

cal. deg.⁻¹ mole⁻¹ was shown to be due to internal rotation, corresponding to a potential barrier of 4700 cal. mole⁻¹.

The entropy at 298.1° K. and 1 atmosphere was found to be 65.91 cal. deg.⁻¹ mole⁻¹.

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

The Chlorophyll-sensitized Photooxidation of Phenylhydrazine by Methyl Red. II. Reactivity of the Several Forms of Methyl Red¹

BY ROBERT LIVINGSTON AND RUDOLPH PARISER

In a previous study² of this reaction a mechanism was suggested which led to the prediction that the quantum yield should increase with increasing concentration of phenylhydrazine. Direct measurements, in the range from 0.01 to 0.20 *M* phenylhydrazine, showed a definite although small decrease in the yield with increasing concentrations. Since it was noticed that the color of methyl red was also affected by this change in concentration, a series of measurements using varying mixtures of phenylhydrazine and phenylhydrazine hydrochloride were made. Both the concentration of a "red" form of the methyl red and the yield of the reaction increased with increasing acidity of the solution, the yield approaching a limiting value of about 0.5. Since methyl red has three colored forms,³ it was necessary to determine the absorption spectra of each of these forms, before it was possible to analyze the solutions spectrophotometrically. Using this method of analysis, it was found that only the intermediate form of methyl red reacted in the solutions used. Making allowance for the variation of quantum yield with dye concentration, it can be shown that the yield is also a (sympatric) function of the phenylhydrazine concentration. The yield appears to be independent of intensity. A relatively simple reaction mechanism is consistent with these observations.

Part I. Spectrophotometric Analysis of Methyl Red

Experimental Methods and Materials

Materials.—The methanol was purified by treating synthetic methanol with an amount of sodium estimated to be three times as much as was required to react with the water present, refluxing with an excess of methyl phthalate,⁴ and then distilling through an efficient packed column. The purification of the methyl red has been described.² Alcoholic hydrochloric acid was prepared by bubbling dry hydrogen chloride into methanol. Sodium methylate solutions were prepared by allowing weighed quantities of clean sodium to react completely with methanol. The concentrations of the acid and base solutions were checked by titration with aqueous standard solutions.

(1) This work was supported jointly by the Graduate School of the University of Minnesota and by the Office of Naval Research (Contract N6ori-212, T. O. I) to whom the authors are indebted.

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

(3) A. Thiel, A. Dassler and F. Wülffkin, *Fortsch. Chem. Physik. physik. Chem.*, **18**, no. 3 (1924).

(4) We are indebted to Dr. R. Arnold of the Organic Division of this department for suggesting this method.

The several solutions were made from stock solutions of methyl red and of either sodium methylate or alcoholic hydrochloric acid. All measurements were made with 2×10^{-5} *M* methyl red. As only ordinary precautions were taken to keep the solutions out of contact with laboratory air, it is probable that the sodium methylate solutions contained some carbonate and hydroxide.

Methods.—The photometric measurements were made with a Beckmann spectrophotometer at room temperature (24 to 27°). Measurements were made at 100 Å. intervals in the range from γ 3600 to 6000 Å. Duplicate preparations and measurements were made for each solution studied.

Experimental Results

The solutions studied were made up to contain, in addition to 2×10^{-5} *M* methyl red, the following added substances: (1) 0.40 *M* HCl, (2) 10^{-3} *M* HCl, (3) 10^{-4} *M* HCl, (4) 10^{-5} *M* HCl, (5) 10^{-6} *M* NaOCH₃, (6) 10^{-5} *M* NaOCH₃, (7) 2×10^{-5} *M* NaOCH₃, (8) 5×10^{-5} *M* NaOCH₃, and (9) 10^{-3} *M* NaOCH₃.

Further increase of the hydrochloric acid concentration above 0.40 *M* did not affect the extinction curve. At the other end of the range, use of concentrated sodium methylate results in a fading of the yellow color. This fading is reversible. It is not complete even in very basic solutions. The extinction coefficients at wave lengths near the maximum decrease about 30% as the concentration of methylate is increased from 10^{-3} to 1 *M*. The absorption spectrum of the dye is practically unchanged in the range from 2×10^{-4} to 5×10^{-3} *M* NaOCH₃.

