[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY, UNIVERSITY OF MINNESOTA, INSTITUTE OF TECHNOLOGY]

The Pheophytin-sensitized Photoreduction of *p*-Dimethylaminoazobenzene by Ascorbic Acid[1]

BY ROBERT LIVINGSTON AND RUDOLPH PARISER

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The pheophytin-sensitized photoöxidation of ascorbic acid by an azo dye, Butter Yellow, exhibits an inducton period. If *p*-dimethylaminoaniline, which is one of the products of the reaction, is added to the reaction mixture, the induction period is eliminated. The following empirical equation represents the quantum yield as a function of the several concentrations.

$$\varphi_{-\mathrm{DD}'} = \frac{1}{2} \times \frac{[\mathrm{AH_2}][\mathrm{DD'}]}{1.6 \times 10^{-5} + 1.69 \times 10^{-3}[\mathrm{AH_2}] + [\mathrm{DD'}] + 1.34 \times 10^{-2}\,[\mathrm{DH_2}] + 6.5 \times 10^{-3}\,[\mathrm{D'H_2}]} \times \left(\frac{1}{A + 5.9 \times 10^{2}\,[\mathrm{DD'}]} + \frac{[\mathrm{DH_2}]}{B + C[\mathrm{DD'}] + [\mathrm{DH_2}]} \times \frac{1}{4.20 \times 10^{-3} + [\mathrm{AH_2}]}\right) \quad (1)$$

The significance of the symbols is as follows: AH_2, ascorbic acid; DD′, butter yellow, DH_2, *p*-dimethylaminoaniline; $D'H_2$, aniline, $A = 1.05 \times 10^{-9} \exp(8700/RT)$, $B = 7.3 \times 10^{-12} \exp(8700/RT)$ and $C = 1.11 \times 10^{-7} \exp(8700/RT)$. The limiting yield is one half. A mechanism is proposed which is compatible with the empirical equation.

A preliminary study[2] of the chlorophyll and pheophytin-sensitized photochemical reductions of azo dyes by each of a wide variety of reducing agents, indicated that the system pheophytin a–butter yellow–ascorbic acid is suitable for intensive study. The compounds can be obtained readily in relatively pure form; they are separately stable in air and in solution over a fairly wide range of acidities; the spacing of their absorption maxima is favorable for spectrophotometric analysis; their sensitized photochemical reaction is conveniently efficient and is not accompanied by a detectable dark reaction.

Accordingly, an extensive study was made of this system in methanolic solutions and the following results were obtained. The maximum value of the quantum yield for the disappearance of butter yellow is one half. The yield is independent of the pheophytin concentration, over the range 0.94×10^{-5} to 2.64×10^{-5} *m*, and of the intensity of absorbed light from 2.5×10^{14} to 5.2×10^{14} quanta/second. At low concentrations, the yield is proportional to the concentration of butter yellow and of ascorbic acid but approaches limiting values as either of these concentrations is increased indefinitely. For buffered or unbuffered solutions of the reactants and sensitizer, the yield is initially low but increases with illumination until an appreciable fraction of the dye has been reduced.

It was at first suspected that the low value of the initial yield was due to the presence of an inhibitor which was introduced as an impurity with one of the reagents, an effect similar to that of oxygen in inhibiting the chlorophyll-photosensitized reduction of methyl red by phenylhydrazine.[3] This postulate was disproven by a series of critical experiments, which demonstrated that the supposed inhibitor is not oxygen and that it was not introduced with the solvent or any of the reagents. It was also shown that the yield is not a function of the time which the reaction mixture stands in the dark before it is illuminated, nor is it affected if the illumination is interrupted by a prolonged dark period. It follows, therefore, that the reaction is autocatalytic. The reduction of butter yellow results in the formation of aniline and *p*-dimethylaminoaniline. The addition of aniline to the reaction mixture in amounts comparable to those produced in the photochemical reaction, produces only a slight retardation of the reaction. However, a similar addition of *p*-dimethylaminoaniline to the initial mixture completely eliminates the induction period. These facts indicate that there are (at least) two reaction paths, an efficient one involving *p*-dimethylaminoaniline and a less efficient mechanism which involves only the stoichiometric reactants.

Although a large number of reasonably accurate measurements of the yields of this system were made, the complexity of the results makes it impossible to obtain a unique equation relating the yield to the concentrations. Correspondingly, the best that can be said for the detailed mechanism, which is suggested in this paper, is that it appears to be consistent with the present data and with other published studies of chlorophyll photochemistry.

