Photochemical Reactions between Methylene Blue and Tri-, Di- and Monomethylamine. II

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(Received September 19, 1956)

Introduction

In the preceding paper[1] the scheme for the reaction was established and a satisfactory rate formula was proposed. Now there will be reported in this paper some quantitative investigations upon the effects of various factors such as amine concentration, pH, light intensity, temperature upon the rate of the reaction. How the rate depends upon three kinds of amines will also be reported, analysing the bleaching curve by the proposed rate formula. Further, the influence of the addition of some metallic ions will be described. Though these experiments are still somewhat preliminary, the results obtained are very interesting and are considered to give further support for the reaction scheme. Lastly, there will be some discussion about the connection between the vacuum photobleaching reaction and the process of oxygen absorption in aerobic condition.

Experimental Results

1. Quantitative Investigations upon the Rate of Photochemical Reaction between Methylene Blue and Trimethylamine.—a. The Effect of pH.—pH was controlled between 7.7 and 9.2 by the use of M/35 borate buffer. Table I gives one series of typical results.

TABLE I

THE EFFECT OF pH

Methylene blue 2.0×10^{-5} M
Trimethylamine 1.0×10^{-3} M
Temperature 30°C

pH	[OH$^-$]	ratio of [OH$^-$]	k_1	k_2	k_3
7.7	5×10^{-7} M	1	0.014	0.023	0.04
8.0	1×10^{-6} M	2	0.056	0.066	0.014
8.55	3.57×10^{-6} M	7.1	0.156	0.126	0.039
9.2	1.59×10^{-5} M	32	0.69	0.64	0.141

It can be said that all the constants are approximately proportional to the hydroxyl ion concentration.

b. The Effect of Light Intensity I_0.—The intensity of light was varied by successively inserting metallic nets between the filter and the condenser lens (See Fig. 1 of the preceding paper[1]). Table II shows two series of typical results.

TABLE II

THE EFFECT OF LIGHT INTENSITY

Methylene blue 2.0×10^{-5} M
pH 9.2
Temperature 30°C

[TA]	Number of metallic nets	Relative intensity	k_1	k_2	k_3
0.1×10^{-3} M	0	15.6	0.048	0.037	0.013
0.1×10^{-3} M	1	6.2	0.019	0.024	0.009
0.1×10^{-3} M	2	2.5	0.008	0.014	0.004
0.6×10^{-3} M	0	15.6	0.157	0.125	0.104
0.6×10^{-3} M	1	6.2	0.066	0.071	0.013
0.6×10^{-3} M	2	2.5	0.023	0.020	0.011
0.6×10^{-3} M	3	1	0.009	0.013	0.004

As is expected, k_1 is almost exactly proportional to the light intensity, but a remarkable result is that k_2 and k_3 also increase with the light intensity. Though the exact relationship cannot be given, the extrapolated k_2 value to zero light intensity is evidently not zero. The values of k_3 are so randomly located that nothing can be said as to whether it has a finite value at zero intensity or not.

As already suggested in the preceding paper[1], it can be concluded that all the steps are photochemical in nature, though there exists a small contribution of the dark back reaction from the intermediate complex. It is to be added here that the absorption of the intermediate is so small, as already established in the preceding paper, that it will never disturb the method of measurement employed in the present investigation.

c. The Effect of Amine Concentration.—

TABLE III

Methylene blue 2.0×10^{-5} M
Temperature 30°C
pH 9.2
Metallic net None

[TA]	Ratio of [TA] to [MB]	k_1	k_2	k_3
6×10^{-4} M	30	0.157	0.071	0.060
4×10^{-4} M	20	0.107	0.076	0.037
2×10^{-4} M	10	0.048	0.037	0.012
1×10^{-4} M	5	0.022	0.032	0.01

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[1] H. Obata and M. Koizumi, This Bulletin, **30**, 136 (1957).

As seen from the above table, k_1 is satisfactorily proportional to the concentration of trimethylamine. k_2 and k_3 also increase with the rise of amine concentration.

d. The Effect of Temperature.—The results are summarized in Table IV.

