, papers by Krasnovsky and Neverof[4–6] claimed to establish the operation of eq 1 on the basis of steady-state experiments, and recently Krasnovsky and Foote[7] have claimed further support for this mechanism on the basis of time-resolved experiments using C_{60} as the $^1\Delta_g$ sensitizer and tetra-*tert*-butylphthalocyanine (TTPC) as the acceptor of dimolecular (dimol) excitation energy. In this paper we report that, in the case of a phthalocyanine with an absorption maximum exactly coincident with the dimol emission maximum at 703 nm, namely 2,3,9,10,16,17,23,24-octahexadecylphthalocyanine (OHPC),[8] the sensitized luminescence proceeds via the stepwise mechanism of eq 2, and that this process is independent of the $^1\Delta_g$ triplet sensitizer. In our opinion, there is no evidence for the dimol-sensitized process of eq 1.

Laser excitation at 355 nm of 2-acetonaphthone (3×10^{-3} mol L^{-1}) as the triplet sensitizer[9] in aerated benzene containing OHPC (10^{-6} mol L^{-1}) led to results in complete experimental agreement with those published by Krasnovsky and Foote[7] using C_{60} and TTPC; i.e., the key findings were (a) delayed OHPC luminescence at 706 nm with a lifetime (15 ± 1 μs) half that of the 1270 nm $^1\Delta_g$ monomol emission (31 ± 2 μs) and (b) initial 706 and 1270 nm emission intensities (I_{706} and I_{1270}) exhibiting respectively quadratic and linear dependencies on laser excitation energy.[10]

Scheme 1 forms the framework for the subsequent mechanistic discussion for a sensitizer S and fluorophor M. The first point to emphasize is that competition for $^3S^*$ (reactions a and b) by oxygen (2×10^{-3} mol L^{-1} in aerated benzene, $k \approx 3 \times 10^9$ L mol^{-1} s^{-1}) and a low triplet energy acceptor M (10^{-6} mol L^{-1}, $k \approx 6 \times 10^9$ L mol^{-1} s^{-1}) means that the relative concentrations of $^1\Delta_g$ and $^3M^*$ produced by these processes would be of the order of 1000:1. If $^3M^*$ lies >4 kcal mol^{-1} above $^1\Delta_g$,[12] the equilibrium between these species, (Scheme 1, f vs g), would lie further to the *left* than this by a factor of >20; i.e. the fast exothermic process (g) would result in the establishment of an equilibrium between $^1\Delta_g$ and $^3M^*$ within 150 ns of the laser pulse. Given this scenario, Scheme 1 includes the three mechanisms which are consonant with the lifetime and laser energy dependence data, i.e., the claimed dimol mechanism[7] (c, d, and e), that previously proposed by Ogryzlo and Pearson[2] and Wilson[3] (f, g, and h), and the classical T–T annihilation process (i, j, and k).[14]

Scheme 1



Since the steady-state fluorescence intensity of OHPC is no different in oxygen than in nitrogen-saturated benzene, there is, in principle, a straightforward way to distinguish between these three processes: variation of the oxygen concentration. When $^3S^*$ is inherently long-lived, as in the cases of 2-acetonaphthone and C_{60}, the initial $^1\Delta_g$ concentration will not be affected by increasing the oxygen concentration above that of aeration, a fact readily verified by monitoring I_{1270}. In addition, while the several orders of magnitude lower equilibrium concentration of $^3M^*$ will *decrease* linearly with *increasing* oxygen concentration, that of $^1\Delta_g$ will be effectively unchanged, again readily verified by monitoring I_{1270}. Thus, assuming one unique mechanism, the three possible consequences on I_{706} of varying the oxygen concentration above that of aeration would be (1) no effect (dimol mechanism,[7] reactions c, d, and e in Scheme 1),[15] (2) inverse proportionality to the oxygen concentration (f, g, and h in Scheme 1), and (3) inverse proportionality to the *square* of the oxygen concentration (T–T annihilation,[14] i, j, and k).

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[2] Ogryzlo, E. A.; Pearson, A. E. *J. Phys. Chem.* **1968**, *72*, 2913.

[3] Wilson, T. *J. Am. Chem. Soc.* **1969**, *91*, 2387.

[4] Krasnovsky, A. A., Jr.; Neverof, K. V. *Biofizika (Sov. Biophys.)* **1988**, *23*, 884.

[5] Krasnovsky, A. A., Jr.; Neverof, K. V. *Chem. Phys. Lett.* **1990**, *167*, 591.

[6] Neverov, K. V.; Krasnovsky, A. A., Jr. *Opt. Spektrosk. (Sov. Opt. Spectrosc.)* **1991**, *71*, 691.

[7] Krasnovsky, A. A., Jr.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 6013.

[8] Clarkson, G. J.; McKeown, N. B.; Treacher, K. E. *J. Chem. Soc., Perkin Trans. 1* **1995**, *1817*.

