due to a change in van der Waals contact between heme and protein, because the low-frequency modes involve significant contribution from the peripheral groups.[22]

The Raman line of ferroHRP at 243 cm^{-1} and that of ferriHRP fluoride at 269 cm^{-1} were previously assigned to the Fe–His stretching vibration on the basis of the observed ^{54}Fe isotopic frequency shift.[15] Due to the analogy of their similar frequencies, the Raman lines of ferriHRP at 279 cm^{-1}, compound II at 287 cm^{-1}, and compound I at 248 cm^{-1} might be assignable to the Fe–His stretching mode. It was recently pointed out that the Fe–His stretching frequency of ferroHRP (243 cm^{-1}) serves as a distinct property in iron coordination environments of plant tissue peroxidases[23] and is caused by a considerably strong hydrogen bond of the proximal histidine.[15b] The frequency shifts of the Fe–His stretching mode from 279 to 248 cm^{-1} upon formation of compound I[24] and to 287 cm^{-1} upon formation of compound II are significantly large, suggesting a concomitant change of the charge distribution of the Fe–His bond and thus involvement of the proximal histidine in activation of the ligated oxygen atom at its trans position.

Registry No. Peroxidase, 9003-99-0.

(22) (a) Choi, S.; Spiro, T. G.; Langry, K. C.; Smith, K. M. *J. Am. Chem. Soc.* **1982**, *104*, 4337. (b) Choi, S.; Spiro, T. G.; Langry, K. C.; Smith, K. M.; Budd, D. L.; LaMar, G. N. *J. Am. Chem. Soc.* **1982**, *104*, 4345.
(23) Teraoka, J.; Job, D.; Morita, Y.; Kitagawa, T., submitted for publication.
(24) If these two Raman lines arose from fairly pure Fe–His stretching mode, the ratio of the stretching force constant of compound I to native ferriHRP would be $k_{I}/k_{\text{ferriHRP}} = (\nu_{I}/\nu_{\text{ferriHRP}})^2 = 0.8$

Photoacoustic Measurement of Photophysical Properties. Lowest Triplet-State Energy of a Free Base Porphyrin

Thomas A. Moore,*[1a] David Benin,[1b] and Roderick Tom[1a]

Department of Chemistry and Department of Physics Arizona State University, Tempe, Arizona 85287

Received August 16, 1982

Via a calorimetric method[2–4] based on the photoacoustic effect,[5,6] we have measured certain photophysical properties of free base *meso*-tetra-*p*-tolylporphyrin. In particular, we determine the product of the quantum yield of intersystem crossing and the triplet-energy level to be 0.93 eV. By contrast, current literature values give a range for this product from 1.07 to 1.26 eV. To demonstrate that our calorimetric method is viable, we have also investigated two other compounds with well-known photophysical properties, zinc tetraphenylporphyrin and 1-chloroanthracene. In these cases, the experimental values we obtain are in agreement with literature values.

When a system of absorbing molecules is exposed to intensity-modulated exciting light, the populations of the excited electronic states produced will also be modulated. Deexcitation of these excited states through nonradiative routes constitutes the heat source for the photoacoustic effect. Since the relaxation of the triplet state is slow, the modulation of the triplet population will be delayed and lag in phase the modulation of other rapidly relaxing states. Quenching the triplet state to a sufficiently short
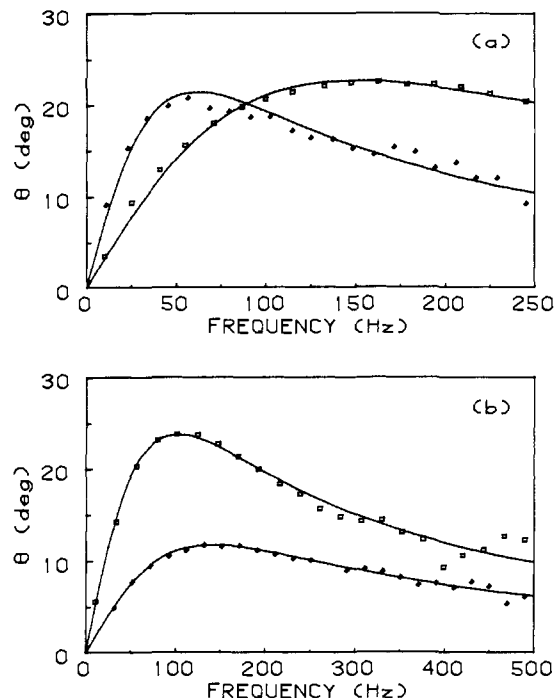
(1) (a) Department of Chemistry; (b) Department of Physics.
(2) Callis, J. *J. Res. Natl. Bur. Stand., Sect. A* **1976**, *80A*, 413–419.
(3) Quimby, R.; Yen, W. *Opt. Let.* **1978**, *3*, 181–183.
(4) Quimby, R.; Yen, W. *J. Appl. Phys.* **1980**, *51*, 1780–1782.
(5) Rosencwaig, A.; Gersho, A. *J. Appl. Phys.* **1976**, *47*, 64–69.
(6) McDonald, F.; Wetsel, G. *J. Appl. Phys.* **1978**, *49*, 2313–2322.