TABLE IV

Methylene blue $2.0\times{}^{-5}$ M
Buffer Not used

Expt. No.	[TA]	Metallic net	Temp.	k_1	k_2	k_3
1	2.0×10^{-3} M	3	45°C	0.178	0.084	0.094
			30°C	0.166	0.067	0.077
			20°C	0.114	0.064	0.049
2	2.0×10^{-4} M	0	45°C	0.031	0.048	0.018
			40°C	0.030	0.046	0.014
			35°C	0.025	0.043	0.016
			25°C	0.018	0.040	0.022

k_1 evidently increases with the rise of temperature and the activation energies calculated from the above data are ca. 3.4 kcal. and 4.9 kcal. for case 1 and 2 respectively. Both k_2 and k_3 also seem to increase a little when the temperature is raised, but the data are not accurate enough to enable an estimation of the activation energy to be made. At any rate the temperature coefficients for k_2 and k_3 are about the same as or less than that of k_1.

e. Quantum yield for the Initial Step.—Quantum yield for the initial step (Process I) can easily be calculated from the value of k_1, the number of dye molecules (1.2×10^{16} per ml.) and the number of photons absorbed by the solution at the initial stage. The last quantity was measured and found to be 3.1×10^{15}/sec. ml. when no metallic nets were inserted. Table V shows the results of two series of various calculations.

TABLE V

QUANTUM YIELD γ

a) Methylene blue 2.0×10^{-5} M
pH 9.2
Temperature 30°C
Metallic net was not used

[TA]	γ
6×10^{-4} M	1.0×10^{-2}
4×10^{-4} M	6.9×10^{-3}
2×10^{-4} M	3.1×10^{-3}
1×10^{-4} M	1.4×10^{-3}

b) Methylene blue 2.0×10^{-5} M
Trimethylamine 6.0×10^{-4} M
pH 9.2
Temperature 30°C

Metallic net	γ
0	1.0×10^{-2}
1	1.1×10^{-2}
2	1.1×10^{-2}
3	1.0×10^{-2}

f. Resumé for the Photobleaching of Methylene Blue by means of TA.—

(1) k_1 can be expressed as follows,

$$k_1=k_{1_0}[\mathrm{OH}^-][\mathrm{TA}]I_0$$

(2) k_2 is proportional to $[\mathrm{OH}^-]$ and increases steadily with the light intensity and the amine concentration.

(3) Roughly speaking, k_3 behaves similarly as k_2.

2. The Photobleaching of Methylene Blue by means of Dimethylamine (DA) and Monomethylamine (MA).—The efficiency for the photobleaching of methylene blue in the evacuated aqueous solution was found to be in the order tri > di > mono. These results conform with those of Weil. In order to make clear which of the three processes-I, II and III is most affected by an amine of any kind, similar experiments as those for trimethyl amine were performed and the results were analyzed in the same way.

a. The Effect of Amine Concentration—The results are summarized in Table VI. They can be compared with the data in Table III, because the experimental conditions are quite similar.

TABLE VI

THE EFFECT OF THE CONCENTRATIONS OF DI-, AND MONOMETHYLAMINE

Methylene blue 2.0×10^{-5} M
M/35 Borate buffer pH 9.2
Temperature 30°C

Species	Amine conc.	Ratio of conc. of amine to [MB]	k_1	k_2	k_3
DA	2.0×10^{-2} M	1000	0.035	0.036	0.016
DA	1.4×10^{-2} M	700	0.026	0.022	0.009
DA	1.0×10^{-2} M	500	0.017	0.019	0.008
DA	0.6×10^{-2} M	300	0.013	0.017	0.007
DA	0.2×10^{-2} M	100	0.005	0.016	0.004
MA	4.0×10^{-2} M	2000	0.046	0.046	0.029
MA	2.8×10^{-2} M	1400	0.026	0.021	0.022
MA	2.0×10^{-2} M	1000	0.019	0.011	0.015
MA	1.2×10^{-2} M	600	0.011	0.009	0.007
MA	0.8×10^{-2} M	400	0.008	0.010	0.006

The values of k_1, k_2 and k_3 are much smaller than those for trimethylamine. They are of the same order of magnitude for 4.0×10^{-2} M of monomethylamine, 2.0×1.0^{-2} M of dimethylamine and 2.0×10^{-4} M of trimethylamine. k_1 is approximately proportional to the amine concentration in the above two cases and the dependency of k_2 and that of k_3 upon the amine concentration resemble that in case of trimethylamine.

b. The Effect of Light Intensity.—The results are summarized in Table VII.

