THE PHOTOCHEMICAL REACTIONS OF COLOURING MATTERS.
I. THE REVERSIBLE PHOTOCHEMICAL REACTION OF MALACHITE GREEN.

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As is well known, colouring matters have played important rôles in the developement of photochemistry both from technical and scientific standpoints, for most of them are more or less sensitive to light and moreover their colour changes offer very convenient analytical methods in spite of complexity of the molecules. Indeed the bleaching effect of light on colouring matters has been very often investigated, and the results of these investigations accord at one point that most of these reactions are photocatalytic. While there are so many photocatalytic reactions in general, very few reversible photochemical reactions are known. Very simple photochemical reactions, such as those of tautomeric changes, will perhaps be favourable for the study of fundamental laws of photochemistry, provided that it is furnished with an easy and simple analytical method.

Berl,(1) Lassareff,(2) and Gebhard(3) formerly studied on the reversibility of methylene blue and Chevreul(4) on Prussian blue. Later J. Lifschitz and Joffé(5) described about photochemical molecular rearrangements in triphenylmethane series in the case of leucocyanides and carbinol bases of the dyes in the solutions of alcohols, ether, chloroform and aqueous mineral acids. A similar reaction was reported by Holmes(6) who used triphenylmethane sulphonic acid.

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(1) Berl, *Ber.*, 43 (1910), 164.
(2) Lassareff, *Z. physik. Chem.*, 78 (1912), 631.
(3) Gebhard, *Z. physik. Chem.*, 79 (1912), 639.
(4) Chevreul, *Fortschritte der Physik*, (1894), 206.
(5) Lifschitz and Joffé, *Ber.*, 52 (1919), 1919; *Z. physik. Chem.*, 97 (1921), 426.
(6) Holmes, *J. Am. Chem. Soc.*, 44 (1922), 1002.

For the purpose of looking for a reversible photochemical reaction I have tried to expose aqueous solutions of various colouring matters contained in a quartz glass tube to the light of a quartz mercury lamp, and carefully measured their colour changes, using Nutting's spectro-photometer. In the course of these experiments, I have found that the colour of malachite green solution, contrary to expectation, became more intense after the exposure to the light of the mercury lamp. Repeating the same experiment with the dye in presence of various chemicals, I found that the dye solution, which was beforehand decolourised by adding alkali, regained its green colour when exposed to the light of the lamp, and loses its colour again in the dark. This reversible colour change of malachite green solution may be suitably observed in a quartz glass vessel illuminated with the light of iron or carbon arc, but the reaction occurs neither with diffused daylight nor with the light of ordinary electric lamp. Intense direct sunlight is able to cause the reaction even in a glass vessel.

Although the similar phenomena were observed in other colouring matters of triphenylmethane group such as fuchsin, methylviolet etc, the present study is concerned only with the experiments which were carried out with malachite green.

Experimental.

In the first place, velocities of the colour changes of malachite green solutions were determined in the following three cases, in using Nutting's spectro-photometer: 1) Decolourisation in alkaline medium. (NaOH was added) 2) Regaining of the colour when exposed to the light of quartz-mercury-vapour-lamp. 3) Reversed decolourisation in the dark.

Experiment 1. 0.0218 gr. of malachite green (from Grueber in Germany) was dissolved in one litre of distilled water and diluted to the four times of its volume.(1) To each 50 c.c. of this solution was added respectively 5 c.c. of NaOH solution of the concentrations of 0.05, 0.03, 0.025, 0.02, 0.015, 0.010, 0.005 and 0.003 normal and the velocities of decolourisation of these solutions were observed.

The absorption tubes of the photometer were furnished with water jackets through which water of constant temperature was allowed to circulate from a thermostat in order to keep the system in a constant temperature. The light absorption was observed at the spectrum region of wave length 600 $\mu\mu$, where exists the absorption maximum of malachite green and, therefore, observations may be very conveniently carried out even in such a dilute solution as this.

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(1) If the solution be in larger concentration, white precipitates would be produced when alkali is added, therefore the experiment must be carried out within the limit of solubility of this difficultly soluble, colourless matter.

As the concentration of the colouring matter is very small in comparison with that of NaOH, we can practically take this reaction as that of first order, leaving, as the further question, the doubt about which of catalytic or of second order is the real nature of this reaction.

The concentration of the substance, the absorption of which is to be measured, can be expressed as follows,

$$C = \frac{-2 \log \cos \alpha}{Ed} \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where α is the angle of the rotation of Nicol's prism, C the concentration of the colouring matter, E the extinction coefficient of the solution, d the thickness of the liquid layer.