Experimental Methods and Materials

Materials.—Methanol was purified as has been described elsewhere.[4] The pheophytin was prepared from purified[3] chlorophyll a by treatment with methanolic HCl and was purified chromatographically. Since the opinion was once current[5] that pheophytin is incapable of acting as a sensitizer, the sample used in these experiments was tested for traces of unchanged chlorophyll both spectrophotometrically[8] and for Mg by a modification of the titan yellow method.[7] Chlorophyll a was not detected by either method and if present was certainly less than 5% of the total pigment. The butter yellow (*p*-dimethylaminoazobenzene) was purified chromatographically on activated alumina and by crystallization. Mallinckrodt USP *l*-ascorbic acid was used without further purification. Chloroacetic acid and ammonium chloroacetate were purified by crystallization. Aniline was purified by distillation and *p*-dimethylaminoaniline by repeated recrystallization.

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(2) R. Pariser, Doctoral Thesis, University of Minnesota, 1950.

(3) R. Livingston, D. Sickle and A. Uchiyama, *J. Phys. Chem.*, **51**, 775 (1947).

(4) R. Livingston and R. Pariser, THIS JOURNAL, **70**, 1510 (1948).

(5) *Cf.*, E. Rabinowitch, "Photosynthesis," Vol. I, Chap. 18, Interscience Pub., New York, N. Y., 1945.

(6) F. Zscheile and D. Harris, *Bot. Gaz.*, **104**, 515 (1943).

(7) Reference 2, p. 30 and E. Sandell, "Colorimetric Determinations of Traces of Metal," Interscience Publishers, New York, N. Y., 1947, p. 305.

Apparatus and Procedure.—The photochemical experiments were performed with apparatus[8] which was an improvement upon, but was essentially similar to, that used by Livingston and Pariser.[4] Both the reaction cell and the thermopile were immersed in a thermostat.

A band of red light, isolated from the output of a tungsten filament lamp by a glass filter and a $CuSO_4$ solution, served as the actinic radiation. Since only pheophytin absorbed in this region, it was possible to calculate, by graphical integrations, the frequency distribution of the absorbed light. The wave lengths ranged from 6000 to 6950 Å. and the mean frequency corresponded to λ 6430 Å.

Reaction mixtures were prepared in dim light and were freed from oxygen by boiling off about 30% of the solvent under vacuum. The period of illumination was broken up into a series of short intervals, each one corresponding to a reduction of the butter yellow concentration by about 10 to 25% of its initial concentration. The concentration of butter yellow was determined and that of pheophytin checked at the end of each interval. For the analysis, the reaction vessel was transferred directly from the photochemical apparatus to a special holder in the Beckman spectrophotometer. Average values of the quantum yield were calculated for each such short interval by dividing the change in the number of dye molecules by the total number of photons absorbed.

The majority of the photochemical experiments were performed with buffered solutions containing 0.075 *m* ammonium chloroacetate. Pheophytin can exist in any of three different forms, depending[9] upon the acidity of the solution. Butter yellow also is an indicator.[2] In strongly acid solutions, its principal absorption maximum is at 5200 Å. and has an extinction coefficient of 4.77×10^4 mole^{-1} cm.$^{-1}$ (using common logarithms). In basic solutions, the principal maximum is at 4080 Å., with $\epsilon = 3.04 \times 10^4$ mole^{-1} cm.$^{-1}$. The absorption of this form is negligible for wave lengths greater than 5100 Å. There are isosbestic points at 3420 and 4590 Å. In the buffered solution, about 99% of the butter yellow exists as the free base and the pheophytin is practically all in its intermediate form.

The chief advantage of the buffer in this work is that it maintains the relative amounts of the several forms of the two pigments invariant and thereby decreases the errors of the spectrophotometric analyses. However, the omission of the buffer has little effect upon the proportion of the different forms of butter yellow and of pheophytin in the initial reaction mixtures. Quantum yield measurements made in unbuffered solutions were similar to those obtained with the corresponding buffered solution, although, on the average, the yields for unbuffered solutions may have been about 3% higher than those for buffered solutions.

