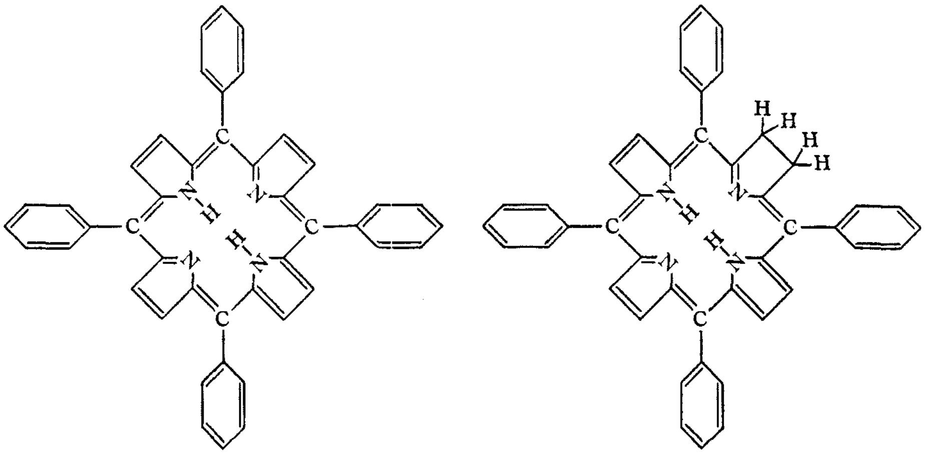
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Possibility of a Triplet State Intermediate in the Photo-oxidation of a Chlorin

BY M. CALVIN AND G. D. DOROUGH[1]

As part of a rather routine examination of the spectra of a number of tetraphenyl porphin and chlorin compounds (see Fig. 1), the zinc salt of tetraphenyl chlorin was prepared and dissolved in benzene. The solution at first was green in color and showed an intense red fluorescence, but upon standing a few hours this fluorescence died out, and the color of the solution changed from green to yellow. The cause of this curious phenomenon was attributed to a light induced oxidation by molecular oxygen, since it was found that benzene solutions of zinc tetraphenyl chlorin were quite stable if either light or air were excluded, or if the air were replaced by carbon dioxide.



a. Tetraphenyl porphin b. Tetraphenyl chlorin

Fig. 1.

The spectrum of such a degraded zinc chlorin solution is given in Fig. 2. This spectrum, upon reference to the spectra of the zinc complexes of porphin and chlorin (Fig. 3), indicates that some of the zinc chlorin still remains, as evidenced by the remnants of a band at about 6200 Å., that some zinc porphin has been formed, as evidenced by a band at 5500 Å. and that some new substance or substances have been formed, as shown by the high absorption in the region 4650 Å., a region where neither porphin nor chlorin have any appreciable absorption. These conclusions were substantiated by removing the zinc from a sample of the photoöxidation product upon which the spectrum had been run, and chromatographing the resulting free base. Found were tetraphenyl porphin and tetraphenyl chlorin and two substances which appeared as dark blue layers on the talc. No attempt was made to identify these blue materials.

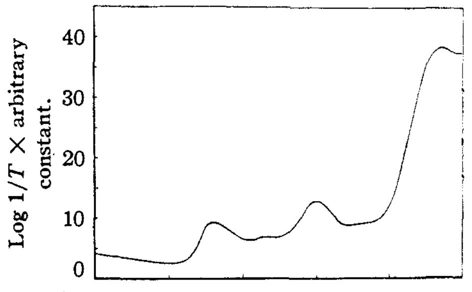


Fig. 2.—Oxygen-degraded zinc chlorin (in benzene).

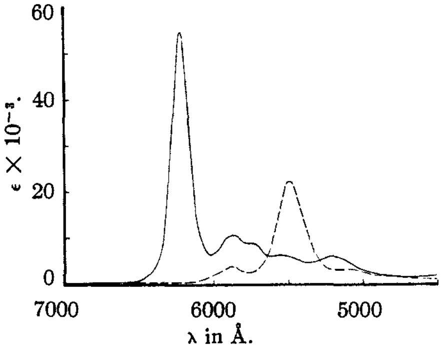


Fig. 3.—Absorption spectra of zinc complexes in benzene: — — — — — —, tetraphenylporphin; ————, tetraphenyl chlorin.

The establishment of a photochemical conversion of chlorin to porphin by molecular oxygen prompted similar experiments with other oxidizing agents. In contrast to the oxygen reaction which gave several products, it was found that a

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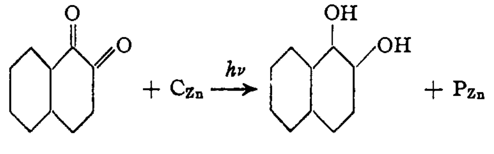
number of ortho and para quinones (*p*-benzo, 1,2-naphtho, 1,4-naphtho, and 9,10-phenanthro) in a deoxygenated benzene solution of zinc tetraphenyl chlorin gave quantitatively with light a single product—zinc tetraphenyl porphin. This latter reaction was thus considered to be of the following type where C_{Zn} and P_{Zn} represent zinc tetraphenyl chlorin and porphin, respectively. It was observed further that para quinones as a class seemed to react more slowly than the ortho quinones. Such a result is not unreasonable, for one might very well expect from spatial considerations alone that an ortho quinone might react in a simple bimolecular manner with the simultaneous removal of both hydrogens from the chlorin, while a para quinone could not sterically do so.