Figure 1. (a): (□) 1×10^{-4} M zinc tetraphenylporphyrin in polystyrene, 422-nm excitation, fitted curve parameters $R = 0.80$, $\tau = 1.6$ ms; (◊) 1×10^{-2} M 1-chloroanthracene in cellulose triacetate, 365-nm excitation, curve parameters $R = 0.87$, $\tau = 3.8$ ms. (b): *meso*-tetra-*p*-tolylporphyrin (◊) 4×10^{-3} M in cellulose triacetate, 420-nm excitation, fitted parameters $R = 1.96$, $\tau = 1.4$ ms; (□) 8×10^{-3} M in polystyrene, 650-nm excitation, parameters $R = 0.74$, $\tau = 2.4$ ms.

lifetime eliminates this phase lag. We measure the phase-angle difference, θ, between the photoacoustic signals of an unquenched sample and of the same sample but with the triplets quenched. This angle is given by the theoretical expression[7]

$$\tan \theta = \omega\tau / [1 + R(1 + \omega^2\tau^2)]$$

$$R = (h\nu - \phi_{fl}E_s - \phi_{isc}E_T)/\phi_{isc}E_T$$

where $h\nu$ and ω are the energy and angular modulation frequency of the exciting light, E_s and E_T are the energies of the O–O transitions of fluorescence and phosphorescence, and τ is the triplet lifetime. ϕ_{fl} and ϕ_{isc} are quantum yields of fluorescence and intersystem crossing. We have assumed $\phi_{fl} + \phi_{isc} + \phi_{ic} = 1$, where ϕ_{ic} is the quantum yield of internal conversion.

Neither fluorescence excitation nor emission spectra of the samples described below indicate any fluorescence other than the transition from the lowest vibrational state of S_1 to the ground-state vibrational manifold, as is consistent with Kasha's Rule.[8] These same spectra also indicate a phosphorescence quantum yield less than 1/100th that of fluorescence; we have accordingly neglected phosphorescence.

The molecules were dissolved into a rigid matrix consisting of a polymer[9–11] of either polystyrene (Aldrich 18,242-7) or cellulose triacetate (Aldrich 18,100-5) (both used without further purification). This was necessary to lengthen the triplet lifetime τ of unquenched samples to the order of milliseconds, so that $\omega\tau \sim 1$ within the normal frequency range of photoacoustic spectroscopy, and an appreciable phase shift will result. Samples were placed in a photoacoustic cell employing nitrogen as the coupling gas for