The extinction curves for solutions 1, 3, 6, 7, and 9 are plotted in Fig. 1. The curves corresponding to solutions 4, 5 and 8 have been omitted from the plot to simplify it. They belong to the same family of curves as those plotted. It should be noted that the curves intersect at one of two points, corresponding to either λ 4360 or 4800 Å. One curve, number II, passes through both points of intersection.

It is apparent that the dye can exist in three different colored forms. From the variation of the absorption curves with the acidity of the solutions, it may be safely assumed that curves 9 and 7 correspond, respectively, to the pure forms I and III.⁵ It is impossible to calculate exactly the extinc-

(5) It is possible that solution 9 contains a trace of the colorless form. However, the practical independence of the curve from the methylate concentrations over a wide range is evidence that the percentage of the dye present in the colorless form is small.

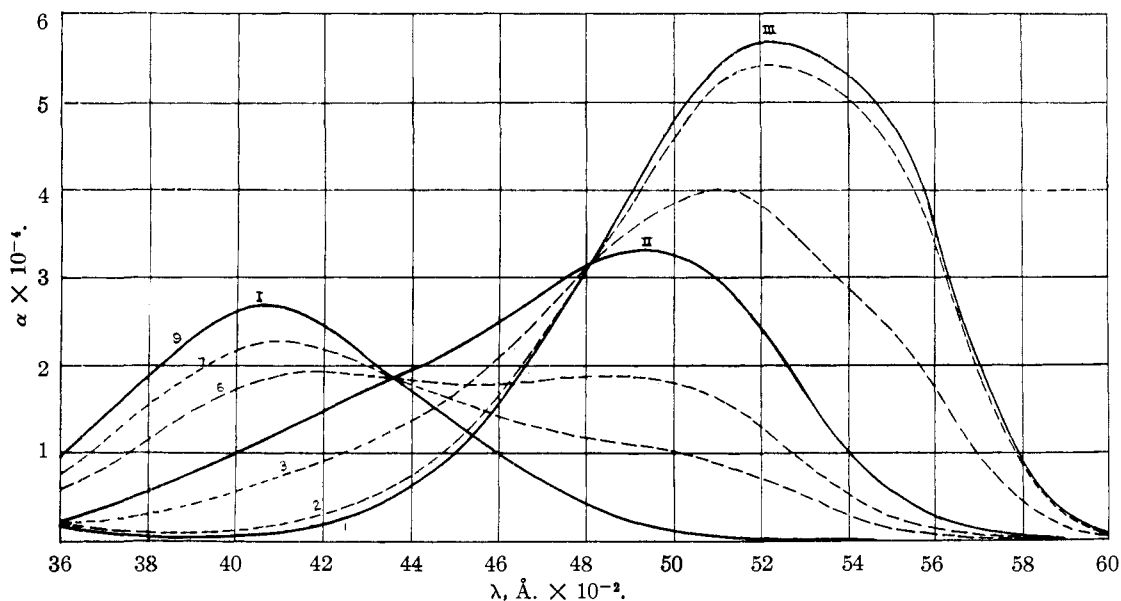


Fig. 1.—Extinction coefficients of methyl red dissolved in methanol containing acid or base.

tion curve of the third form from the curves for the two pure forms and from any number of curves for mixtures.⁶ However, a reasonably precise numerical approximation, to the curve of form II, may be readily obtained.^{3,6} The curves which pass through the point at 4360 Å. correspond to solutions which are free from form III; and those which cross at 4800 Å. represent solutions free from form I. The analysis of the data was simplified by the fact that one curve (for solution number 4) which is not shown on Fig. 1 passes very close to both points of intersection. Accordingly this solution must contain chiefly form II of the dye. For those solutions whose curves cross at 4360 Å. the observed extinction coefficient β_1 equals

$$\beta_{1,\lambda} = \alpha_{1,\lambda}C_1 + \alpha_{2,\lambda}C_2$$

when C_1 and C_2 are the concentrations of form I and II in the i th solution and $\alpha_{1,\lambda}$ and $\alpha_{2,\lambda}$ are the extinction coefficients of the pure form I and II at the wave length λ . Similarly for curves crossing at 4800 Å.