A few experiments were performed with a more acid, buffered solution in which about 70% of the pheophytin and 14% of the butter yellow were in their acid forms. Under these conditions, the quantum yield was less than 0.01. In a solution made basic by the addition of sodium methoxide, the reaction occurred with reduced efficiency, the maximum quantum yield being about 0.22.

The Reaction Products.—Catalytic reduction of butter yellow with H_2 produces a transient colorless solution which changes to a yellow solution containing aniline, dimethylaminoaniline and unchanged butter yellow.[10] Unlike hydrazobenzene, solutions of *p*-dimethylaminohydrazobenzene appear to disproportionate rapidly. A simple chromatographic technique[11] was used in an attempt to determine the products of the photochemical reaction. The solid medium was blotting paper, the solvent was a mixture of methanol and petroleum ether and Cl_2 gas was used to "develop" the chromatogram. By the use of this technique, the components of a synthetic mixture of pheophytin, butter yellow, aniline and *p*-dimethylaminoaniline can be separated and identified. Addition of ascorbic acid to the mixture does not interfere with the separation nor increase the number of bands observed. Comparison of such synthetic mixtures with a solution, prepared by concentrating a partially reacted photochemical solution, showed that the principal products of the photochemical reduction of butter yellow are aniline and *p*-dimethylaminoaniline. The oxidation product of ascorbic acid was not identified, but was assumed to be dehydroascorbic acid.[12]

Kinetic Results and Interpretation

The relation between the quantum yield and the

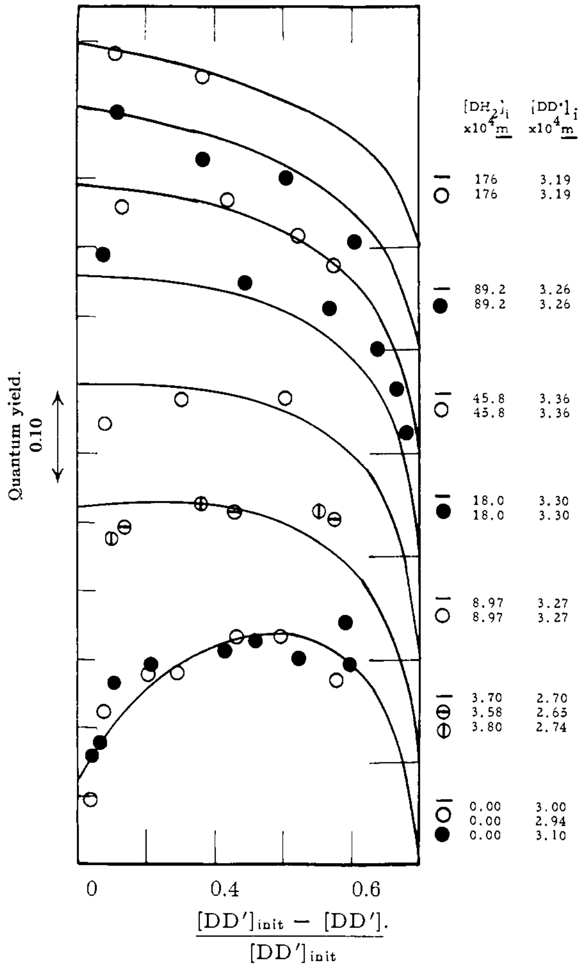

Fig. 1.—The quantum yield as a function of the ratio of the change in the concentration of Butter Yellow to its initial concentration. The effect of added *p*-dimethylaminoaniline. The ordinate origin corresponding to each curve is indicated by a horizontal line on the right-hand side of the figure. The scale of the ordinates is given by the length of the doubleheaded arrow which corresponds to an increment of 0.10 in φ. The double column of figures lists the parameters used in calculating the curves and the initial concentrations of the experiments whose measured yields are represented by circles.

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(8) A detailed description of the apparatus, experimental methods and calculations is given in the Doctoral Thesis of R. Pariser, University of Minnesota, 1950, and for reasons of brevity is not repeated in the present paper.

(9) R. Livingston, R. Pariser, L. Thompson and A. Weller, THIS JOURNAL, **75**, 3025 (1953).

(10) Reference 2, pp. 42–3. See also A. Andrews and A. Lowry, *ibid.*, **56**, 1411 (1934).

(11) W. Brown, *Nature*, **143**, 377 (1939).

(12) J. Penney and S. Silva, *Biochem. J.*, **37**, 403 (1943).