(Illustrating with β-naphthoquinone):



The cleanness of the oxidation of zinc chlorin by the quinones led to a very detailed study of the reaction with one of them, β-naphthoquinone. The reaction was followed by measuring the simultaneous decrease and increase in absorption at 6212 Å. and 5500 Å., respectively, due to the disappearance of chlorin and the formation of porphin as the reaction proceeds (see Fig. 3). By modifying a Beckman spectrophotometer to permit thermostating, it was possible to run the reaction right in this instrument, using the tungsten light of the Beckman both for illumination of the solution and for the measurement of absorption. From rate studies carried out in this manner and other related experiments, it was possible to establish the following facts (see experimental section for details): (1) β-naphthoquinone reacts with zinc tetraphenyl chlorin to give zinc tetraphenyl porphin and β-naphthohydroquinone. (2) Light is required for the reaction—more particularly, only light that is absorbed by the chlorin is required, for illumination was always carried out at 6212 Å. where the naphthoquinone and the zinc porphin have no appreciable absorption. (3) Traces of oxygen inhibit the reaction, *i. e.*, cause the rate to be slower without reacting with the chlorin. (4) The rate of the reaction is independent of the naphthoquinone concentration down to a value of 1.8×10^{-6} *M;* the quantum yield corresponding to this rate is about 0.02. (5) The function of chlorin concentration, $(C_{Zn}) + \log A/\Sigma d$, gives a straight line when plotted against time. (6) The reaction rate increases with decreasing temperature. (7) The reaction rate is directly proportional to the light intensity. (8) There is no evidence for complex formation between the quinone and the chlorin. (9) An ortho quinone of lower oxidation–reduction potential, phenanthro, behaves in a manner identical to the above, but with a rate a factor of three smaller.

The primary step in this reaction must be the absorption of a 6212 Å. photon to give a chlorin molecule excited to the first electronic state. Furthermore, it would appear that the quinone does not react with this excited state, for if it did the rate would be proportional to the quinone concentration. This is due to the fact that the quantum yield is only 2%, and thus 98% of the excited chlorin molecules must be deactivated by a number of processes, fluorescence, solvent and wall deactivation, etc., and it is apparent that if the reaction with quinone were competing with these processes, then the probability of a reaction and thus the rate would increase with increasing quinone concentration. But this is not so; the reaction is independent of the quinone concentration down to a very small value. Thus, if the quinone does not react with the ground state, and does not react with the excited state, then one is forced to the conclusion that it reacts with some intermediate state which is only obtainable from the excited state.

We have considered this intermediate state to be the phosphorescent state, partly because of the ease with which such an assumption will explain the known facts. Figure 4 shows an energy level diagram of this state in relation to the ground and excited states. Now the ground state is a singlet state, that is, there are no unpaired electrons. Since transitions between states of different multiplicity are of low probability, the excited state must also be a singlet, for this transition is obviously of high probability (the extinction coefficient is high). G. N. Lewis[2,3,4] has considered the phosphorescent state to be of a different multiplicity, namely, a triplet state, and accounts for the slow emission of light to the ground state, *i. e.*, phosphorescence, by the low transition probability between these two states. The S′-T transition (dotted line) is a non-radiative transfer, which not being bound by the usual selection rules permits the transition to occur during the very short life time of the S′ state, about 10^{-9} seconds.

Experiments established that zinc tetraphenyl chlorin had a phosphorescence at about 8000 Å. (see Fig. 5) and an intrinsic lifetime of the triplet state of about 8×10^{-3} seconds. If one assumes that every molecule which gets into the triplet state reacts with quinone, then the rate would be independent of the quinone concentration down to the point where the time between collisions became so large as to allow other deactivating processes to occur. Collision number calculations based on the gas laws showed that a triplet state chlorin would, on the average, make an effective collision with quinone in about 10^{-5} second if the quinone concentration were at the point where

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[2] Lewis, Lipkin and Magel, THIS JOURNAL, **63**, 3005 (1941).

[3] Lewis and Kasha, *ibid.*, **66**, 2100 (1944).

[4] Lewis and Kasha, *ibid.*, **67**, 994 (1945).

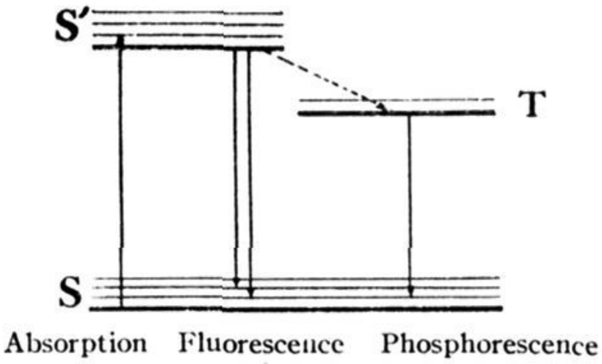

Fig. 4.—Energy level diagram.

quinone independence was experimentally observed to break down. That a triplet state molecule with an intrinsic lifetime of nearly a hundredth of a second could last more than 10^{-5} second in a media where solvent deactivation is inefficient is indeed reasonable.

The inhibitory effect of the oxygen could be accounted for by its paramagnetism. If an excited molecule such as a triplet state chlorin is placed in an inhomogeneous magnetic field, it will radiate due in effect to the breakdown of the selection rules forbidding the transition. Thus a triplet state chlorin approached closely by an oxygen would have a very large probability of being deactivated by radiation to the ground state, due to the magnetic field associated with the oxygen molecule. Thus an observed decrease in the rate of the reaction in the presence of small amounts of oxygen is explained.