$$\beta_{1,\lambda} = \alpha_{2,\lambda}C_2 + \alpha_{3,\lambda}C_3$$

Approximately the values of $\beta_{4,\lambda}$ are equal to those of $\alpha_{2,\lambda}$. Curve II has been obtained from the values of solution No. 4 by a process of successive approximations, as follows. Minor adjustments were made in these approximate values of $\alpha_{2,\lambda}$ until all of the mixture curves (2, 3, 5, 6, 7 and 8) could be fitted in terms of the preceding two equations and a series of values of $\alpha_{1,\lambda}$, $\alpha_{2,\lambda}$ and $\alpha_{3,\lambda}$. It is assumed that these values are close approximations to the true values for the extinction coefficients of the three pure forms of the dye. The three solid curves of Fig. 1 are plots of these values which are listed in Table I.

(6) Compare E. Q. Adams and L. Rosenstein, *THIS JOURNAL*, **86**, 1452 (1914).

TABLE I
EXTINCTION COEFFICIENTS OF THE COLORED FORMS OF
METHYL RED

λ , Å.	$\alpha_1 \times 10^{-4}$ (lit./mole) ^a	$\alpha_2 \times 10^{-4}$ (lit./mole) ^a	$\alpha_3 \times 10^{-4}$ (lit./mole) ^a
3600	0.99	0.243	0.187
3700	1.44	.40	.117
3800	1.91	.55	.075
3900	2.32	.79	.057
4000	2.64	1.00	.065
4060	2.71 ^b		
4100	2.67	1.26	.112
4200	2.45	1.50	.212
4300	2.07	1.75	.39
4400	1.72	1.97	.66
4500	1.37	2.22	1.05
4600	1.01	2.53	1.61
4700	0.70	2.87	2.32
4800	.44	3.18	3.13
4900	.262	3.33	3.94
4910		3.34 ^b	
5000	.138	3.27	4.78
5100	.085	2.99	5.42
5200	.038	2.44	5.70
5210			5.71 ^b
5300	.020	1.72	5.60
5400	.010	1.04	5.35
5500	.005	0.57	4.79
5600	.005	.270	3.56
5700	.005	.130	2.02
5800	.000	.075	0.89
5900	.000	.025	.295
6000	.000	.000	.082

^a The values of the extinction coefficients are in terms of common logarithms. ^b The maximum value of the extinction coefficient.

It is interesting to compare these results with those obtained by Thiel, Dassler and Wülfskin (ref. 3, Fig. 13) for aqueous solutions of methyl

red. The data of Table II⁷ suggest that, while two of the colored forms are chemically identical in methanol and in water, the remaining forms differ.

TABLE II

COMPARISON OF MAXIMUM ABSORPTION IN AQUEOUS AND METHANOL SOLUTIONS

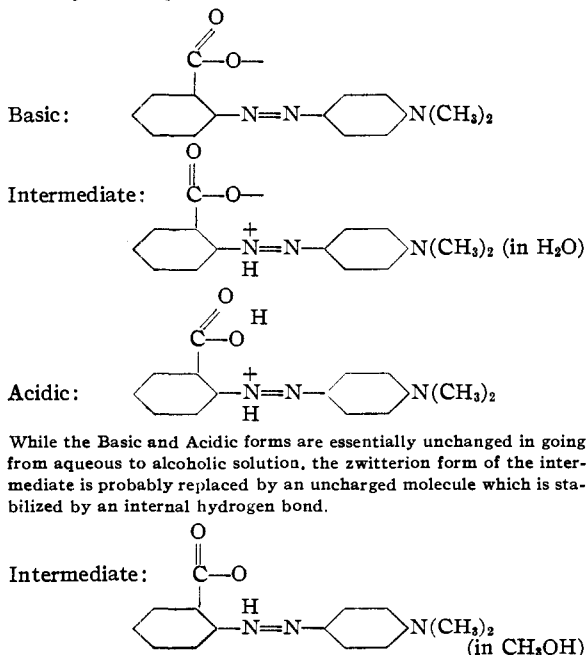
Solution	Aqueous solutions		Methanol solutions	
	λ , Å.	$\alpha \times 10^{-4}$	λ , Å.	$\alpha \times 10^{-4}$
Basic	4470	2.08	4060	2.71
Intermediate	5300	5.33	4910	3.34
Acidic	5170	5.25	5210	5.71

