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Studies on Metastable States of Porphyrins. II. Spectra and Decay Kinetics of Tetraphenylporphine, Zinc Tetraphenylporphine and Bacteriochlorophyll[1]

BY LAURI PEKKARINEN AND HENRY LINSCHITZ

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The flash technique used earlier to study the metastable states of chlorophyll[2] has been applied to the above compounds in toluene and pyridine solution. The spectra all show a main band just below the Soret peak, as well as other regularities. The decay law is again $-\mathrm{d}C^*/\mathrm{d}t = k_1C^* + k_2(C^*)^2 + k_3(C^*)(C_g)$ (C^* = excited state; C_g = ground state). The respective rate constants for all the compounds are almost the same, except for a much faster first-order decay in bacteriochlorophyll. Little or no flash-bleaching is observed with the Cu^{++}, Co^{++} and Ni^{++} complexes of tetraphenylporphine.

The absorption spectra and decay kinetics of metastable (triplet) states of chlorophyll-a and b have been studied recently in this Laboratory, using flash-excitation apparatus with a time-resolution of 10^{-5} second.[2] We have now extended this investigation to bacteriochlorophyll, tetraphenylporphine (TPP) and zinc tetraphenylporphine (ZnTPP) and have also examined other metal complexes of TPP. In addition, absorption spectra of the metastable states of these compounds, as well as chlorophyll-a and b, have been followed into the infrared, as far as 10,500 Å. These new data permit us to begin systematic, comparative study of the triplet states of these spectroscopically interesting and biochemically significant compounds.

Experimental

1. **Method.**—The method used in this work involves the almost complete conversion of dissolved dye to its metastable state, by means of a brief and intense light flash, and the measurement of the magnitude and time course of resulting spectral changes in the solution using a scanning beam, monochromator, photo-cell and oscilloscope. A full description of the apparatus,[3] operational techniques and mode of calculation of results has been given previously.[2] For measurements in the region from 7000 to 10,500 Å., the usual photomultiplier was replaced by an infrared sensitive tube (DuMont, Type 6911). At 10,500 Å. using a 100-watt zirconium arc source and red filter, this tube gave a signal-to-noise ratio of better than 10, at a monochromator slit width of 200 Å. At 7000 Å. slit widths could be reduced to 40 Å.

All test solutions were prepared on the vacuum line from stock solutions of the pigments in toluene.[2]

2. **Spectrum Measurements.**—The determination of the spectra of the metastable states of the porphyrins is rendered difficult by the large variation in intensity of the several triplet and singlet absorption bands. The change in absorbance in each region of the spectrum therefore was measured at a concentration giving the optimum precision for the particular band in question, up to a point at which the initial fractional conversion began to fall off seriously. The region under the extremely sharp Soret bands of TPP and ZnTPP, which is especially sensitive to slit-width errors, was studied at concentrations near 2×10^{-7} M, while the relatively weak triplet bands in the near infrared required measurements near 10^{-5} M. Overlapping data at suitable wave lengths were taken at intermediate concentrations, so that, assuming Beer's law, fractional conversions could be checked over the full concentration range. The per cent. conversions, extrapolated back to "zero time" of the flash,[2] were estimated from the height of residual peaks under the original bands. At the lowest concentrations, using the Soret band, conversions were (within 5% error) 100 and 92% for TPP and ZnTPP, respectively, and using the far red peak, 90% for bacteriochlorophyll. In all cases, these remained at 90% or higher up to about 1×10^{-5} M, as judged by the constancy (within 10%) of the ratio $\Delta D_\lambda/C$ over this interval (ΔD_λ = change in absorbance at a convenient wave length; C = dye concentration). Only these runs were used to establish the spectra so that corrections to 100% conversion are small, except under the Soret bands. In kinetic runs on TPP, at 1.4×10^{-5} M, the initial conversion was about 70% complete.

3. **Kinetic Measurements.**—For convenience in this and the following paper, we briefly review here the kinetic analysis given earlier.[2] We let

(C_0) = total concn. of dye
(C^*) = concn. of metastable state
(C_g) = concn. of ground state

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[1] This work was assisted by a grant from the U. S. Atomic Energy Commission to Brandeis University (Contract No. AT (30-1)-2003).