The increase in the rate of the reaction with decreasing temperature is not in disagreement with a triplet state mechanism, but neither can it be said that it supports it. What the observation means is that the probability of the S′–T non-radiative transition is increased with decreasing temperature. The direction of change of this probability with temperature depends upon the relative positions of the two states and shapes of their representative potential energy curves, especially at their crossing point. The change may be in either direction.

A mechanism for this reaction may be summarized as

$$\mathrm{C_{Zn}} + h\nu \xrightarrow[k_1]{} \mathrm{C^{S'}{}_{Zn}} \qquad (1)$$

$$\mathrm{C^{S'}{}_{Zn}} \xrightarrow[k_4]{} \mathrm{C_{Zn}} + (h\nu \text{ or } kT) \qquad (4)$$

$$\mathrm{C^{S'}{}_{Zn}} \xrightarrow[k_2]{} C^{T}{}_{\mathrm{Zn}} \qquad (2)$$

$$\mathrm{C^{T}{}_{Zn}} + \mathrm{Q} \xrightarrow[k_3]{} \mathrm{P_{Zn}} + \mathrm{H_2Q} \qquad (3)$$

$$\mathrm{C^{T}{}_{Zn}} + \mathrm{Q} \xrightarrow[k_5]{} \mathrm{C_{Zn}} + \mathrm{Q} + kT \qquad (5)^5$$

k_1 is the primary absorption act
k_2 is the transition from excited singlet to the triplet state
k_3 is the reaction of triplet state molecules with quinone leading to oxidation to porphin
k_4 is the deactivation of excited singlet states by all processes leading to the ground state (fluorescence and thermal deactivation by solvent)
k_5 is the thermal deactivation of triplet state molecules by quinone leading back to ground state chlorin molecules.

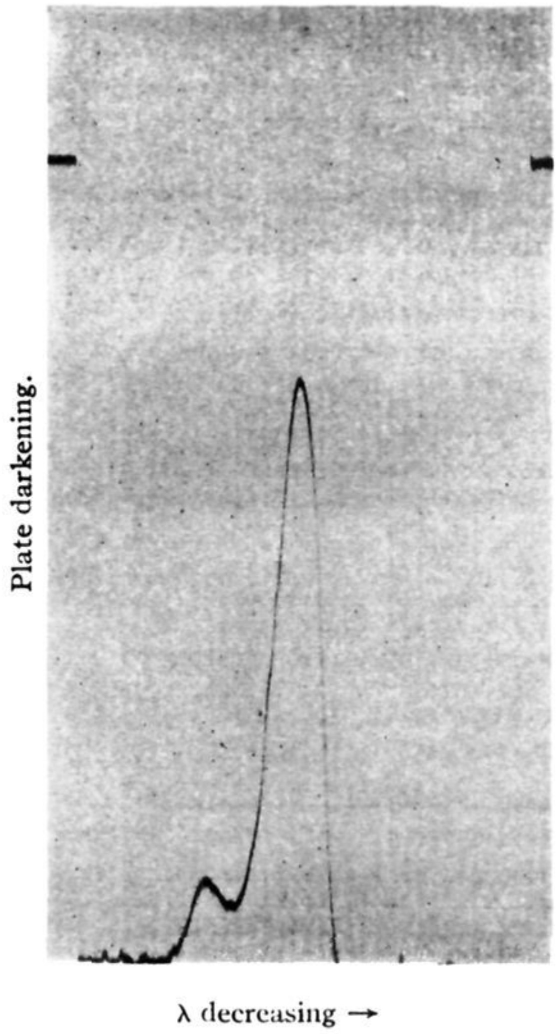

Fig. 5.—Tracing of spectrographic plate showing phosphorescence of zinc tetraphenylchlorin. Peak positions are at approximately 8000 Å. for the tall peak and 9000 Å. for the second peak.

The net rate of disappearance of Zn chlorin is given by

$$-\mathrm{d(C_{Zn})}/\mathrm{d}t = k_3(\mathrm{C^{T}{}_{Zn}})(\mathrm{Q}) \qquad (6)$$

The steady state expression for $\mathrm{C^{S'}{}_{Zn}}$ molecules is

$$K_{\mathrm{a}}I_{\mathrm{absorbed}} = (k_2 + k_4)(\mathrm{C^{S'}{}_{Zn}}) \qquad (7)$$

where K_{a} is a unit conversion factor involving the volume of solution and Avogadro's number to convert photons absorbed per second into moles of photons per liter absorbed per second. And the steady state expression for $\mathrm{C^{T}{}_{Zn}}$ molecules is

$$k_2(\mathrm{C^{S'}{}_{Zn}}) = k_3(\mathrm{C^{T}{}_{Zn}})(\mathrm{Q}) + k_5(\mathrm{C^{T}{}_{Zn}})(\mathrm{Q}) \qquad (8)$$

Combining (7) and (8) for $(\mathrm{C^{T}{}_{Zn}})$ and substituting in (6), we have

$$\frac{-\mathrm{d(C_{Zn})}}{\mathrm{d}t} = \frac{k_2}{k_2 + k_4} \times \frac{k_3}{k_3 + k_5} \times K_{\mathrm{a}}I_{\mathrm{abs}} \qquad (9)$$

I_{abs} may be expressed in terms of Beer's and Lambert's law

$$I_{\mathrm{abs}} = I_0A = I_0(1 - 10^{-\Sigma \mathrm{C_{Zn}}d})$$

where I_0 is the impinging light intensity, A is the fraction of the impinging light absorbed, Σ is the molar extinction coefficient for the wave length band used in these experiments, and Σ is the thickness of the solution through which the light passes.