Part II. Photochemical Measurements Experimental Methods and Materials

The reagents used were similar to those described by Livingston, Sickle and Uchiyama.² The method of purifying methanol is described in the first part of the paper. The apparatus, described by them,² was slightly improved mechanically and by the use of a voltage stabilizer with the light source. Cylindrical reaction vessels, 12 mm. in length, were used in all of the present experiments.

Except for the analytical method, the experimental procedure and the routine computations were similar to those previously described.² All solutions were analyzed for methyl red concentra-

(7) As was pointed out by Thiel in 1924,³ the probable structures of methyl red in aqueous solutions are as follows.



While the Basic and Acidic forms are essentially unchanged in going from aqueous to alcoholic solution, the zwitterion form of the intermediate is probably replaced by an uncharged molecule which is stabilized by an internal hydrogen bond.

It is noteworthy that the wave length maxima for the basic and intermediate forms are shifted strongly to the violet when the solvent is changed from water to methanol. In both of these cases the principal resonance of the excited states involves a separation of charges. In the acid form where a similar resonance can occur without a separation of charge, the effect of the solvent upon the wave length of the extinction maximum is slight. As a result of these shifts, the maximum of the Acidic form lies between the maxima of the Basic and intermediate forms in aqueous solution, but to the red side of that of the Intermediate form in alcoholic solution.

tion, before and after illumination, with the Beckmann spectrophotometer. Two or more wave lengths were used and the measured values were corrected for the (small) absorption due to chlorophyll. Control experiments showed that this method of analysis did not produce any change in the concentration and that it gave results consistent with the analytical method used in the earlier measurements.²

The results of a number of determinations of the quantum yield, in terms of the disappearance of methyl red, are presented in Table III. Chlorophyll A at a concentration of $5 \times 10^{-6} M$ was used in all experiments. The solvent was methanol. The experiments were performed at room temperature, which varied between 25 and 28°. The actinic light was a red band, having a maximum at 6200 Å., cutting off sharply at 6000 Å., and tailing off gradually to about 7300 Å. The special symbols used in the table have the following significance: I, number of quanta absorbed per second in the reaction cell, (Ph), molarity of phenylhydrazine, (PhHCl), molarity of phenylhydrazine hydrochloride, $(D)_0$, initial molarity of the total methyl red, and $(D'')_0$, initial molarity of the intermediate form of methyl red. The quantum yield, $\bar{\varphi}$, is the average value and is defined by the equation

$$\bar{\varphi} = \frac{[(D)_0 - (D)_{\text{final}}](\text{moles/liter})}{I (\text{quanta/sec.}) [T_0 - T_{\text{final}}] (\text{sec.})} V(l) \times N (\text{molecules/mole})$$

The significance of the values tabulated in the last three columns is discussed in a later section of the paper.

The average value of the quantum yield, $\bar{\varphi}$, corresponding to those solutions in which there was no phenylhydrazine hydrochloride, is 0.14. This is in reasonable agreement with the value of 0.12 obtained by Livingston, Sickle and Uchiyama.² The statement by these latter authors, that the yield is independent of the methyl red concentration, was based upon preliminary unpublished experiments and appears to be in error.

Attempts to make quantum yield measurements in more acid solutions were unsatisfactory, due partly to the instability of chlorophyll in acid solutions, and partly to a dark reaction between phenylhydrazine and methyl red, which becomes appreciable as the phenylhydrazine is completely neutralized with hydrogen chloride.⁸ A few experiments were performed with solutions which contained 0.10 *M* phenylhydrazine hydrochloride but no free base. In these solutions, the dye was partly in form II and partly in form III. The quantum yields obtained were lower than in less acid solutions, and suggest that form III (like form I) of methyl red is incapable of undergoing a photosensitized reaction with phenylhydrazine.

When purified methylaniline is substituted for phenylhydrazine no detectable reaction occurs.