(7) This expression results from solving rate equations for a three-level system with sinusoidal light modulation; see: Hunter, T.; Rumbles, D.; Stock, M. *Faraday Trans 2* **1974**, *70*, 1010–1021.
(8) Kasha, M. *Discuss. Faraday Soc.* **1950**, *9*, 14–19.
(9) Melhuish, W.; Hardwick, R. *Trans. Faraday Soc.* **1962**, *58*, 1908–1911.
(10) West, M.; McCallum, K.; Woods, R.; Formosinho, S. *Trans. Faraday Soc.* **1970**, *66*, 2135–2147.
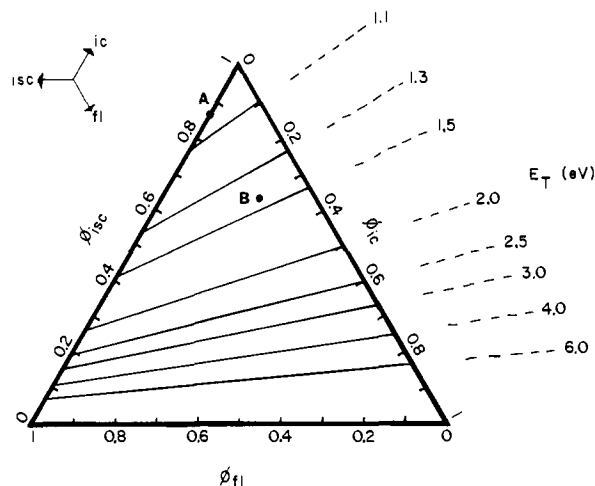(11) Hormats, E.; Unterleitner, F. *J. Phys. Chem.* **1965**, *69*, 3677–3681.

Figure 2. Triplet energy contours for *meso*-tetra-*p*-tolylporphyrin as a function of quantum yields. Shown are contour lines E_T = constant, for E_s = 1.90 eV, $\phi_{isc}E_T$ = 0.93 eV. Sample points: A (ϕ_{fl} = 0.13, ϕ_{isc} = 0.87, ϕ_{ic} = 0, E_T = 1.07eV), B (ϕ_{fl} = 0.13, ϕ_{isc} = 0.64, ϕ_{ic} = 0.23, E_T = 1.45 eV).

the unquenched triplet case. Oxygen was used for the quenched case; triplets are then quenched by oxygen diffusing into the polymer.[11,12] All samples were thermally thick over the frequency range employed. The above theoretical expression was fitted to the measured θ at several frequencies, with use of a least-squares criterion to determine the two fitting parameters R and τ. All measurements were taken at room temperature.

Two compounds, 1-chloroanthracene (Aldrich, purified by sublimation) and zinc tetraphenylporphyrin (chlorin-free, supplied by D. Gust) served as standards to establish the validity of this procedure. Phase data and fitted theoretical curves are shown in Figure 1a. For zinc tetraphenylporphyrin, with singlet-state parameters ϕ_{fl} = 0.033 and E_s = 2.08 eV,[13] the fitted curve parameters give $\phi_{isc}E_T$ = 1.59 ± 0.02 eV.[14] The current literature value is[13] (0.97)(1.60 eV) = 1.55 eV, in reasonable agreement. Similarly, using ϕ_{fl} = 0.08 and E_s = 3.31 eV for 1-chloroanthracene,[15,16] we obtain $\phi_{isc}E_T$ = 1.68 ± 0.04 eV, as compared to the literature value of[16] (0.92)(1.83 eV) = 1.69 eV.

In free base *meso*-tetra-*p*-tolylporphyrin (chlorin-free, supplied by D. Gust), two measurements were made at different excitation wavelengths (Figure 1b). With photophysical parameters ϕ_{fl} = 0.13 and E_s = 1.90 eV,[13] these two measurements give values for $\phi_{isc}E_T$ of 0.92 ± 0.01 and 0.96 ± 0.03 eV. Current literature values of ϕ_{isc} range from 0.74[17] to 0.87;[18] we have measured $\phi_{isc} \approx 0.9$ in styrene by flash spectroscopy.[19] A triplet energy of 1.45 eV for tetraphenylporphyrin has been quoted in the literature.[20–22] However, this value is questionable because no heavy-atom effect or excitation spectrum was observed.[21,22] Although these literature values are based on free base tetraphenylporphyrin, negligible

perturbations are expected due to the para substituent.[13] Thus the literature product $\phi_{isc}E_T$ ranges from 1.07 to 1.26 eV, inconsistent with our results.