[2] H. Linschitz and K. Sarkanen, THIS JOURNAL, **80**, 4826 (1958).

[3] We wish to thank the Chemistry Department and Instrumentation Section of the Brookhaven National Laboratory for kind permission to use components of the flash apparatus that were developed and constructed there.

$\Delta D_0\lambda$ = obsd. change in absorbance at wave length λ (referred to the original soln.), at some arbitrary time, $t = 0$, after the flash

$\Delta D\lambda$ = obsd. change in absorbance at wave length λ, at time t after the arbitrary starting point

$\alpha\lambda^*, \alpha_g\lambda$ = molar extinction co-efficients of metastable and ground state

l = cell length

$$a\lambda = \frac{1}{(\alpha\lambda^* - \alpha_g\lambda)l}$$

The rate law found to describe the decay of the triplet state of chlorophyll is[2]

$$-\frac{\mathrm{d}C^*}{\mathrm{d}t} = k_1C^* + k_2(C^*)^2 + k_3(C^*)(C_g) \qquad (1)$$

Since $C^* = a\lambda\Delta D\lambda$, this becomes

$$\frac{\mathrm{d}}{\mathrm{d}t}\ln(\Delta D_0/\Delta D)\lambda = A + B\lambda\Delta D\lambda \qquad (2)$$

in which

$$A = k_1 + k_3C_0$$

and

$$B\lambda = a\lambda(k_2 - k_3)$$

Tangents drawn to plots of log $(\Delta D_0/\Delta D)\lambda$ *vs.* t give the derivative directly, and the values of A and $B\lambda$ are then found from plots of this derivative against $\Delta D\lambda$. K_1 and k_3 are separated by measuring the change in A with C_0. The spectrum measurements give $a\lambda$ for the wave length at which $\Delta D\lambda$ is observed, and k_2 is thus evaluated. Our results to date on a number of compounds all indicate that $k_2 >> k_3$. Moreover, in dilute solutions $k_1 >> k_3C_0$, and the latter term can be neglected.

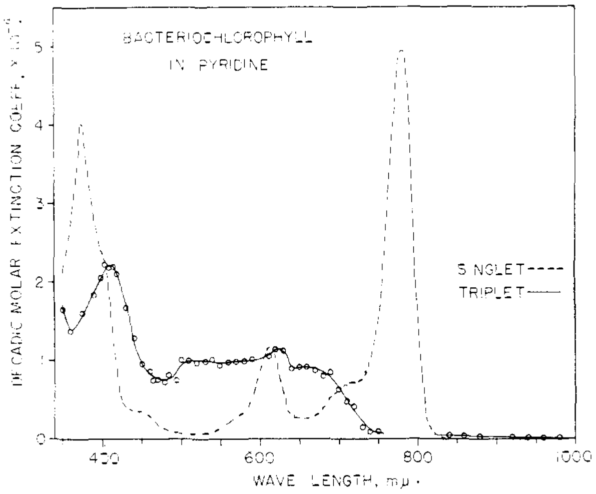

Fig. 1.—Absorption spectra of bacteriochlorophyll (dashed line) and its triplet state (solid line), corrected to 100% conversion, in pyridine.

Kinetic measurements were made on bacteriochlorophyll in pyridine and on the porphyrins in toluene and pyridine. Copper, cobalt and nickel complexes of TPP were flashed in 10^{-5} *M* toluene solution.

Irreversible decomposition of the degassed dye solutions was very slight, as judged by changes in absorption spectrum. Bacteriochlorophyll in pyridine is especially stable, less than 1% change resulting after 300 flashes.

All measurements were made at room temperature.

4. **Materials.**—Crystalline chlorophyll-a and b were prepared from spinach[4] and bacteriochlorophyll from lyophilized *Rhodospirillum Rubrum*.[5] The lyophilized bacteria were first moistened and then processed as recommended by Holt and Jacobs.[5] If dry material is used directly, Curby found that other products are obtained. The absorption spectrum of our bacteriochlorophyll in ether checked within experimental error with that of Holt and Jacobs,[5] with regard to location and relative height of the various peaks, but our molar extinction coefficients were uniformly low by about 60%. However, we assume that the absorption of the metastable state relative to the ground state is still reliable. The rate constant k_1 is independent of the absolute extinction, in any case. In passing from ether to pyridine, an especially large shift of the "orange peak" occurs, as noted by Weigl[6] for other solvents. The main bacteriochlorophyll peaks (our preparation) in pyridine lie at 780, 612 and 373 mμ, compared with 770, 574 and 358 mμ in ether. The subsidiary peak in ether, at 392 mμ, is not resolved in pyridine (Fig. 1).