(8) Ghosh and Sen Gupta, *J. Ind. Chem. Soc.*, **11**, 69 (1934).

TABLE III
 SUMMARY OF THE EXPERIMENTAL MEASUREMENTS

No.	$I \times 10^{-15}$	(Ph)	(PhHCl)	(D) ₀ × 10 ⁴	(D'') ₀ × 10 ⁴	$\bar{\varphi}$	$\bar{\varphi}'$	(\bar{D}) × 10 ⁴	Φ
45	8.3	0.100	^a	1.22	0.089	0.11	0.12	0.065	0.49
44	7.5	.050	^a	1.19	.110	.10	.10	.072	.44
9	4.7	.100	0	1.19	.107	.13	.14	.074	.52
4	3.9	.200	0	1.19	.109	.12	.13	.081	.43
3	3.9	.100	0	1.19	.125	.13	.14	.096	.44
8	4.7	.100	0	1.19	.135	.13	.15	.100	.44
214	5.5	.050	0	1.09	.134	.11	.14	.105	.40
211	6.6	.050	0	1.10	.137	.18	.22	.106	.63
213	5.9	.050	0	1.10	.141	.16	.19	.109	.54
206	1.0	.050	0	1.09	.140	.13	.16	.109	.44
14	5.3	.050	0	1.19	.165	.15	.18	.116	.50
5	3.4	.200	0	1.19	.147	.12	.12	.117	.34
119	1.1	.050	0	1.12	.141	.14	.17	.119	.38
2	3.8	.050	0	1.12	.162	.14	.16	.132	.41
1	4.8	.050	0	1.17	.181	.16	.19	.137	.48
23	1.6	.500	0.250	0.24	.208	.21	.21	.142	.52
6	3.7	.025	0	1.19	.304	.15	.22	.195	.43
7	3.9	.020	0	1.19	.359	.14	.22	.222	.41
37	3.1	.250	0.750	0.61	.610	.31	.32	.348	.50
38	2.4	.250	.750	0.61	.610	.34	.35	.357	.54
29	2.5	.100	.200	1.19	0.87	.29	.30	.438	.43
24	2.4	.050	.250	1.19	1.05	.32	.33	.468	.46
33	2.4	.100	.005	1.19	0.81	.23	.25	.468	.35
30	3.0	.500	.100	1.23	1.03	.31	.31	.478	.44
34	2.8	.100	.005	1.22	0.85	.27	.30	.498	.42
31	2.5	.100	.010	1.19	.91	.26	.28	.543	.38
32	2.9	.500	.005	1.23	0.97	.28	.28	.578	.38
25	2.5	.500	.250	1.19	1.05	.29	.29	.605	.39
26	2.4	.250	.750	1.19	1.14	.35	.36	.690	.46
28	2.4	.250	.750	1.19	1.19	.34	.34	.735	.43
42	1.4	.250	.750	6.10	6.10	.45	.45	2.49	.49
36	2.5	.250	.750	5.95	5.95	.41	.42	2.54	.45
35	2.2	.250	.750	5.95	5.95	.49	.49	2.68	.53
39	7.9	.250	.750	6.10	6.10	.45	.46	3.12	.48

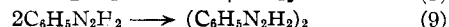
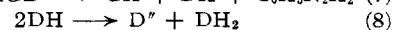
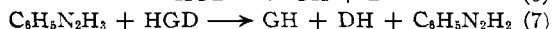
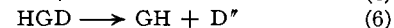
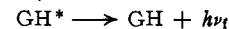
^a Contained 10^{-4} M NaOCH₃.

Two experiments were performed with solutions containing 5×10^{-6} M chlorophyll A, 2×10^{-6} M methyl red, and 0.050 M methylaniline. If any reduction of methyl red occurred its quantum yield was less than 0.005. In contrast to this result, hydrazobenzene undergoes a reaction comparable to that obtained with phenylhydrazine. Quantum yields of 0.17 and 0.19 were obtained with solutions containing 5×10^{-6} M chlorophyll A, 1×10^{-4} M methyl red, and 0.050 M hydrazobenzene. In these (four) experiments the solvent was methanol, and the light intensity and temperature were comparable to those reported in Table III.