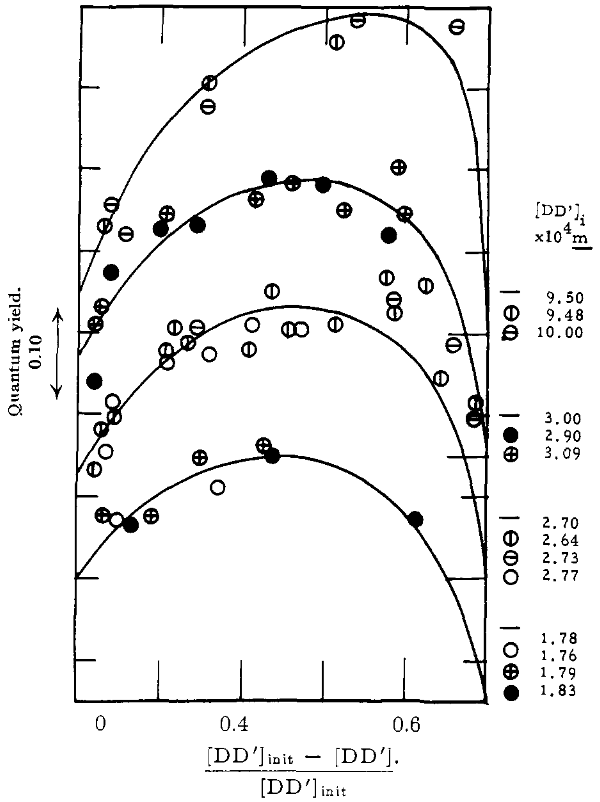

Fig. 2.—The quantum yield as a function of the ratio of the change in the concentration of Butter Yellow to its initial concentration: the effect of varying the initial concentration of Butter Yellow.

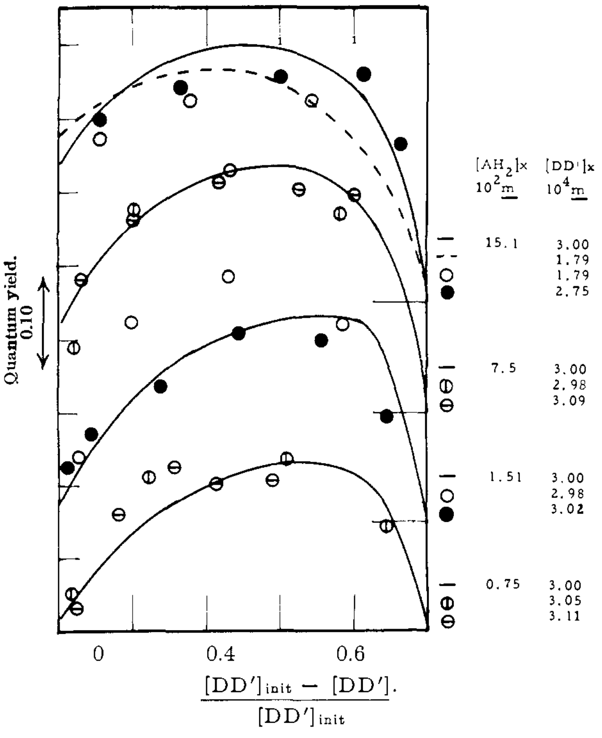

Fig. 3.—The quantum yield as a function of the ratio of the change in the concentration of Butter Yellow to its initial concentration: the effect of varying the initial concentration of ascorbic acid.

concentrations of reactants and products is illustrated by Figs. 1, 2 and 3. The points correspond to the experimental average yields and the curves are plots of an empirical equation (equation 1) which was fitted to the data. All of the data represented by these figures were obtained with buffered solutions at approximately 27°.

The measurements corresponding to Fig. 1 were made with solutions whose initial concentrations of ascorbic acid and butter yellow were 7.5×10^{-2} *m* and approximately 3×10^{-4} *m*, respectively. It is apparent from these results that the yield falls off as the azo dye is used up and that a relatively small initial concentration ($\sim 5 \times 10^{-4}$ *m*), of *p*-dimethylaminoaniline is sufficient to eliminate the initial induction period. Higher concentrations of this substance retard the reaction.

Figure 2 represent data which were obtained with solutions initially free from *p*-dimethylaminoaniline. These values illustrate both the slow rise due to the accumulation of the substituted aniline and the rapid drop which occurs when the dye is practically exhausted. It is also apparent that the maximum yield increases with the dye concentration.