TPP was obtained by condensing pyrrole and benzaldehyde in a sealed tube[7,8] and was chromatographed several times. The metal complexes[9] were purified similarly.

The spectra of TPP and ZnTPP checked well with previous measurements.[9] Solvents were reagent-grade. Pyridine was refluxed and fractionated over KOH. Toluene was washed with H_2SO_4, water, dried and fractionated over sodium.

Results and Discussion

1. **Absorption Spectra.**—Figures 1–3 give the absorption spectra of the metastable states of bacteriochlorophyll, TPP and ZnTPP. Peak locations and decadic molar extinction coefficients are summarized in Table I. Figure 4 shows the near infrared absorption spectra for the chlorophyll-a and b triplets and extends the spectral data given earlier for the visible region.[2]

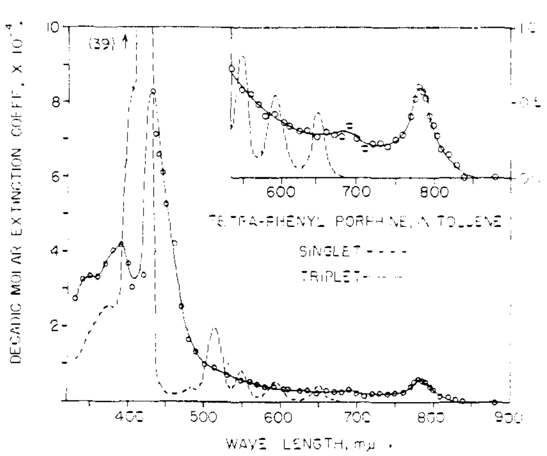

Fig. 2.—Absorption spectra of tetraphenylporphine (dashed line) and its triplet state (solid line), corrected to 100% conversion, in toluene.

The largest errors in determining the spectra occur under the Soret peaks and arise mainly from the uncertainty in fractional conversion. Elsewhere this is not serious, and the scatter of the points gives an idea of the precision. For bacteriochlorophyll, the spectrum under the main red band is also in doubt (dotted portion, Fig. 1) because of a large scattered light signal in this region, apparently due to fluorescence. In the near infrared, this compound shows a very small but definite absorption. The chlorophyll triplets also show weak infrared absorption, which is more pro-

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[4] E. E. Jacobs, A. E. Vatter and A. S. Holt, *Arch. Biochem. Biophys.*, **53**, 228 (1954).

[5] A. S. Holt and E. E. Jacobs, *Am. J. Botany*, **41**, 718 (1954). We wish to thank Mr. W. Curby and Dr. R. Bartsch for this sample and for their assistance in the bacteriochlorophyll measurements.

[6] J. W. Weigl, THIS JOURNAL, **75**, 999 (1953).

[7] P. Rothemund and A. R. Menotti, *ibid.*, **70**, 1808 (1948); **63**, 267 (1941).

[8] R. H. Ball, G. D. Dorough and M. Calvin, *ibid.*, **68**, 2278 (1946).

[9] G. D. Dorough, J. R. Miller and F. M. Huennekens, *ibid.*, **73**, 4315 (1951).

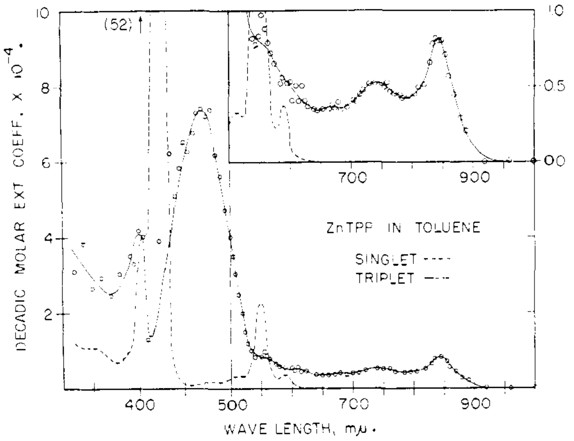

Fig. 3.—Absorption spectra of zinc tetraphenylporphine (dashed line) and its triplet state (solid line), corrected to 100% conversion, in toluene. Note change in wave length scale at 500 mμ.

nounced for -a than for -b. The b absorption decreases steadily and is lost in noise at about 10,000 Å., while the a spectrum remains flat and continues beyond 10,500 Å. The TPP and ZnTPP peaks in the near infrared are unmistakable, and the indicated lesser peaks seem outside experimental error.