Discussions and Computations

The data presented in Table III are consistent with any of several different mechanisms. The following series of steps has been adopted for purposes of discussion. It is as simple as any and has the further advantage that it is in agreement with the interpretation of the reversible bleaching of chlorophyll which was recently suggested by

McBrady and Livingston.^{9,10} The special symbols used have the following significance: GH, chlorophyll, HG, long-lived activated chlorophyll, D'', methyl red in form II, and DH₂, reduced methyl red. Making the usual assumption that a



steady state exists, an equation for the steady-

(9) J. McBrady and R. Livingston, *J. Phys. Colloid Chem.*, **52**, in press (1948).

(10) Unpublished results on the quenching of fluorescence, obtained recently in this Laboratory by Dr. W. Watson, indicate that the photochemical properties of chlorophyll are modified by methyl red due to the formation of an addition compound. If this postulate is confirmed, the present mechanism can be modified to conform to it.

state can be obtained¹¹

$$\varphi_{-D} = \frac{1}{2} \times \frac{k_3}{k_2 + k_3} \times \frac{k_7 (\text{C}_6\text{H}_5\text{N}_2\text{H})}{k_6 + k_7 (\text{C}_6\text{H}_5\text{N}_2\text{H}_3)} \times \frac{k_5 (D'')}{k_4 + k_5 (D'')} \quad (1)$$

For the concentrations used in the present experiments, the factor involving the concentrations of phenylhydrazine as well as the ratio of (D'') to (D) remain sensibly constant during each run, and therefore we write

$$\varphi_{-D} = -\frac{1}{I'} \times \frac{d(D)}{dt} = -\frac{1}{I'} \times \frac{(D)_0}{(D'')_0} \times \frac{d(D'')}{dt} \quad (2)$$

and

$$-\frac{d(D'')}{dt} = \frac{(D'')_0}{(D)_0} I' A \frac{(k_5/k_4)(D'')}{1 + (k_5/k_4)(D'')} \quad (3)$$

where I' is the intensity of the absorbed light expressed in Einsteins per liter per second and

$$A = \frac{k_7(\text{C}_6\text{H}_5\text{N}_2\text{H}_3)}{k_6 + k_7(\text{C}_6\text{H}_5\text{N}_2\text{H}_3)}$$

The definite integral corresponding to equation (3) is

$$\frac{k_4}{k_5} \ln \frac{(D'')_0}{(D'')} + (D'')_0 - (D'') = \frac{(D'')_0 A I' t}{(D)} \quad (4)$$

Introducing the experimentally determined average value for the quantum yield

$$\bar{\varphi} = \frac{(D)_0 - (D)}{I' t} = \frac{(D)_0}{(D'')_0} \frac{(D'')_0 - (D'')}{I' t} \quad (5)$$

we obtain

$$\frac{k_4 \ln \frac{(D'')_0}{(D'')} - \ln \frac{(D)_0 - (D)}{(D'')_0 - (D'')}}{k_5} + 1 = \frac{A}{\bar{\varphi}}$$

Rearranging and introducing the symbol (\bar{D}'') for the logarithmic mean¹²

$$\frac{(D'')_0 - (D'')}{\ln (D)_0 / (D'')}$$

we obtain equation (5) for the mean quantities, which has the same form as equation (1) relating to the instantaneous values.

$$\bar{\varphi} = \frac{1}{2} \times \frac{k_3}{k_2 + k_3} \times \frac{k_7/k_6 (\text{C}_6\text{H}_5\text{N}_2\text{H}_3)}{1 + k_7/k_6 (\text{C}_6\text{H}_5\text{N}_2\text{H}_3)} \times \frac{k_5/k_4 (\bar{D}'')}{1 + k_5/k_4 (\bar{D}'')} \quad (6)$$

Assuming the validity of this equation, we may compute $\bar{\varphi}'$, the values which $\bar{\varphi}$ would approach at high concentrations of phenylhydrazine.

$$\bar{\varphi}' = \bar{\varphi} \left[1 + \frac{k_6}{k_7} \times \frac{1}{(\text{C}_6\text{H}_5\text{N}_2\text{H}_3)} \right] \quad (7)$$

The values of $\bar{\varphi}'$, listed in the eighth column of Table III, were computed in this way, using an

(11) It is interesting to note that the preceding mechanism and the derived equation for the quantum yield are formally similar to those presented by Ghosh and Sen Gupta.⁹ The chief differences are the nature of the activated chlorophyll molecule, the restriction of the reaction to the intermediate form of the dye, and the postulated final products. The latter differences lead to a limiting quantum yield of one-half in the present case and of unity in the earlier paper.