The results are quite analogous to those of trimethylamine. Thus k_1 is proportional to the light intensity; k_2 and k_3 also increase with the light intensity, indicating the participation of the photochemical process in processes II and III.

TABLE VII

THE EFFECT OF LIGHT INTENSITY

Methylene blue	2.0×10^{-5} M
pH	9.2
Temperature	30°C

	Metallic net	Relative light intensity	k_1	k_2	k_3
Dimethyl-	0	15.6	0.053	0.045	0.023
amine	1	6.2	0.019	0.026	0.015
(2.0×10^{-2} M)	2	2.5	0.007	0.014	0.011
	3	1	0.004	0.012	0.008
Monomethyl-	0	15.6	0.074	0.043	0.049
amine	1	6.2	0.031	0.016	0.017
(4.0×10^{-2} M)	2	2.5	0.015	0.015	0.015
	3	1	0.005	0.004	0.006

c. The Effect of Hydrogen Ion Concentration.—The rate constants in the low pH values could not be measured because it was impossible to adjusted pH values by the use of borate buffer at the high concentration of amine. Though the data in Table VIII are scanty, it will be possible to say that k_1, k_2 and k_3 are all proportional to $[OH^-]$, the results being the same as that for trimethylamine.

TABLE VIII

THE EFFECT OF HYDROGEN ION CONCENTRATION

Methylene blue	2.0×10^{-5} M
Dimethylamine	2.0×10^{-2} M
1/35 M Borate buffer	
Temperature	30°C

pH	Relative conc. of $[OH^-]$	k_1	k_2	k_3
10.1	7.94	0.26	0.24	0.227
9.2	1	0.039	0.044	0.040

The data for monomethylamine are similar to the above.

d. The Effect of Temperature.—This was investigated only for the case of dimethylamine.

TABLE IX

THE EFFECT OF TEMPERATURE

Methylene blue	2.0×10^{-5} M
Dimethylamine	2.0×10^{-2} M
pH	9.2

Temp. °C	k_1	k_2	k_3
40	0.078	0.052	0.047
30	0.039	0.043	0.041
20	0.025	0.030	0.022
10	0.012	0.013	0.010

The activation energy for process I was calculated as 8.6 kcal./mol. This is evidently much greater than that for trimethylamine. The temperature coefficients for k_2 and k_3 are somewhat smaller than that for k_1, but they are conspicuously greater than the corresponding ones for trimethylamine. (compare with Table IV.)

3. The Influence of the Addition of Cu^{++} and Fe^{+++}.—For the further elucidation of the reaction mechanism and of the nature of the intermediate, the investigation about the influence of some metallic ions upon the reaction seems to be very helpful, because perhaps some of the ions may selectively act on three processes-I, II and III. Taking into account the data of oxidation-reduction potential, Fe^{+++} ($E^0_h=0.772$ V.) and Cu^{++} ($E^0_h=0.167$ V.) were selected and the bleaching reaction was examined in the presence of these ions.

a. The photobleaching reaction can be examined without any difficulty in the case of Fe^{+++}, so long as the concentration is not very large. Apparently the bleaching proceeds in the same way as when no metallic ion is added. The results of the analysis of the bleaching curve are given in Table X.

TABLE X

THE EFFECTS OF THE VARIOUS CONCENTRATIONS OF Fe^{+++}

Methylene blue	2.0×10^{-5} M
Trimethylamine	6.0×10^{-4} M
pH	9.2
Temperature	30°C

$[Fe^{+++}]$	Ratio of $[Fe^{+++}]$ to [MB]	k_1	k_2	k_3
4.5×10^{-4} M	22.5	0.085	0.046	0.006
3×10^{-4} M	15	0.084	0.045	0.007
0.75×10^{-4} M	3.75	0.100	0.045	0.027
0	0	0.099	0.041	0.075

From the above data it is clear that k_1 and k_2 are scarcely affected, while k_3 is decreased by the addition of Fe^{+++}. Corresponding to this result, the absorption of the intermediate at 950 mμ could be observed more prominently. Table XI (a) gives the value of $\log(I_0/I)$ of

TABLE XI

Methylene blue	2.0×10^{-5} M
Trimethylamine	6.0×10^{-4} M
$FeCl_3$	6.0×10^{-4} M
pH	9.2

(a) The absorption spectra of the intermediate at 950 mμ.