TABLE I

SPECTRA OF METASTABLE STATES OF TETRAPHENYLPORPHINE, ZINC TETRAPHENYLPORPHINE AND BACTERIOCHLOROPHYLL

Decadic Molar Extinction Coefficients

TPP (toluene)		ZnTPP (toluene)		Bacti-chl. (pyridine)[a]	
λ (mμ)	α^* × 10^{-4}	λ (mμ)	α^* × 10^{-4}	λ (mμ)	α^* × 10^{-4}
390 (max.)	4.2	370 (min.)	2.5	360 (min.)	1.38
405 (min.)	3.3	400 (max.)	4.2	410 (max.)	2.22
430 (max.)	8.3	410 (min.)	1.3	472 (min.)	0.75
690 (max.)	0.35	470 (max.)	7.4	620 (max.)	1.15
780 (max.)	0.60	745 (max.)	0.53	655 (max.)	0.93
		790 (min.)	.40		
		845 (max.)	.82		

[a] These may be systematically low by about 60% (see section on "Materials"). Relative values should be correct.

Certain general characteristics of the triplet state absorption in porphyrins and chlorins already appear in these five examples. In every case, the strongest band lies just to the red of the main Soret peak. *This feature seems to be as typical of these compounds as the Soret band itself.* All the spectra taken here show also a second peak[2] lying on the high-energy side of the Soret absorption. Below the main band, the triplet spectra show a peculiarly broad absorption, extending into the infrared. These same general aspects also have been found by Livingston and Fujimori[10] in photographic flash experiments on various porphyrins, chlorins and phthalocyanines and may be regarded now as well established. A difference between the chlorin and porphyrin spectra appears in that the chlorophylls and bacteriochlorophyll have broad plateaus in the yellow-green, while the porphyrins show steadily decreasing absorption here. The infrared porphyrin bands are also sharper than those of the chlorophylls. The TPP and ZnTPP spectra are generally similar, the bands of the metal complex being shifted toward longer wave lengths. In both cases, the main peak lies very nearly at twice the energy of the first transition.

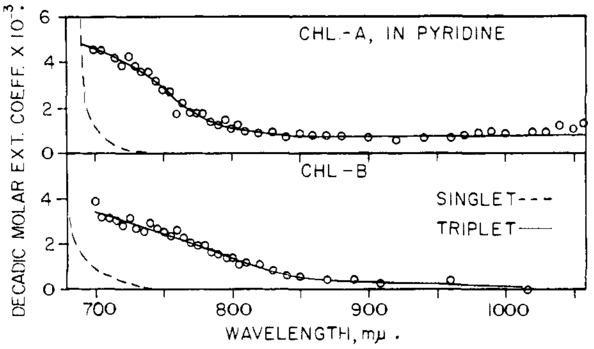

Fig. 4.—Near infrared absorption spectra of triplet states (solid lines) of chlorophyll-a (upper curve) and b (lower curve), in pyridine.

Several authors have discussed the analogies between the spectra of the triplet state and other reversibly bleached forms of the chlorophylls.[11,12] We now note yet another example in the remarkably similar spectra of the photoöxidation product of bacteriochlorophyll[13] and its triplet state. The reason for these close spectral relations is obscure.