Figure 3 shows the effect of the ascorbic acid concentration upon both the initial and the maximum yield.

The effect of temperature upon the yield is illustrated by the data of Fig. 4. The initial concentrations were similar to those used in the experiments of Fig. 2, and the 27° values are taken directly from Fig. 2. The data are not sufficiently precise to determine whether the temperature coefficient is the same for the initial and maximum yields, although this appears to be true.

Since the experimental data are not exact and the relation between the concentrations and the yield is relatively complicated, it is impossible to fit an unique, simple equation to the data. Equation 1 was adopted, since it represents the data within their apparent limits of errors and has a form which is consistent with a plausible mechanism. However, it must be admitted that the data can be represented equally well by equations of simpler form which may be compatible with other mechanisms.

The relatively large temperature coefficient places a severe restriction upon the group of acceptable mechanisms, since for reactions of the type which are likely to be encountered in the present system, it is most improbable that a rate constant can be at once large (*i.e.*, $\gg 10^9$ mole^{-1} sec.$^{-1}$) and be associated with a high energy of activation. It would be intuitively appealing to assume that the role of dimethylaminoaniline is that of a catalyst for the (thermal) reduction of the "semiquinone," D_2H, of the azo dye, D_2, and that in the absence of this substituted aniline the semiquinone disproportionates, leading to a maximum yield of $^1/_4$ rather than $^1/_2$. However, an equation consistent with this mechanism predicts initial yields systematically larger than those observed.

The symbols used in equation 1 have the following meanings: AH_2, ascorbic acid; DD', butter yellow; DH_2, *p*-dimethylaminoaniline and $D'H_2$, aniline.

$$\varphi_{-\mathrm{DD}'} = \frac{1}{2} \times \frac{[\mathrm{AH_2}][\mathrm{DD}']}{1.6 \times 10^{-5} + 1.69 \times 10^{-3}\,[\mathrm{AH_2}] + [\mathrm{DD}'] + 1.34 \times 10^{-2}\,[\mathrm{DH_2}] + 6.5 \times 10^{-3}\,[\mathrm{D'H_2}]} \times \left(\frac{1}{A + 5.9 \times 10^{2}\,[\mathrm{DD}']} + \frac{[\mathrm{DH_2}]}{B + C[\mathrm{DD}'] + [\mathrm{DH_2}]} \times \frac{1}{4.20 \times 10^{-3} + [\mathrm{AH_2}]}\right) \quad (1)$$

where A, B and C are, respectively, equal to $1.05 \times 10^{-9} \exp(8700/RT)$, $7.3 \times 10^{-12} \exp(8700/RT)$ and $1.11 \times 10^{-7} \exp(8700/RT)$. The last two terms in the denominator of the first factor are negligible except when aniline or *p*-dimethylaminoaniline is added to the initial mixture.