Now it is also readily seen that $k_2/(k_2 + k_4)$ represents the quantum yield of the triplet state,

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(5) This step was suggested to us by Prof. G. Rollefson and Mr. F. Hueunekens.

and that $k_3/(k_3 + k_5)$ represents the fraction of the triplet state molecules going to porphin. Thus

$$\frac{k_2}{k_2 + k_4} \times \frac{k_3}{k_3 + k_5} = \gamma$$

the quantum yield for the over-all reaction. Using these substitutions in (9) we have

$$-\mathrm{d}(\mathrm{C_{Zn}})/\mathrm{d}t = \gamma K_a I_0 (1 - 10^{-\Sigma \mathrm{C_{Zn}} d})$$

which upon integration gives

$$(\mathrm{C_{Zn}}) + \frac{1}{\Sigma d} \log A = \gamma K_a I_0 t + \pi \text{ (integration constant)} \tag{10}$$

All of our runs showed excellent straight line agreement when the left side of equation (10) was plotted against time.

Another piece of evidence supporting this mechanism was provided by experiments with the copper salt. It was predicted that the copper salt of tetraphenyl chlorin would have a very short lived triplet state due to the magnetic field resulting from the odd electron in the copper orbitals. As a result, it was predicted that copper chlorin, if it reacted with quinone at all, should react very slowly. Experiments were run to test these predictions. It was found that the phosphorescence was so short lived as to be beyond the scope of the phosphoroscope used, which means a life of less than 10^{-5} second. A rate run with copper chlorin and β-naphthoquinone showed the rate to be considerably less than one hundredth that of zinc chlorin. In view of the close chemical similarity between copper and zinc chlorin, and the ease with which the copper chlorin is oxidized by other reagents, we feel this is supporting evidence for the triplet state mechanism.

From equation (9) it is apparent that although the rate of the reaction is independent of the quinone concentration, it is not independent of which quinone is used. The ratio $k_3/(k_3 + k_5)$ will be a characteristic of the quinone used, and increases with the oxidation potential of the quinone and is larger for the ortho quinones than it is for the para quinones. It is interesting to point out the parallelism of these results with those reported by Aronoff[6] on the production of oxygen by illuminated grana using a series of quinones as hydrogen acceptors.

If this reaction of zinc tetraphenyl chlorin is characteristic of the chlorin ring in general, then it may be that the knowledge gained from this reaction may find application in the study of photosynthesis. Using a sample of what we believed to be a pure mixture of chlorophylls *a* and *b*, we found[7] a phosphorescence of fair intensity at about 8000 Å. Whether this phosphorescence was due to chlorophyll is now open to question, for when we extended the work to the separated components of chlorophyll using samples the high purity of which we were absolutely certain, we found that the *b* component phosphoresced weakly at about 8600 Å. with a life of 0.03 second, while no phosphorescence could be detected for chlorophyll *a* below 8600 Å. Nevertheless, the possibility that chlorophyll could act in such a role is not yet excluded, for the S′–T transition under the conditions of the living plant could well be such as to give a high yield of chlorophyll in the metastable state.

It should be pointed out that this photoreduction of quinone by zinc chlorin is in all probability not a conversion of light energy into chemical energy since whatever estimates can be made of its free energy[8] indicate that its value is negative, at least with β-naphthoquinone. However, the reduction by chlorophyll of the pyridine enzymes (TPN or DPN) with the simultaneous formation of the corresponding porphyrin, might be expected to be somewhat endergonic to the extent of about 10 kcal. It could thus be part of the primary photo-chemical transformation.

Experimental

Part I. Apparatus and Materials

The Beckman Spectrophotometer.—The basic unit about which the apparatus was built was a Beckman Quartz Spectrophotometer Model DU. Illumination of the sample was always carried out at a slit width of 0.8 mm. and a wave length setting of 6212 Å., under which conditions the width of the spectral segment was about 300 Å. Absorption measurements which must be run with spectral segments of only a few Ångströms were made at slit width settings around 0.02, where the light intensity was only about 1/1600 of that used for illumination. This light intensity was so low that the reaction was virtually stopped, allowing as many absorption readings to be made as desired with no appreciable light reaction occurring.

Light Source.—The light source for the Beckman is 6–8 v. tungsten filament Mazda 2331 automobile headlight, ordinarily operated at 6 volts. In this work it was run at 9.0 volts, for the intensity from such a lamp is about tripled when the voltage is raised from 6 to 9, thus permitting the use of smaller slit widths and correspondingly narrower spectral ranges for illumination.

Thermostating.—Water from a large reservoir thermostated by conventional means was circulated through a specially designed cell compartment to maintain the temperature within 0.1°. Due to the fact that room temperature was usually below 25°, the benzene in the evacuated cell had the tendency to distil to the upper part of the cell when runs were made at this temperature. To prevent this, the upper part of the cell compartment was heated by a warm stream of air from a heated copper coil (see Fig. 6).