2. **Kinetic Results.**—The kinetic data are summarized in Fig. 5 and Tables II and III. Figure 5 shows some of the TPP data in toluene, plotted

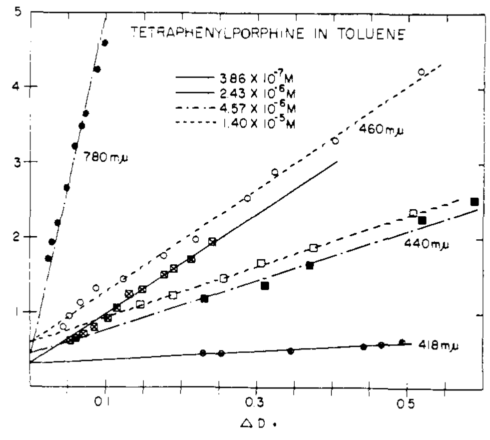

Fig. 5.—Decay kinetics of tetraphenylporphine in toluene; application of eq. 2.

according to eq. 2. Very similar results were obtained in pyridine and with ZnTPP. It is seen that at each wave length parallel lines result, displaced for the various concentrations, and that lines for equal concentrations converge to the same intercept. The kinetic scheme established for the chlorophylls thus applies also to these porphyrins. As with chlorophyll, the shift in intercept with total concentration is small and permits only an

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(10) R. Livingston and E. Fujimori, THIS JOURNAL, **80**, 5610 (1958).

(11) R. Livingston, "Research in Photosynthesis," Interscience Publishers, Inc., New York, N. Y., 1950, p. 10–11.

(12) A. Weller, THIS JOURNAL, **76**, 5819 (1954).

(13) J. C. Goedheer, *Biochim. Biophys. Acta*, **27**, 478 (1958).

order of magnitude estimate of k_3. In Table II, k_1 has been taken to be equal to the intercept A. If an (uncertain) correction for the k_3C_0 term were applied, the k_1's would be decreased by perhaps 10%. The k_1 and k_2 values in Table II are estimated to be accurate to ± 20%. For ZnTPP in pyridine, the uncertainty in k_2 is larger. For both TPP and ZnTPP, constant values of k_1 and k_2 were obtained from data taken throughout the spectrum, and we conclude that essentially only one photoproduct is formed in the reversible flash reaction. For both compounds, however, measurements at the subsidiary peaks (TPP, 513 mμ; ZnTPP, 548 mμ, in toluene) gave plots in which points at high ΔD tended to fall below the expected line. It is possible that small amounts of other products are formed, which absorb in this region.

TABLE II

RATE CONSTANTS FOR TRIPLET STATE DECAY: TETRAPHENYLPORPHINE AND ZINC TETRAPHENYLPORPHINE

	TPP				ZnTPP			
	Toluene		Pyridine		Toluene		Pyridine	
k_3 (l. mole^{-1} sec.$^{-1}$)	5×10^7		...		2×10^7		...	
k_1 (sec.$^{-1}$)[a]	740		670		800		870	
	$k_2 \times 10^{-9}$ (l. mole^{-1} sec.$^{-1}$)							
	λ	k_2	λ	k_2	λ	k_2	λ	k_2
	780	3.2	480	2.2	840	2.8	562.5	1.7
	460	3.0[b]	470	2.4	520	3.2	500	3.7
	460	3.0[c]	460	2.8	465	2.9	460	1.9
	450	2.5			450	3.1		
	440	2.2[b]						
	440	2.1[c]						
Av. $k_2 \times 10^{-9}$ (l. mole^{-1} sec.$^{-1}$)		2.7		2.5		3.0		2.4

[a] No correction for k_3C_0. This may make these values about 10% too high. [b] Concentration = 1.40×10^{-5} M. [c] Concentration = 4.57×10^{-6} M.

At low concentrations, bacteriochlorophyll gave good first-order plots of log $(\Delta D_0/\Delta D)$ *vs.* time. Only at higher concentrations did deviations from first-order kinetics appear, in the expected direction. In Table III, values of the constant k_1 are given, obtained in dilute solutions from the first-order plots and in more concentrated solution by the intercept method. The agreement is good. Since k_1 is relatively very large, the value of k_2 is somewhat uncertain and k_3 cannot be obtained at all.

The rate constants for chlorophyll-a, -b, TPP and ZnTPP are all strikingly similar. The k_1's and k_2's agree to within a factor of two, and the k_3's are experimentally indistinguishable. Apparently neither the side groups nor the introduction of the metal ion have a marked effect on the quenching transitions. Thus the ZnTPP rate constants are not changed appreciably in passing from toluene to pyridine, although spectral changes show the formation of pyridine complexes.[14] The considerable difference in viscosity between toluene and pyridine would in fact lead one to expect a larger effect than is actually observed in k_2.