Reaction steps	v_i = rate of step
$h\nu + \mathrm{GH} \longrightarrow \mathrm{GH^*}$	I
$\mathrm{GH^*} \longrightarrow \mathrm{GH} + h\nu$	$k_2[\mathrm{GH^*}]$
$\mathrm{GH^*} \longrightarrow \mathrm{GH'}$	$k_3[\mathrm{GH^*}]$
$\mathrm{GH'} \longrightarrow \mathrm{GH}$	$k_4[\mathrm{GH'}]$
$\mathrm{AH_2} + \mathrm{GH'} \longrightarrow \mathrm{GH{\cdot}AH_2}$	$k_5[\mathrm{AH_2}][\mathrm{GH'}]$
$\mathrm{DD'} + \mathrm{GH'} \longrightarrow \mathrm{GH{\cdot}DD'}$	$k_6[\mathrm{DD'}][\mathrm{GH'}]$
$\mathrm{DH_2} + \mathrm{GH'} \longrightarrow \mathrm{GH} + \mathrm{DH_2}$	$k_7[\mathrm{DH_2}][\mathrm{GH'}]$
$\mathrm{D'H_2} + \mathrm{GH'} \longrightarrow \mathrm{GH} + \mathrm{D'H_2}$	$k_8[\mathrm{D'H_2}][\mathrm{GH'}]$
$\mathrm{GH{\cdot}AH_2} \longrightarrow \mathrm{GH} + \mathrm{AH_2}$	$k_9[\mathrm{GH{\cdot}AH_2}]$
$\mathrm{DD'} + \mathrm{GH{\cdot}AH_2} \longrightarrow \mathrm{GH} + \mathrm{AH} + \mathrm{DD'H}$	$k_{10}[\mathrm{DD'}][\mathrm{GH{\cdot}AH_2}]$
$\mathrm{GH{\cdot}DD'} \longrightarrow \mathrm{GH} + \mathrm{DD'}$	$k_{11}[\mathrm{GH{\cdot}DD'}]$
$\mathrm{DH_2} + \mathrm{GH{\cdot}DD'} \longrightarrow \mathrm{DH_2{\cdot}GH{\cdot}DD'}$	$k_{12}[\mathrm{DH_2}][\mathrm{GH{\cdot}DD'}]$
$\mathrm{DD'} + \mathrm{GH{\cdot}DD'} \longrightarrow \mathrm{GH} + 2\mathrm{DD'}$	$k_{13}[\mathrm{DD'}][\mathrm{GH{\cdot}DD'}]$
$\mathrm{DH_2GH{\cdot}DD'} \longrightarrow \mathrm{GH} + \mathrm{DD'} + \mathrm{DH_2}$	$k_{14}[\mathrm{DH_2{\cdot}GH{\cdot}DD'}]$
$\mathrm{AH_2} + \mathrm{DH_2{\cdot}GH{\cdot}DD'} \longrightarrow \mathrm{GH} + \mathrm{DH_2} + \mathrm{AH} + \mathrm{DD'H}$	$k_{15}[\mathrm{AH_2}][\mathrm{DH_2{\cdot}GH{\cdot}DD'}]$
$\mathrm{AH_2} + \mathrm{DD'H} \longrightarrow \mathrm{DD'H_2} + \mathrm{AH}$	
$2\mathrm{DD'H_2} \longrightarrow \mathrm{DD'} + \mathrm{DH_2} + \mathrm{D'H_2}$	
$2\mathrm{AH} \longrightarrow \mathrm{A} + \mathrm{AH_2}$	

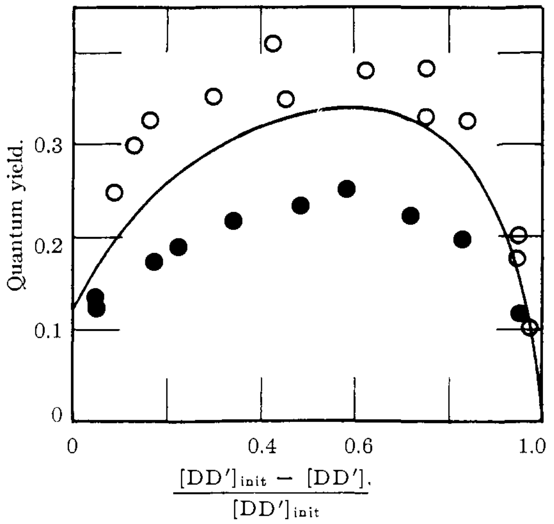

Fig. 4.—The quantum yield as a function of the ratio of the change in the concentration of Butter Yellow to its initial concentration. The effect of temperature: open circles, 34°, dots, 11.7°, line, 27°.

The following mechanism was devised to be consistent with equation 1 and with published observations on the photochemistry of chlorophyll. Figure 5 is a flow sheet of the unstable intermediates.

According to this mechanism, the rate of disappearance of butter yellow is

$$-\frac{\mathrm{d}[\mathrm{DD}']}{\mathrm{d}t} = {}^1\!/_2(v_{10} + v_{15}) \quad (2)$$

the first term corresponding to the direct and the second to the autocatalyzed reaction. Introducing the probabilities, Pi, that the intermediate in question will disappear by step i rather than by any other possible reaction, it follows that

$$-\mathrm{d}[\mathrm{DD}']/\mathrm{d}t = I = {}^1\!/_2 P_3(P_5P_{10} + P_6P_{12}P_{15}) \quad (3)$$