(12) We are indebted to Dr. B. Crawford, Jr., for pointing out that the function $(x_1 - x_2) / \ln x_1/x_2$ is known as the logarithmic mean and is commonly used in engineering problems.

empirical value of k_7/k_6 of 1.0×10^2 (liter/mole). In making this correction, the total concentration of phenylhydrazine, rather than the concentration of the free base, was used. While this procedure seems to be in better agreement with the data, they are not sufficiently precise to prove that it is correct.

Figure 2 is a plot of $1/\bar{\varphi}'$ against $1/(\bar{D}'')$. While the points show considerable scatter, they unmistakably conform to the expected linear relation. The values of the constants, corresponding to the line drawn in the figure, are $k_5/k_4 = 5.0 \times 10^4$ (liter/mole) and $\Phi = 1/2 \times k_3/k_2 + k_3 = 0.46$ (molecules/quantum). The latter quantity is the maximum value for the quantum yield and corresponds to a value of $k_3/(k_2 + k_3)$ of 0.92. If the electronically excited chlorophyll, GH^* , is incapable of directly sensitizing the reaction (as is assumed in the mechanism), this value is in close agreement with the commonly quoted value of 0.08 for the fluorescence efficiency of chlorophyll in solution.

The values of Φ , listed in the last column of Table III, were computed from the corresponding values of $\bar{\varphi}'$ and of (\bar{D}'') by means of equation (8).

$$\Phi = \bar{\varphi}' \left[1 + \frac{k_4}{k_5} \frac{1}{(\bar{D}'')} \right] \quad (8)$$

The mean of the tabulated values of Φ is 0.45, with a standard deviation of the mean of 0.06. The several values of Φ show no significant correlation with any of the experimental variables (concentrations or intensity). In other words equation (6) fits the data within the limit of their random variation. It was not found possible to fit to the data any simple equation which contained, in place of (D'') , the total concentration of the dye, the concentration of its basic form or the concentration of its acidic form. Accordingly, we are forced to the conclusion that only the intermediate form of the dye enters, directly, into the reaction. This result, which was unexpected, is probably related to the relative stabilities of the semiquinones of the several forms of the dye.

The mechanism proposed here is based as much upon the reversible bleaching data (5) as it is upon the kinetics results. Therefore, the values of the rate constants of the individual reaction steps must be consistent with both sets of data. The mean life of the activated state, HG, was determined¹³ from the reversible bleaching measurements to be equal to or less than 4×10^{-8} seconds. Combining this with the present value for k_5/k_4 , we obtain

$$k_5 \leq 10^9 \text{ (liter/moles) per sec.}$$

In terms of the simple collision theory, the value for k_5 corresponds to a collision efficiency of about 1%. In other words, step 5 would require little or no heat of activation, and its rate would be practically independent of temperature.

(13) R. Livingston, *J. Phys. Chem.*, **45**, 1312 (1941).