Claesson, Lindqvist and Holmstrom have independently measured the decay kinetics of the chlorophyll-b triplet in benzene.[15] Their results agree very well with those of Linschitz and Sarkanen,[2] taking into account particularly that three rate constants must be derived from the data, that the decay is exceedingly sensitive to traces of oxygen and that evaluation of the bimolecular constants requires quantitative determination of the triplet absorption spectrum. The respective k_1's agree to 25%, the k_2's agree to 7%, and the rather uncertain k_3's are in each case of the same order of magnitude. It is noteworthy that the chlorophyll-b triplet absorption spectrum given by Claesson, *et al.*, was obtained by photographic techniques.

TABLE III

RATE CONSTANTS FOR TRIPLET STATE DECAY: BACTERIOCHLOROPHYLL IN PYRIDINE

Concn. $\times 10^6$ (mole/l.)	λ (mμ)	$k_1 \times 10^{-4}$ (sec.$^{-1}$)	$k_2 \times 10^{-9}$ (l. mole^{-1} sec.$^{-1}$)
		(1st-order plot)	
2.94	375	1.25	
	430	1.25	
	760	1.13	
		(av. A)	
12.3	430		1.2
	520	1.09	0.9
	655		0.5
	Av.	1.18×10^4 (± 15%)	0.9×10^9 (± 50%)

Of particular interest is k_1, which represents primarily a radiationless transition from the lowest triplet to the ground state. If this transition requires "crossing" of the triplet and ground state energy surfaces, involving mainly electronic excitation and vibrations of the central ring, the lack of side-group effect is reasonable. However, for bacteriochlorophyll, k_1 is roughly 20-fold greater than for the other compounds. It is most unlikely that traces of oxygen in the solution could be responsible for this high value, first because of the stringent degassing procedure,[2] and second because closely concordant k_1 values were obtained in entirely independent experiments (Table III). If the effect were due to presence of quenching impurities, one would have to assume bimolecular quenching rate constants certainly much higher than 10^{10} l. mole^{-1} sec.$^{-1}$, which seems improbable. The further possibilities of rapid decay, due to bimolecular back-reactions of primary photochemical products leading to the ground state, or caused by a high k_3, are both ruled out definitely by the observed kinetics. We conclude that the high k_1 value is real and is an intrinsic property of the molecule.

The effect must in some way involve the change in size and shape of the region of conjugation, in passing from the porphyrins and chlorins to the tetrahydroporphyrins, since the spin-orbit coupling cannot be appreciably modified. In this series, as the number of atoms involved in the conjugation is decreased, fewer nuclear coördinates need be matched to permit passage to the ground state, and critical quenching configurations may be reached more frequently.[16] It is also possible that different coupling of electronic and nuclear

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[14] J. R. Miller and G. D. Dorough, THIS JOURNAL, **74**, 3977 (1952).

[15] S. Claesson, L. Lindqvist and B. Holmstrom, *Nature*, **183**, 661 (1959).

[16] J. Franck, *Ann. Rev. Plant Physiol.*, **2**, 53 (1951).

oscillations in "long-field" molecules compared with "round-field" molecules[17,18] may favor internal conversion. Should data on aromatic hydrocarbons embodying these geometries (coronene *vs.* perylene, for example) bear out this expectation, some clue will be afforded toward the understanding of internal conversion in complex molecules.

3. Complexes of TPP and Transition Metals.—Entirely negative results were obtained in attempts to observe triplet states of copper and cobalt TPP complexes by flash-excitation. Even in the region adjoining the Soret band, and with oscillograms taken under very favorable scattered light conditions, no change in absorption was observed. Assuming the triplet absorption to be comparable to that of TPP or ZnTPP, a 5% conversion lasting 1×10^{-5} second would have been detected readily.