The Reaction Cell.—Figure 6 shows the details of the reaction cell and stirrer. The section in the optical path was constructed from 1-cm. Pyrex square mandrel tubing with one pair of opposite faces ground optically flat. The blank cell for the solvent was a twin to the reaction cell. The reaction cell had to be evacuated in order to exclude oxygen. The solution in the cell had to be stirred since the reaction took place only in the light beam, and thermal diffusion was not fast enough to keep the solution mixed. These two conflicting requirements, evacuation and stirring, were satisfied by the use of an all glass enclosed magnetic stirrer. Since there was no direct mechanical connection between the motor and the reaction cell, this type of stirrer also allowed the blank cell to be placed in the light beam for the balancing of the instrument when taking absorption readings.

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(6) Aronoff, *Plant Physiol.*, **21**, 393–409 (1946).

(7) Calvin and Dorough, *Science*, **106**, 433 (1947).

(8) Fischer–Orth, "Die Chemie des Pyrroles," Vol. II, Akademische Verlagesellschaft (1937).

Filter Slide.—In addition to the very extensive modifications made on the cell compartment of the Beckman, a minor change was made on the filter slide. This slide has three openings which may be placed in front of the light path. For this work, the first opening was left blank, the second was replaced by a wire screen transmitting 38.0% of the light, and the third was filled with a piece of black cardboard. The filter slide was thus capable of use as a shutter, and as a means of varying the light intensity without varying the special composition of the light.

Preparation of Solutions. Zinc Chlorin.—The preparation was carried out in as dim a light as possible. About 2 mg. of free base chlorin was dissolved in 10 cc. of dioxane and boiled for several minutes with solid zinc acetate. The resulting zinc chlorin was then transferred to benzene, washed and dried, and made up to a volume of 100 cc. This gave a volume of roughly 3×10^{-5} *M*. The exact concentration was determined from the log $1/T$ value of the peak at 6212 Å.

$$C = \frac{\log 1/T}{\epsilon} = \frac{\log 1/T}{5.49 \times 10^4} \quad \text{for a 1 cm. cell}$$

Such solutions were found to be quite stable if stored in the dark and sampled in only the minimum of light.

Preparation of Solutions. β-Naphthoquinone.—Stock aminonaphthol was recrystallized and oxidized by ferric chloride according to "Organic Syntheses."[9] A number of stock benzene solutions were made up with the pure β-naphthoquinone in concentrations varying from 1.89×10^{-5} to 4.72×10^{-3} *M*.

Preparation of Samples for Rate Experiments.—Small aliquots of the order of 1 or 2 cc. of the chlorin and quinone solutions that would give the desired final concentrations were mixed in a small flask. This solution was then used to fill a small delivery cup equipped with an overflow spout. The delivery cup when filled delivered 2.56 cc. of solution, as shown by standardizations with benzene. During the evacuation of the cells, however, a little benzene was usually lost by distillation even though the solutions were frozen during pumping. A correction for this was made by the simple equation

$$V_0 = 2.56\ (C_M/C_O)$$

Where V_0 is corrected volume, C_M is concentration of chlorin when measured into the cell, and C_O is initial value of the chlorin concentration after pumping (determined spectrally). These sampling operations for the reaction mixture were also carried out in the very minimum of light. Solutions for the spectral blank were made with identical quinone concentrations, but without the chlorin.

Evacuation of Samples.—After the sample had been transferred to the reaction cell, the stirrer assembly was attached and the whole unit connected to a vacuum line. The solution was frozen in liquid nitrogen, and the system evacuated. The stopcock on the reaction cell was then closed and the solution thawed out and shaken. The cell was then refrozen, repumped and rethawed in an identical manner. The cell was now filled with hydrogen at nearly atmospheric pressure, and again frozen, pumped and thawed as before. Hydrogen was then twice more admitted. The cell was not thawed the last time; it was taken directly to the Beckman and placed in the thermostated cell compartment.

These operations, too, were carried out in a very minimum of light. As an added precaution, the reaction cell was kept covered by a small "skirt" of black cloth.

Method of Taking Rate Measurements.—After the reaction cell had attained temperature equilibrium, the rate experiments were conducted by illuminating the solution with stirring for intervals of five to fifteen minutes, and recording absorption readings at 6212 Å., 5500 Å., and 4640 Å. before and after each illumination period. The intensity of illumination was determined with a standardized thermopile-galvanometer circuit.

Absorption Spectra.—All absorption spectra were measured on a Beckman Quartz Spectrophotometer Model DU. Points were taken every 50 Å. by even fifties. The curves given represent smooth curves drawn through all points.

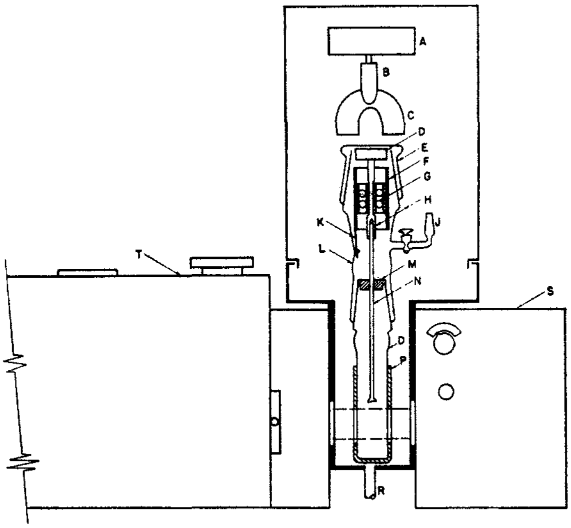

Fig. 6.—Reaction cell and stirrer assembly: A, motor; B, chuck; C, magnet; D, iron bar; E, 29/42 standard taper joint; F, brass column; G, double row ball bearing; H, chuck for stirrer; J, 10/30 standard taper inner joint; K, spring clip to hold column (F); L, Pyrex glass to standard taper 19/38 joint; M, brass bearing; N, glass stirrer; O, Pyrex cell (1 cm. square mandrel tubing); P, cell holder; R, thermostated water inlet; S, photocell compartment of Beckman; T, monochromator case of Beckman.