	Initial	Directly after 2 min. exposure	After 10 min. in the dark
$\log(I_0/I)$	0.008	0.025	0.011

(b) Dark back reaction in the presence of Fe^{+++}. (The increase of the optical density at 665 mμ)

	After 5 min. illumination	After 10 min. illumination	After 20 min. illumination
Initial	0.760	0.754	0.750
Immediately after exposure	0.298	0.095	0.027
10 min. in the dark	0.380	0.120	0.038
24 hr. in the dark	0.618	0.296	0.137

the intermediate at 950 mμ immediately after two minutes exposure and Table XI (b) gives the variation of $\log(I_0/I)$ at 665 mμ of methylene blue in the dark after a certain time of illumination.

If one compares Table XI (a) with Table II in the preceding paper, it is clear that the quantity of the intermediate is larger in the present case. Table XI (b) shows that the recovery of dye takes place in the dark.

Since the recovery of the color can never be observed if the bleaching is made to proceed completely, the above data are only related with process II in which the intermediate goes back to the original dye. It is noteworthy that ferric ion only affects the intermediate, namely stabilizes the intermediate, and only reduces the value of k_3.

b. When cupric chloride was added to the system the induction period appeared, after which the photobleaching began to take place, and during the induction period, cuprous chloride was precipitated. The existence of this precipitate made it very difficult to pursue the photobleaching quantitatively. Taking into account the light dispersion by the precipitate of Cu^+, it seemed that the rate of photobleaching does not differ so markedly compared with the rate obtained in the absence of Cu^{++}. A typical example for the variation of photocurrent is shown in Fig. 1. The induction period was found to be proportional to the added Cu^{++} ion concentration as shown in Table XII.

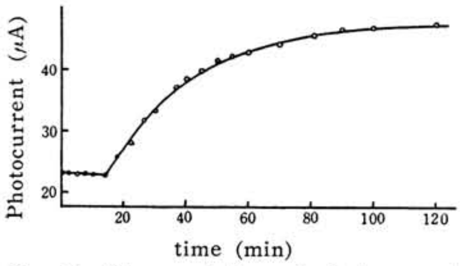

Fig. 1. The variation of photocurrent in the presence of Cu^{++}.
MB 2.0×10^{-5} M, TA 6.0×10^{-4} M,
$CuCl_2$ 6.0×10^{-5} M, pH 9.2,
Metallic net was not used, Temp. 30°C

TABLE XII

INDUCTION PERIOD IN THE PRESENCE OF Cu^{++}

Methylene blue	2.0×10^{-5} M
Trimethylamine	6.0×10^{-4} M
Temperature	30°C
pH	9.2

Ratio of [Cu^{++}] to [MB]	1.5	3	7.5	10	15
Induction period (min.)	7	14	25	48	65

Discussion

The photobleaching of methylene blue by means of mono-, di- and trimethylamine takes place via the common scheme with only different specific rates. There is no doubt that an intermediate having quite a long life participates in the reaction and a probable scheme can be written as follows:

$$MB^+ + H_2O + TA \underset{\text{II }(k_2)}{\overset{\text{I }(k_1)}{\rightleftharpoons}} \text{Intermediate} \underset{\text{IV}}{\overset{\text{III }(k_3)}{\rightleftharpoons}} MBH + TAO \quad (1)$$

Recently Kutsaya and Dain[2] reported that methylene blue in alcohol was decolorized under degassed condition on exposure to light. They explained the reaction according to the following two-step's. The first step is the formation of a colored photoproduct between dye and alcohol, and the further action of light reduces this product to the colorless leuco dye. Their scheme seems to conform well with our present one.