A very short-lived phosphorescence and no observable fluorescence was found by Becker and Kasha[19] in nickel and copper porphyrins in rigid EPA (ether–isopentane–alcohol), compared with strong fluorescence and weak phosphorescence in non-paramagnetic complexes. This was attributed to enhancement of spin–orbit interactions by the paramagnetic ion[20] which both increased the yield of triplet by radiationless transition from the excited singlet and shortened the lifetime for radiative transition between the triplet and ground state. In view of this, we assume that the negative results of our flash experiments with copper and cobalt porphyrins are not due to failure to excite the triplet to a measurable extent but rather to the very short lifetime of the triplet state. Becker and Kasha's measurements gave about 10^{-4} sec. as an upper limit to the triplet lifetime of copper or nickel porphyrins in rigid EPA. The intensity of phosphorescence also suggested that the transition between triplet and ground states was mainly radiative. In fluid solvents, assuming good initial triplet yields, the lifetime of the copper or cobalt TPP complexes must be considerably less than 10^{-5} sec. to show no effect in our experiments. In this case, radiationless as well as radiative transitions may, of course, contribute to the decay. In any event, the extremely short lifetime of these transition-metal porphyrins compared to diamagnetic complexes may again be ascribed to lessening of spin restrictions on the triplet → ground state transition by the paramagnetic ion. The nickel–TPP complex gave a very slight increase in absorption at 4600 Å. when flashed, but the transient decayed with about 10^{-4} sec. half-life and is probably due to a trace of free TPP.

Similar experiments by Livingston and Fujimori on iron and copper porphyrins, done independently of our work and with somewhat longer time resolution, are in entire accord with our results and have been interpreted in the same way.[10]

WALTHAM, MASSACHUSETTS

[17] J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

[18] H. C. Longuet-Higgins, C. W. Rector and J. R. Platt, *ibid.*, **18**, 1174 (1950).

[19] R. S. Becker and M. Kasha, THIS JOURNAL, **77**, 3669 (1955).

[20] P. Yuster and S. I. Weissman, *J. Chem. Phys.*, **17**, 1182 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BRANDEIS UNIVERSITY]

The Quenching of Triplet States of Anthracene and Porphyrins by Heavy Metal Ions[1]

BY HENRY LINSCHITZ AND LAURI PEKKARINEN

RECEIVED JULY 23, 1959

Lifetime measurements have been made on triplet states of anthracene and porphyrins in tetrahydrofuran and pyridine solution containing various salts, and the bimolecular quenching constants have been evaluated. Although the paramagnetic transition metals generally have rate constants near 10^8 l. mole^{-1} sec.$^{-1}$, that for Mn^{++} is much lower ($\sim 10^6$) and various strongly paramagnetic rare earth salts have constants smaller than 5×10^5. The addition of water frequently causes a sharp drop in the quenching constant, which may be correlated with changes in solvation indicated in the absorption spectrum. It is concluded that the quenching is not simply related to the paramagnetism of the salt, and a charge-transfer mechanism is proposed.

The development of the flash-excitation method and its application to solutions makes it possible to observe directly the spectra, decay processes and chemical reactions of excited molecules. Present flash techniques permit the study of states having lifetimes longer than about 3×10^{-6} seconds.[2] While quenching of excited singlet states may be conveniently followed in fluid solvents by observation of fluorescence changes, the necessity for using highly viscous or rigid solvents to observe phosphorescence[3] makes it difficult to study bimolecular quenching of triplets by luminescence measurements. However, the flash method is very well adapted to this purpose. The well-known quenching reactions of oxygen with both singlet[3] and triplet[4] excited states and the effects of chelated heavy metals on singlet–triplet transition rates[5–7] makes the study of paramagnetic quenchers especially interesting. In our previous work on chlorophyll, it was pointed out that, while certain paramagnetic transition metal salts strongly quench the triplet state, rare earth and manganous salts are relatively weak quenchers.[2] In this paper we present further studies on this problem. In-

[1] This work was assisted by a grant from the U. S. Atomic Energy Commission to Brandeis University (Contract No. AT (30-1)-2003).

[2] H. Linschitz and K. Sarkanen, THIS JOURNAL, **80**, 4826 (1958).

[3] (a) P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, Inc., New York, N. Y., 1949. (b) T. Förster, "Fluoreszenz Organischer Verbindungen," Vandenhoeck and Ruprecht, Gottingen, 1951.

[4] G. Porter and M. Windsor, *Discussions Faraday Soc.*, **17**, 178 (1954).

[5] L. Pekkarinen and H. Linschitz, THIS JOURNAL, **82**, 2407 (1960).

[6] R. S. Becker and M. Kasha, *ibid.*, **77**, 3669 (1955).

[7] P. Yuster and S. I. Weissman, *J. Chem. Phys.*, **17**, 1182 (1949).