[9] Gorman, A. A.; Rodgers, M. A. J. *Chem. Phys. Lett.* **1978**, *55*, 52.

[10] All laser experiments[11] were single shot with excellent first-order fits of emission decays extrapolated to zero time. Both 1270 and 706 nm emission experiments used the same reaction cell arrangement with identical excitation geometries. Detection was at right angles to the laser beam. Detection of the 1270 nm emission was as described.[11] The 706 nm emission was focused by a pair of lenses onto the monochromator entrance slit and detected by means of a Hamamatsu R928 photomultiplier. The output was fed via a 1 kΩ load resistance to the input of a Tektronix 7A13 differential comparator coupled to a Tektronix 7912 AD programmable digitizer.

[11] Gorman, A. A.; Hamblett, I.; Lambert, C.; Prescott, A. L.; Rodgers, M. A. J.; Spence, H. M. *J. Am. Chem. Soc.* **1987**, *109*, 3091.

[12] This must certainly apply here, a value of 28.7 kcal mol^{-1} having been quoted for the parent phthalocyanine on the basis of energy transfer experiments.[13]

[13] McVie, J.; Sinclair, R. S.; Truscott, T. G. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1870.

[14] Clearly this would appear less likely than the $^1\Delta_g/^3M^*$ reaction, simply on the grounds of concentration.

[15] As an alternative to the dimol mechanism, Foote and Krasnovsky[7] have considered and rejected the reaction of an M–$^1\Delta_g$ exciplex with a second $^1\Delta_g$ molecule. Neither would be affected by changing the oxygen concentration above that of aeration.

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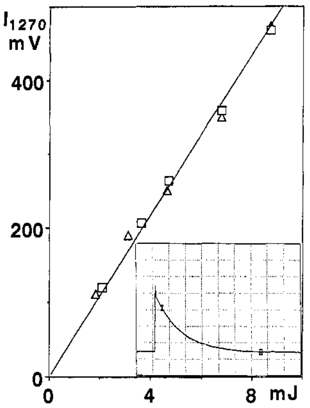

Figure 1. Plot of the initial emission intensity at 1270 nm, I_{1270}, vs the laser energy per pulse for 2×10^{-3} (△) and 10^{-2} mol L^{-1} (□) oxygen concentrations. Inset: Time-resolved 1270 nm emission decay with first-order fit after laser excitation of 2-acetonaphthone (3×10^{-3} mol L^{-1}) at 355 nm in aerated benzene containing OHPC (10^{-6} mol L^{-1}), 6.8 mJ/pulse, 100 mV/division, 20 μs/division, $k' = 3.3 \times 10^4$ s^{-1}, $I_{1270} = 350$ mV.

We have performed a series of experiments of the type already described using a range of oxygen concentrations (2×10^{-3} (aerated)-2×10^{-2} mol L^{-1}). There was absolutely no change in the kinetic parameters of the emissions. However, whereas as anticipated the 1270 nm emission intensity remained unchanged (Figure 1), the delayed fluorescence intensity at 706 nm was linearly and inversely proportional to the oxygen concentration. In Figure 2, it is demonstrated that plots of I_{706} vs $I_{1270}{}^2$ (*cf.* ref 7) are linear, but the gradients are inversely proportional to the oxygen concentration, the ratio of the slopes for 2×10^{-3} and 5×10^{-3} mol L^{-1} oxygen being almost exactly 2.5, in complete accord with the mechanism summarized by steps f, g, and h in Scheme 1 (*cf.* eq 2). We have demonstrated the same behavior in corresponding C_{60}-sensitized experiments (*cf.* ref 7), and the clear conclusion is that in these systems, there is no evidence for dimol sensitization. Since, as emphasized, the *absorption* maximum of OHPC is exactly coincident with the dimol *emission* maximum, it would appear that other chemical systems are also unlikely to exhibit dimol sensitization.

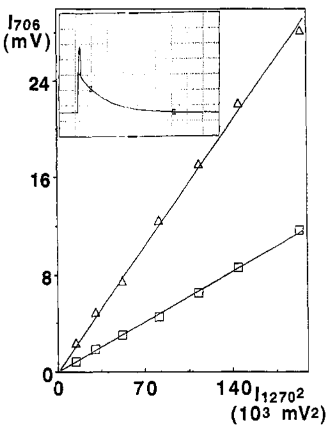

Figure 2. Plots of I_{706} vs $I_{1270}{}^2$ for 2×10^{-3} (△) and 5×10^{-3} mol L^{-1} (□) oxygen concentrations. The ratio of the slopes is 2.52. Inset: Time-resolved 706 nm emission decay with first-order fit after laser excitation of 2-acetonaphthone (3×10^{-3} mol L^{-1}) at 355 nm in aerated benzene containing OHPC (10^{-6} mol L^{-1}), 8.3 mJ/pulse, 10 mV/division, 10 μs/division, $k' = 6.4 \times 10^4$ s^{-1}, $I_{706} = 26.3$ mV.

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