Phosphorescent Spectra.—The methods and apparatus used to determine spectra were identical to those described by Lewis and Kasha[4]; in fact, it was the same apparatus. The lifetime of the phosphorescences were measured on a photo-electric phosphoroscope.[10] Light from the phosphorescing sample is allowed to impinge on an infrared sensitive photo-multiplier tube, the signal from which is imposed on the vertical plates of an oscillograph. From the resulting decay curve trace and a knowledge of the sweep time, the life time can be calculated.

Part 2. Calculations

Determination of Concentrations During a Run.—In any region of light absorption where the absorption is due to only chlorin and porphin, Beer's law may be used to derive an expression for the chlorin concentration (for a 1.0-cm. cell)

$$C_c = \frac{\log 1/T - \epsilon_p C_T}{\epsilon_c - \epsilon_p}$$

where C_c is the concentration of the chlorin in moles/l, C_T is the total concentration of pigment, $C_c + C_p$; T is the fraction of light transmitted; and ϵ_p and ϵ_c are the molar absorption coefficients for phorphin and chlorin. Two wave lengths could be used

$$\text{at 6212 Å.} \quad C_c = \frac{\log 1/T(\text{obs.}) - 180C_T}{54700}$$

$$\text{at 5500 Å.} \quad C_c = \frac{22200C_T - \log 1/T\ (\text{obs.})}{16{,}300}$$

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[9] "Org. Syntheses," Vol. XVII, p. 11, paragraph 1, p. 68.

[10] D. M. McClure, to be published.

Since the porphin has practically no absorption at 6212 Å., this wave length was used in most of the calculations. The values from measurements at 5500 Å. were used only for an occasional check.

Determination of Quantum Yield.—From the previously derived rate law (equation 10) it is seen that the quantum yield is easily calculated from the slope of the straight line obtained by plotting the left side of the equation against time

$$\gamma = \text{slope}/K_aI_0 \qquad (11)$$

Now K_a is merely a unit conversion factor, being equal to the reciprocal of the product of Avogadro's number and the volume of the solution in liters. The quantity I_0 is derived from the intensity of the light leaving the Beckman as measured by a standardized thermopile–galvanometer unit (sensitivity of 91.3×10^{-6} watt/sq. cm./cm. of deflection), the area of the light beam at the point of measurement (1.77 sq. cm.), the magnitude of the correction for the amount of light reflected, scattered, and absorbed before reaching the solution (1.6%), and the assumption that the average energy of the photons of the illuminating beam were that of a 6212 Å. photon. Substituting these quantities into equation (11)

$$\gamma = 2.0 \times 10^4 \times \frac{\text{slope} \times V}{D} \qquad (12)$$

V is the volume of the solution in ml., and D is the galvanometer deflection in cm.

It may seem curious that the final rate law should be used for the calculation of the quantum yield, since the quantum yield is an obvious factor in the determination of the rate law. As it turns out, however, the form of the rate law of equation (10) is rather general in character, and will be given by a number of other mechanisms, as well as the one from which it was derived here. In these other cases, however, the quantum yield would be a function of the quinone concentration such that the slope of the line represented by the equation would vary with the quinone. The fact that it does not tells us that these mechanisms are incorrect, but the fact that the equation gives a straight line plot indicates the form of the equation is right, and that we can use the simple equation (12) for calculating quantum yield rather than the more involved and laborious direct calculation which makes no assumption as to mechanism. Comparison of the two methods for a number of runs gave exactly identical results.

Part 3. Experimental Results

Effect of Oxygen and Quinone Concentration.—The first runs that were made (see Table I) were not swept out with hydrogen as is described in the section on the evacuation of samples, but were merely alternately pumped and thawed three times. Now all of these runs individually gave good straight line plots for the function $(C_{Zn}) + (\log Z/\Sigma d)$ against time, and all of the runs showed no trace of an oxygen reaction (no increase in absorption at 4640 Å.). But it is evident from the table that the runs reproduce each other very poorly, and that the rather large variation in quinone concentration has had little effect on the rate (quantum yield). In fact, the data seemed to indicate that the reaction was independent of the quinone concentration, with the quantum yields grouping around 0.015. If one assumed that this were so, then the variance among the different runs might be accounted for by an inhibition of the reaction by oxygen, since the oxygen content of the solutions is the only thing which might logically vary from one run to another. This hypothesis was tested by reducing the oxygen content of the solutions to a very low level, and noting whether or not the rate of the reaction increased. Control experiments were first made to get some sort of measure of the amount of oxygen in the solutions. Table II shows the results of two blank runs which were made in every respect like other runs except that the quinone was left out. Thus the only thing that could occur was the oxygen reaction. Experiment 8 was pumped in a manner identical to those experiments listed in Table I; experiment 9 was swept with hydrogen as described in the section on the evacuation of the reaction cell. Whereas experiment 8 showed a percentage change in the 6212 Å. band of 12.5% in thirty minutes, experiment 9 showed only a change of 13.3% in 105 minutes.