We do not believe this discrepancy is due to differences in molecular environment. For both standards the products $\phi_{isc}E_T$ we determine from polymer matrix data are the same as literature values from solutions. Moreover, for tetratolylporphyrin two different polymer matrices give the same value of $\phi_{isc}E_T$, within experimental error. Thus the only effect here of the matrix is to lengthen the triplet lifetime, to values typical of glasses at 77 K formed by rapid cooling of solutions.[23]

Our results may be summarized graphically in a contour diagram of the triplet energy surface as a function of the quantum yields (Figure 2). The photophysical parameters of tetratolylporphyrin must lie at a point on this surface, but the current literature values of ϕ_{isc}, ϕ_{fl}, and E_T do not satisfy this requirement. For instance, if internal conversion is small, then since $\phi_{fl} < 0.2$,[13] the photophysical parameters lie near point A of Figure 2, where the triplet energy is of the order of 1.1 eV, rather than 1.45 eV. Alternatively, with $E_T \simeq 1.45$ eV and $\phi_{fl} < 0.2$, internal conversion cannot be a minor decay path: $\phi_{ic} \gtrsim 0.2$ in the vicinity of point B. Note that at the upper apex of the triangle of the contour diagram, E_T is only weakly dependent on ϕ_{fl} and ϕ_{ic} at a constant ϕ_{isc} (horizontal line).

This calorimetric measurement should prove to be a powerful method for determining photophysical properties unobtainable by purely optical techniques. For molecules whose lowest triplet energy level can be determined by phosphorescence, it is an alternative method of measuring the intersystem crossing quantum yield.

(23) Gradyushko, A.; Tsvirko, M. *Opt. Spectrosc.* **1971**, *31*, 291–295.

Intra- and Intermolecular Organoactinide C–H Activation Pathways. Formation, Properties, and Reactions of Thoracyclobutanes

Joseph W. Bruno and Tobin J. Marks*

Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Victor W. Day*

Department of Chemistry, University of Nebraska
Lincoln, Nebraska 68588, and Crystalytics Company
Lincoln, Nebraska 68501

Received August 2, 1982

The scope and mechanisms of intramolecular C–H activation processes that result in saturated hydrocarbon cyclometalation are justifiably topics of considerable current interest,[1–7] as are the

(12) Czarnecki, S.; Kryszewski, M. *J. Polym. Sci. Polym. Chem. Ed.* **1963**, *A1*, 3067–3077.

(13) Quimby, D.; Longo, F. *J. Am. Chem. Soc.* **1975**, *97*, 5111–5117.

(14) The errors quoted for parameters determined by curve fitting represent the 95% confidence interval for a t distribution with the appropriate number of degrees of freedom.

(15) Padhye, M.; McGlynn, S.; Kasha, M. *J. Chem. Phys.* **1956**, *24*, 588–594.

(16) Bowen, E. *Trans. Faraday Soc.* **1954**, *50*, 97–102.

(17) Petsold, O.; Byteva, I.; Gurinovich, G. *Opt. Spectrosc.* **1973**, *34*, 343–344.

(18) Solov'ev, K.; Tsvirko, M.; Gradyushko, A.; Kozhick, D. *Opt. Spectrosc.* **1972**, *33*, 480–483.

(19) Measurement made by T. Moore, D. Gust, and M. A. J. Rodgers at the Center for Fast Kinetic Research, University of Texas, Austin, TX, using the comparative method.

(20) Harriman, A.; Porter, G.; Searle, N. *Faraday Trans. 2* **1979**, *75*, 1515–1521.

(21) Gouterman, M.; Khalil, G. *J. Mol. Spectrosc.* **1974**, *53*, 88–100.

(22) Dolphin, D., Ed. "The Porphyrins"; Academic Press: New York, 1978; Vol. 3, Pt A, p 1–165.

(1) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 211–228.

(2) (a) Whitesides, G. M. *Pure Appl. Chem.* **1981**, *53*, 287–292. (b) Ibers, J. A.; DiCosimo, R.; Whitesides, G. M. *Organometallics* **1982**, *1*, 13–20. (c) DiCosimo, R.; Moore, S. S.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 124–133. (d) Moore, S. S.; DiCosimo, R.; Sowinski, A. F.; Whitesides, G. M. *Ibid.* **1981**, *103*, 948–949. (e) Foley, P.; DiCosimo, R.; Whitesides, G. M. *Ibid.* **1980**, *102*, 6713–6725.

(3) Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448–2450.

(4) (a) Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1979**, 472–477. (b) Andersen, R. A.; Jones, R. A.; Wilkinson, G. *Ibid.* **1978**, 446–453.

(5) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149–194 and references therein.

(6) (a) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991–1995. (b) Cramer, R. E.; Maynard, R. B.; Gilje, J. W. *Ibid.* **1980**, *19*, 2564–2569.