Substitution of the values of the several probabilities *e.g.*, $P_5 = k_5[\mathrm{AH_2}]/(k_4 + k_5[\mathrm{AH_2}] + k_6[\mathrm{DD}'] + k_7[\mathrm{DH_2}] + k_8[\mathrm{D'H_2}])$ gives

$$\varphi_{-\mathrm{DD}'} = \frac{k_3}{2(k_2 + k_3)} \times \frac{[\mathrm{AH_2}][\mathrm{DD}']}{\frac{k_4}{k_6} + \frac{k_5}{k_6}[\mathrm{AH_2}] + [\mathrm{DD}'] + \frac{k_7}{k_8}[\mathrm{DH_2}] + \frac{k_8}{k_6}[\mathrm{D'H_2}]} \times \left(\frac{1}{\frac{k_6k_9}{k_5k_{10}} + \frac{k_6}{k_5}[\mathrm{DD}']} + \frac{[\mathrm{DH_2}]}{\frac{k_{11}}{k_{12}} + [\mathrm{DH_2}] + \frac{k_{13}}{k_{12}}[\mathrm{DD}']} \times \frac{1}{\frac{k_{14}}{k_{15}} \times [\mathrm{AH_2}]}\right) \quad (4)$$

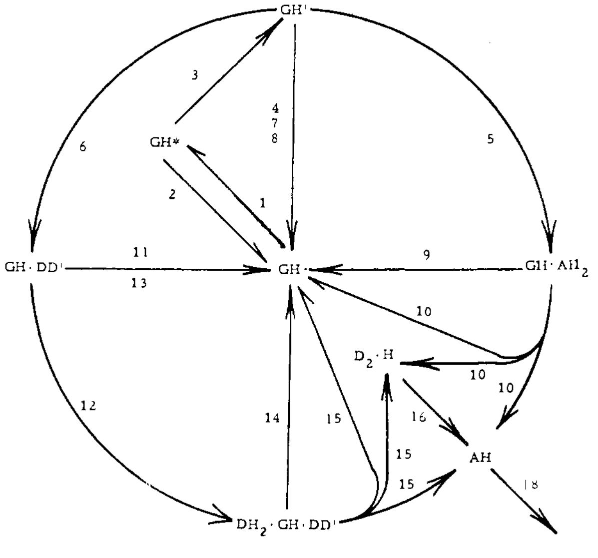

Fig. 5.—Flow sheet for the reaction intermediates.

A comparison of the coefficients of equations 1 and 4[13] confirms the view that the present mechanism is a reasonable one, compatible with the experimental data. Subsequent to the empirical evaluation of the coefficients of equation 1, a measurement of the maximum quantum yield of the fluorescence of pheophytin a[14] demonstrated that the factor, $k_3/2(k_2 + k_3)$, should be about 0.44 rather than 0.50. The introduction of this value would necessitate minor changes in the other coefficients. It is doubtful whether these differences would be significant.

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[13] See reference 2, pp. 93–97.

[14] L. Forster and R. Livingston, *J. Chem. Phys.*, **20**, 1315 (1952).

[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY, UNIVERSITY OF MINNESOTA, INSTITUTE OF TECHNOLOGY]

Some Photochemical Oxidation–Reduction Reactions Sensitized by Chlorophyll a and by Pheophytin a[1]

BY ROBERT LIVINGSTON AND RUDOLPH PARISER

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The efficiency of the chlorophyll-photosensitized (and the pheophytin-photosensitized) reduction of azo dyes is strongly dependent upon the nature of the reducing agent. Of 23 reducing agents which were tested, only the following five reduced methyl red with a quantum yield greater than 0.005: phenylhydrazine, hydrazobenzene, semicarbazide hydrochloride, *t*-hexyl mercaptan and phenylhydroxylamine. The available, admittedly incomplete, data are consistent with the equation $\varphi = {}^1/_2[[AH_2]/(K' + [AH_2])]\ [[DD']/(K + [DD'])]$ where $[AH_2]$ and $[DD']$ represent, respectively, the concentrations of the reducing agent and of the dye.

Chlorophyll-sensitized photochemical autoöxidations of a wide variety of reducing agents occur with good to fair efficiency.[2] Since O_2, but not allylthiourea,[3] is known to accelerate greatly the "triplet"-to-ground transition of chlorophyll molecules in solution,[4] it appears probable that the primary act in the autoöxidations is an interaction between an O_2 molecule and a chlorophyll molecule, in a long-lived excited state, leading to the formation of a labile, reactive moloxide. This view is supported by the results of a recent quantitative study of the chlorophyll-sensitized autoöxidation of allylthiourea in solvents of widely varying viscosity.[5] At first glance, it might appear probable that azo dye molecules would play a role in oxidation–reduction reactions similar to that of O_2 in autoöxidations. However, it is difficult to reconcile this postulate with some of the available data.