Table I

Runs Not Swept with Hydrogen

Temperature, 25°; chlorine concn. $\cong 10^{-5} M$

Run	Concn. of quinone, M	Quantum yield
1	3.15×10^{-4}	0.019
2	3.15×10^{-4}	.015
3	9.44×10^{-4}	.012
4	9.44×10^{-4}	.010
5	9.44×10^{-4}	.016
6	3.15×10^{-3}	.016
7	3.15×10^{-3}	.014

Table II

Effect of Hydrogen Sweeping

Time, min.	log 1/T 6212 Å.	log 1/T 4640 Å.	% change 6212 Å.
Run 8. No hydrogen sweeping			
0	0.865	0.050	
5	.840	.063	2.9
10	.820	.078	5.2
20	.785	.103	9.2
30	.757	.121	12.5
Run 9. With hydrogen sweeping			
0	0.905	0.050	
10	.880	.068	2.7
35	.855	.090	5.5
60	.830	.106	8.3
105	.785	.136	13.3

Knowing now that the oxygen content could be reduced by sweeping with hydrogen, a new series of experiments were conducted with hydrogen sweeping incorporated into the procedure. Table III summarizes the results of these experiments. It is seen that the reduction in the amount of oxygen has indeed caused a marked increase in the quantum yield, and that over a very wide range in concentration of quinone, the quantum yield remains virtually constant. Undoubtedly these values do not represent the limiting value of the quantum yield, since a trace of oxygen is still present, but they are probably quite close to it.

TABLE III

RUNS SWEPT WITH HYDROGEN AT 25°

Run	Concentration of chlorin, M	Concentration of quinone, M	Quantum yield
10	1.10×10^{-5}	6.65×10^{-6}	0.0204
11	1.2×10^{-5}	1.81×10^{-5}	.0191
12	1.12×10^{-5}	3.99×10^{-4}	.0219
13	1.08×10^{-5}	1.63×10^{-3}	.0215

Run 10 is an extremely interesting one, for the quinone is present in smaller amounts than the chlorin. Yet the rate remained at the same high level until the quinone had fallen to only 1.8×10^{-6} M, and even at that low concentration the rate broke only slightly (see Fig. 7). It was not until the quinone was nearly gone that a reaction with the trace of oxygen present began to occur.

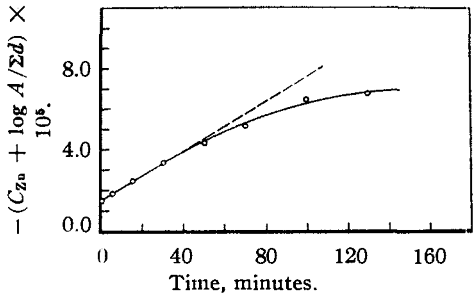

Fig. 7.—Run 10, slope: 5.97×10^{-7}.

Quinone-Chlorin Complex Formation.—An attempt was made to observe complex formation between zinc chlorin and β-naphthoquinone. This was done by running the spectrum of the zinc chlorin in the presence and absence of quinone. Absolutely no deviation was found in the two spectra in the region 6500 to 3000 Å., thus indicating that such complex formation does not exist.

Effect of Temperature.—The effect of temperature was studied by lowering the constant temperature bath from 25 to 10°. The results of two such runs are summarized in Table IV. Although the agreement between the runs is not exceptional, there is no doubt that the rather remarkable result of increasing rate with decreasing temperature has been found.

TABLE IV

RUNS SWEPT WITH HYDROGEN

Temperature, 10°; chlorin concn. ≅ $10^{-5} M$

Run	Quinone concn., M	Quantum yield
14	3.36×10^{-4}	0.0254
15	$1\ 67 \times 10^{-3}$	0.0224

Effect of Light Intensity, Run 16.—The variation of the rate with light intensity was measured by the use of the screen described in the section on the filter slide. This screen transmitted 38.0% of light hitting it. A run was started with the screen in the light path, and then about half way through the run, the screen was removed and the run continued. The ratio of the slope of the rate curve for the second part of the run to the first part (see Fig. 8) was 2.65. The ratio of the light intensities for the second part of the run to the first part is

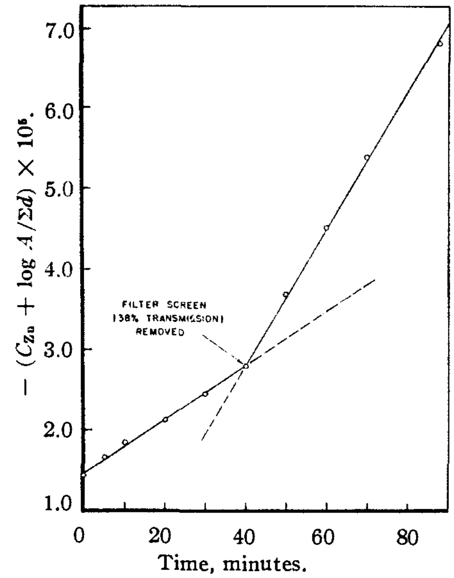

Fig. 8.—Run 16, slopes: 0–40 minutes, 3.2×10^{-7}; 40–88 minutes, 8.52×10^{-7}.

$$\frac{(I_0)_2}{(I_0)_1} = \frac{1}{0.38} = 2.63$$

Thus, the rate is proportional to the light intensity.

TABLE V

RUN 16

Corrected volume (V)	2.36 ml.
Quinone concn., M	3.42×10^{-4}
Temperature, °C.	10
Av. galv. defl. (D)	1.49 cm.