The nature of the intermediate is not yet certain, but it is conceivable that the intermediate may have a structure such as $MBH^{\cdot}\cdots O^-\cdots TA$ which is produced by the following process.

$$MB^+ + OH^- + TA \longrightarrow MB^+\cdots HO^-\cdots TA$$

The fact that k_1 can be expressed as $k_1=k_{1_0}[OH^-][TA]I_0$ is consistent with the above picture of the intermediate. Although the scheme (1) cannot be said to have been definitely established, most of the experimental results can be interpreted well by the rate formula derived on the ground of scheme (1). Some of the results will be discussed along this line.

(1) The Life of an Intermediate.—Putting the concentration of methylene blue and the intermediate as x and y at time t, and the initial concentration of the former as c differential equations for the rate process are

$$\begin{cases} -\dfrac{dx}{dt}=k_1x-k_2y \\ -\dfrac{dy}{dt}=(k_2+k_3)y-k_1x \end{cases}$$

and the solution for x is

$$x=Ae^{-(k+s)t}+Be^{-(k-s)t}$$

as shown in the previous paper.

On the other hand, y can be expressed as follows.

$$y=\frac{c}{2}\frac{k_1}{s}\left\{e^{-(k-s)t}-e^{-(k+s)t}\right\} \quad (2)$$

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[2] B. F. Kutsaya and B. Ya. Dain, *Ukrain. Khim. Zhur*, **17**, 820 (1951); *C. A.* **49**, 13789c (1955).

Time relations of x and y, for one example, are shown in Fig. 2. The analytical formula for this case are

$$\begin{cases} x=0.6e^{-0.2t}+0.9e^{-0.03t} \\ y=0.87(e^{-0.03t}-e^{-0.2t}) \end{cases}$$

As shown in Fig. 2, the concentration of the intermediate must reach its maximum value a few minutes after the start. This conforms well with the observed magnitude of the absorption of the intermediate.

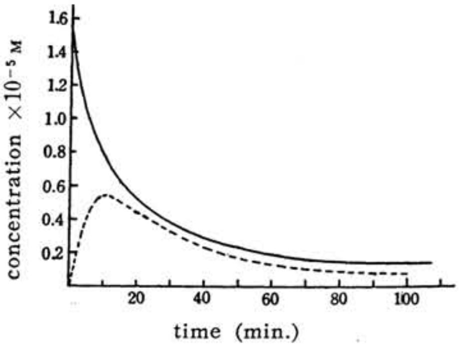

Fig. 2. Concentration curves of MB and the intermediate.
Full line: MB (x)
Broken line: intermediate (y)
MB 2.0×10^{-5} M, TA 6.0×10^{-4} M,
pH 9.2, Temp. 30°C.
Metallic not was not used

In the case of the addition of Fe^{+++} ion where k_3 is reduced remarkably while k_2 and k_3 are scarcely affected, equation (2) requires that y gets quite a large value. This was clearly demonstrated experimentally. Perhaps the discovery of such a unique effect of Fe^{+++} will be considered to be the strongest support for the scheme (1).

(2) **The Effect of Cu^{++} Ion.**—The data in Table XII can be interpreted as follows. From the fact that the induction period is proportional to the concentration of Cu^{++}, it can be said that the rate of its disappearance is of the zeroth order in $[Cu^{++}]$. Hence Cu^{++} must attack the intermediate or the leuco dye as soon as it is produced. The following calculation shows that the first alternative is favorable. If the Cu^{++} ion destroys the intermediate as soon as it is formed, the rate of the reaction, $Cu^{++}\rightarrow Cu^{+}$, is written as

$$-\frac{d[Cu^{++}]}{dt}=k_1[MB], \qquad (3)$$

while in case Cu^{++} attacks the leuco dye, the rate of the reaction, $Cu^{++}\rightarrow Cu^{+}$, must be represented as

$$-\frac{d[Cu^{++}]}{dt}=\frac{k_1k_3}{k_1+k_2+k_3}[MB]. \qquad (4)$$

Using the values of k_1, k_2 and k_3 in the corresponding experimental conditions which are 0.157, 0.071 and 0.063 respectively, equations (2) and (3) can be written in the forms of (5) and (6) respectively.

$$\begin{cases} -\frac{d[Cu^{++}]}{dt}=0.157[MB]=3.14\times10^{-6} & (5) \\ -\frac{d[Cu^{++}]}{dt}=0.034[MB]=6.8\times10^{-7} & (7) \end{cases}$$

In the following Table XIII, the induction period as calculated from (5) and (6) assuming that it comes to an end when Cu^{++} is eliminated, are compared with the experimental one (Table XII).