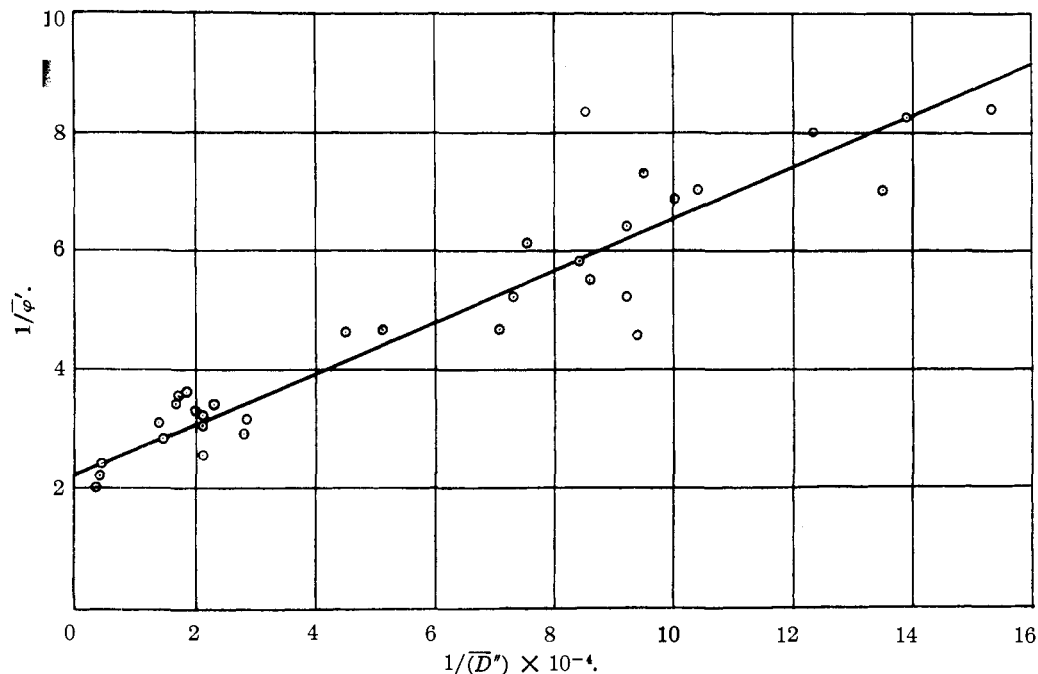


Fig. 2.—The reciprocal of the (corrected) average quantum yield, $\bar{\varphi}'$, plotted as a function of the reciprocal of the logarithmic mean, \bar{D}' , of the dye concentration.

The mean life of the complex, HGD, was not determined⁹ at all precisely, but is approximately 1 second. If we identify HGD with the bleached form of chlorophyll in solutions containing methyl red and further assume⁹ that its disappearance is due to a monomolecular reaction (step 6), we may conclude that $k_6 \approx 1 \text{ sec.}^{-1}$. The corresponding value of k_7 is apparently 10^2 (liter/mole) per second. Since this is smaller than the maximum value for a second order rate constant, it indicates that step 7 must require a considerable energy of activation. It is to be expected, therefore, that the reaction should exhibit a marked dependency upon temperature when the phenylhydrazine concentration is low, but not when it is high.

The simple form of equation (1) or (2) is a direct consequence of the use of the analytically determined concentration of the intermediate form of methyl red. An equation containing the stoichiometric concentration of methyl red would be of much more complex form. It would contain a function of the concentration of phenylhydrazine hydrochloride as well as of the free base.

The present case is the first chlorophyll-sensitized photooxidation which has been studied quantitatively over a wide range of experimental conditions. It is, therefore, particularly gratifying that it can be represented by a relatively simple empirical relation. The available facts do not determine a mechanism uniquely, but they do constitute a definite step in that direction and

suggest that further measurements of this type may be of real aid to our understanding of the "inner mechanism" of photosynthesis.

Summary

Methyl red can exist in three colored forms in methanol. The relative concentration of these forms depends upon the acidity of the solution. The absorption coefficients for each of these pure forms has been determined in the range $\lambda 3600$ to 6000 \AA .

In the chlorophyll-sensitized photooxidation of phenylhydrazine, only the intermediate form of methyl red reacts.

The maximum quantum yield for the reaction is about 0.5.

The quantum yield, φ , is an empirical function of the stoichiometric concentration of phenylhydrazine, (Ph), and of the concentration of the intermediate form of methyl red, (D'')

$$\varphi = 0.46 \frac{10^2(\text{Ph})}{1 + 10^2(\text{Ph})} \times \frac{5 \times 10^4(D'')}{1 + 5 \times 10^4(D'')}$$

Over a fairly wide range, φ is independent of the light intensity and of the concentration of chlorophyll.

A relatively simple mechanism is proposed which is consistent with the preceding facts and with recently published results⁹ on the reversible photobleaching of chlorophyll.

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