	Experimental log $1/T$					Calculated
Time	6212 Å.	5500 Å.	4640 Å.	Chlorin concn., 6212 M	A	$(C_{Zn}) + (\log A/d)$
			38% screen filter in			
0	0.632	0.078	0.025	1.15×10^{-5}	0.365	-1.43×10^{-5}
5	.590	.085	.028	1.07×10^{-5}	.342	-1.67×10^{-5}
10	.562	.095	.029	1.02×10^{-5}	.328	-1.83×10^{-5}
20	.508	.109	.028	0.925×10^{-5}	.303	-2.12×10^{-5}
30	.457	.123	.027	0.832×10^{-6}	.278	-2.44×10^{-6}
40	.404	.137	.027	0.735×10^{-6}	.251	-2.75×10^{-5}
			38% screen filter out			
50	0.298	0.168	0.027	0.542×10^{-6}	0.291	-3.69×10^{-5}
60	.222	.188	.025	$.440 \times 10^{-6}$	.146	-4.52×10^{-5}
70	.162	.206	.025	$.295 \times 10^{-6}$	.108	-5.39×10^{-5}
88	.094	.223	.025	$.171 \times 10^{-6}$	.065	-6.80×10^{-5}

Details of Rate Data.—Complete experimental and calculated data for all the completed runs would consume far too much space to serve any useful purpose. To make completely clear our methods, however, Table V has been prepared summarizing the calculations for run number 16 (see also Fig. 8). The data of all completed runs were entirely consistent.

Acknowledgment.—The authors wish to acknowledge the many helpful suggestions and assistance of Prof. G. K. Rollefson, Drs. M. Kasha and R. V. Nauman, and Messrs. F. M. Huennekens and D. M. McClure. The junior author also wishes to express his appreciation for the assistance of the National Research Council.

Summary

1. The photochemical oxidation of a simple chlorin molecule to the corresponding porphin by oxygen and a number of ortho and para quinones is described.

2. From evidence based on rate experiments, a mechanism for the photochemical oxidation of tetraphenyl chlorin by β-naphthoquinone is derived involving the triplet state of the chlorin molecule as an intermediate.

3. A possible significance of the triple state of chlorophyll is indicated.

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXXI. Conductance of Some Electrolytes in Pyridine at 25°[1]

BY DAVID S. BURGESS[2] AND CHARLES A. KRAUS

I. Introduction

In the last paper of this series,[3] it was shown that various quaternary onium salts are normal electrolytes in pyridine. Silver picrate and perchlorate, however, proved to have much larger dissociation constants than was to have been expected. Certain unreported results for sodium and potassium salts were erratic, indicating sources of error that had not been brought under control.

In view of these circumstances a comprehensive study of solutions in pyridine seemed worth-while.

It was suspected that inconsistencies in the results obtained with the alkali metal salts may have been due to the presence of small amounts of alcohol even though the conductance of the solvent was very low. On treating the pyridine with aluminum chloride, solvent was obtained that yielded consistent results with all salts. The marked effect of alcohol and, perhaps, other impurities that were eliminated by aluminum chloride, led to a study of the effect of the addition of small polar molecules, such as water, ammonia and methanol, on the characteristic constants of electrolytes dissolved in pyridine.

An investigation was made of several lithium, sodium and potassium salts and, in view of the unusual behavior of silver salts, silver picrate was included among the salts studied.

Certain quaternary ammonium salts which have been investigated in ethylene chloride and nitrobenzene, were measured for purposes of comparison. These salts were: tetra-*n*-butylammonium nitrate and acetate, tetramethylammonium picrate, ethyltrimethyl-, hydroxyethyltrimethyl-, bromoethyltrimethyl-, bromomethyltrimethyl-, and phenyldimethylhydroxy-ammonium picrate.

Measurements with pyridonium and piperidonium nitrates, as well as with phenylpyridonium picrate, are of obvious interest in view of the strong proton affinity of the solvent.

Measurements were also carried out with ammonium picrate, iodide and nitrate. The nitrate yielded inconsistent values for the conductance of the ammonium ion; publication of results for this salt is withheld pending further investigation.

In order to evaluate ion conductances, measurements have been made with tetrabutylammonium triphenylborofluoride and a value for the conductance of the tetrabutylammonium ion has thus been obtained according to Fowler's[4] method.

II. Experimental

Materials.—Pyridine prepared by the method of Luder[3] failed to yield consistent results; the procedure was, accordingly, modified so as to provide for elimination of residual traces of alcohol. This was accomplished by distillation from aluminum chloride. The distillate was then fractionally distilled, refluxed over aluminum oxide and finally fractionated. Pyridine obtained in this manner had a specific conductance below 1×10^{-9} and reproducible conductance values were obtained with salts which had previously yielded inconsistent results.

Methanol was refluxed over aluminum amalgam and finally distilled. Its specific conductance was 5×10^{-8}; a 0.275 M, solution in pyridine showed a specific conductance of 2×10^{-9}.

Ammonia was dried by distillation from sodium amide. A 0.0733 M solution of ammonia in pyridine had a specific conductance of 6×10^{-9}.

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(1) This paper is based on a portion of a thesis presented by David S. Burgess in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1940.

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(3) Luder and Kraus, THIS JOURNAL, 69, 2481 (1947).

(4) Fowler and Kraus, *ibid.*, 62, 2237 (1940).