Semi-quantitative Screening Experiments

A series of screening experiments were performed to determine which reducing agents are effective in the chlorophyll-sensitized photochemical reduction of methyl red. Methanolic solutions were prepared which contained 5×10^{-6} *m* chlorophyll a, 10^{-4} *m* methyl red and a reducing agent at 10^{-1} *m*. The solutions were contained in closed Pyrex tubes and were freed from oxygen by boiling off about 20% of the solvent under vacuum. About eight vessels were exposed at a time to equal intensities[6] of red light. The extent of the reaction was determined by comparing visually the solution in the reaction vessel to a series of solutions containing known, graded concentrations of methyl red in similar vessels. When, after suitable illumination, no bleaching was detectable by this method, the solution was transferred to a Beckman cell for spectrophotometric analysis. Two check experiments were performed with each reducing agent. A sample, identical with that which was illuminated, was kept in the dark during the period of illumination. If any bleaching was observed in the illuminated vessel, the dark vessel was analyzed for methyl red to determine whether thermal reaction had occurred. To discover whether a direct photochemical reaction occurred, a third solution, containing no chlorophyll but otherwise similar to the other two, was exposed to the same actinic light.

The standard reaction mixture contained phenylhydrazine as the reducing agent. The average quantum yield, corresponding to a 90% reduction of the methyl red in such a solution, was taken as 0.15.[7] In these screening experiments, the average yield for other solutions was calculated as 0.15 of the ratio of the times required for 90% completion of the reaction of the standard to that of the experimental solution.

The purification of the solvent and pigments have been described elsewhere.[7] The reducing agents were either of reagent grade or were carefully purified[6] before use.

Of the 23 reducing agents which were investigated, only 5 reduced methyl red with a quantum yield greater than 0.005. The effective reagents and their quantum yields are as follows: phenylhydrazine, 0.15; hydrazobenzene, 0.15, semicarbazide hydrochloride, 0.07; *t*-hexyl mercaptan + 0.05 *m* HCl, 0.02; and phenylhydroxylamine, 0.02. The following substances did not exhibit any detectable reaction: *t*-hexyl mercaptan in neutral solution, acetanilide, acetoacetanilide, methyl acetanilide, aniline, dimethylaniline, phthalimide, piperidine, pyridine, urea (alone or with 0.05 *m* HCl). allythiourea, urethan, hydroxylamine (alone or with 0.05 *m* or 0.10 *m* HCl), benzidine, benzoin, hydroquinone, oxalic acid and oxalacetic ester. In addition, negative results were obtained with the following pairs of oxidizing and reducing agents: azobenzene–ascorbic acid, nitrobenzene–piperidine, nitrobenzene–hydroxylamine hydrochloride, nitrobenzene–hydroquinone and azo turkey red ($C_{10}H_7 \cdot N_2 \cdot C_{10}H_6 \cdot CH_3$)–piperidine.

The chlorophyll-sensitized oxidation of phenylhydrazine (alone or with 0.05 *m* HCl) by azobenzene is a moderately efficient reaction, having a yield of about 0.01. The yield of the oxidation by azo turkey red of phenylhydrazine and of phenylhydrazine + 0.05 *m* HCl are 0.02 and 0.06, respectively.

Effect of Dye Concentration upon Quantum Yield.—The effect of the changing concentration of azo dye, DD′, upon the quantum yield was determined for four different systems. In each

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[1] This paper is based upon part of a Doctoral Dissertation submitted in 1950 by Rudolph Pariser to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The work was made possible by the support of the Office of Naval Research to which the authors are indebted.

[2] E. Rabinowitch, "Photosynthesis," Vol. I, Interscience Publishers, New York, N. Y., 1945, Table 18, I:B.

[3] H. Gaffron, *Ber.*, **60**, 755 (1927); *Biochem. Zeit.*, **264**, 251 (1933).

[4] R. Livingston, THIS JOURNAL, **77**, 2179 (1955).

[5] K. Owens, Doctoral Dissertation, University of Minnesota, 1955.

[6] R. Pariser, Doctoral Dissertation, University of Minnesota, 1950.

[7] R. Livingston and R. Pariser, THIS JOURNAL, **70**, 1510 (1948).