TABLE XIII

THE COMPARISON OF THE INDUCTION PERIOD

Ratio of $[Cu^{++}]$ to [MB]	1.5	3	7.5	10	15
Induction period (min.) calc. from (5)	9.5	19	48	63	95
〃 calc. from (6)	44	88	220	290	440
〃 obs. (Table 12)	7	14	25	48	65

From the above results it seems highly probable that Cu^{++} attacks the intermediate as soon as it is produced. It is to be noted, however, that the absorption spectra of the intermediate are still observed in the presence of Cu^{++}, hence further study seems to be necessary.

(3) **The Relation between the Vacuum Photobleaching and the Experiment of Weil.**—The fact that the absorption of the reaction intermediate is still observed in the presence of oxygen strongly supports the view that oxygen attacks only leuco dye. If this attack takes place very rapidly, the rate of the oxygen uptake must be expressed by the following equation after the arrival of the stationary state.

$$\frac{d[O_2]}{dt}=\frac{1}{2}\,\frac{k_1k_3}{k_1+k_2+k_3}[MB]$$

Hence the rate of the oxygen uptake must be independent of the pressure after a certain induction period. According to Kihara's unpublished experiments using ethanol as a solvent, oxygen absorption really takes place with the same rate irrespective of the pressure of oxygen, and some induction period really exists.

The above scheme is noteworthy since it differs greatly much from the postulate, as proposed by Schenck and other investigators, that oxygen attacks directly the triplet state of dye molecules in general[3]. The question will be further studied in future.

To sum up, it can be concluded that the proposed scheme is very satisfactory. Yet there still remain many things to be solved in future. Above all, each of the processes I, II and III are considered to be complex of itself, since all the apparent reaction constants, k_1, k_2, k_3 depend upon various factors. Another thing which seems to be very curious is that all these rate constants decrease in about the same manner when trimethylamine is replaced by dimethylamine and monomethylamine. When the detailed mechanism of each step is clarified, the reason for this will also be clear.

Summary

The effects of various factors upon the photobleaching of methylene blue in the evacuated aqueous solution by means of mono-, di- and trimethylamine, were studied experimentally, and the result were analyzed by the rate formula presented in the preceding paper on the basis of the following scheme;

$$\mathrm{MB^+} + \mathrm{H_2O} + \mathrm{TA} \underset{\mathrm{II}\,(k_2)}{\overset{\mathrm{I}\,(k_1)}{\rightleftharpoons}}$$

$$\text{Intermediate} \underset{\mathrm{IV}}{\overset{\mathrm{III}\,(k_3)}{\rightleftharpoons}} \text{Product}$$

The results obtained can be summarized as follows: k_1 is written in the form; $k_1 = k_{1_0}[\mathrm{OH^-}][\mathrm{TA}]I_0$. k_2 and k_3 are also proportional to $[\mathrm{OH^-}]$ and they both increase monotonously with the light intensity and amine concentration.

In addition, the photobleaching was examined in the presence of $\mathrm{Fe^{+++}}$ and $\mathrm{Cu^{++}}$. It was found that in the case of $\mathrm{Fe^{+++}}$, k_3 is much decreased while k_1 and k_2 are scarcely affected. The absorption spectra of the intermediate were observed more prominently than when no $\mathrm{Fe^{+++}}$ was present. From these results it was concluded that $\mathrm{Fe^{+++}}$ stabilizes the intermediate. In case of $\mathrm{Cu^{++}}$ some induction period was observed during which Cu precipitates, and its duration was found to be proportional to the concentration of $\mathrm{Cu^{++}}$. From these results it was tentatively concluded that $\mathrm{Cu^{++}}$ attacks the intermediate.

The cost of this research has been partially defrayed from the Scientific Research Grant from the Ministry of Education.

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3) For example. G. O. Schenck, *Naturwiss.*, **40**, 205, 229 (1953); M. Pestemer, *Z. Elektrochem.* **59**, 121 (1954).