Therefore, the velocity constant of the reaction, $K = \frac{1}{t} \log \frac{C_0}{C}$ can be expressed in terms of $\cos \alpha$ as follows,

$$K = \frac{1}{t} \{\log(-\log \cos \alpha_0) - \log(-\log \cos \alpha)\} \ldots\ldots(2)$$

TABLE 1.

t	α	$-\log \cos \alpha$	$\log(-\log \cos \alpha)$	$\log \frac{C_0}{C}$	$K = \frac{1}{t} \log \frac{C_0}{C}$
0	85.0	1.0597	0.025	—	—
3	79.0	0.7194	$\bar{1}.857$	0.168	.056
6	70.6	0.4787	$\bar{1}.680$	0.315	.058
10	61.5	0.3213	$\bar{1}.507$	0.518	.052
16	47.5	0.1703	$\bar{1}.230$	0.795	.050
28	22.0	0.0328	$\bar{2}.516$	0.509	.054

The control observation which was specially planned, showed that the extinction coefficient was constant throughout the concentration used, that is, the Beer's law holds.

The velocity increases with the concentration of NaOH linearly as may be seen in Table 2.

TABLE 2.

NaOH	0.03 N	0.025 N	0.02 N	0.015 N	0.01 N	0.005 N	0.003 N
$K \times 10^3$	86	74	54	43	30	16	9.2

Experiment 2. The solution of malachite green which was previously decolourised by adding NaOH, was exposed to the light of a quartz-mercury-vapour-lamp (from Heraeus of Hanau, Germany) at the distance of 15 cm.

and after various intervals of time, a definite quantity of the solution was taken out of the reaction vessel and light absorption of this solution was measured in the same manner as in Experiment 1.

The mercury lamp with its illuminating part of 1.65 cm. in length was lighted with 100 volts D. C., the current being 3 amps. throughout the experiment. In ten minutes after the lamp had been started, its light became constant in intensity. Both of the reaction vessel and light thermostat were made of cylindrical tubes of quartz glass, the former being inserted in the latter, through which water of constant temperature was circulated from a larger thermostat by means of a pump. The solution was agitated with a stirrer during the exposure.

I have prepared three kinds of malachite green solutions with different concentrations, one of these (solution A) is in about the same concentration as in the Exp. 1, while those of the other two (solution B and C) are respectively in the two thirds and one half of the first. To each 250 c.c. of the solution A, B and C, 5 c.c. of 0.01 N. NaOH was added. The solutions thus decolourized were exposed to the light of the lamp, the intensity of which, being found to be too strong was reduced to one fourth by inserting a rotating sector with two 45° apertures (800–1000 rotations per min.) between the light source and the reaction vessel and the change of colour was observed, keeping temperature constant at 25°.

In this case, the velocity constant of the light reaction was calculated in the following way: in the first place, it was considered that the amount of light sensitive substances which suffer changes by light is proportional to the light energy absorbed and consequently the reaction velocity can be put,(1)

$$\frac{dM}{dt}=KA=KS(I_0-I) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

and if Beer's law holds

$$\frac{dM}{dt}=KS(I_0-I_0e^{-idc}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

where M is the amount of the substance, and A the quantity of absorbed light. This relation is satisfied only in such a case that the reacting system is contained in a rectangular vessel and exposed to parallel beams of light which are perpendicular to the wall of the vessel. In the present experi-

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(1) Literatures on photochemical kinetics give us two different conceptions: 1. The equations of reaction velocity are same for photochemical and dark reaction. 2. The amount transformed is proportional to the absorbed light quantity. The light reaction of malachite green, however, being unimolecular, both of these conceptions lead us to the same conclusion.

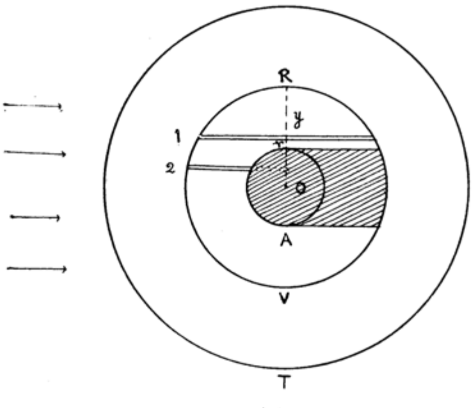
ment, however, the cylindrical vessel having been used, following considerations will be necessary for the calculation of the velocity constant.

Now if we take the elementary slices 1 and 2 in Fig. 1, their volumes are,

$$2\sqrt{R^2-y^2}\,h\,dy \quad \text{and} \quad \{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}\,h\,dy \ldots(5)$$

respectively, and the light absorbed by them are

$$I_0\left\{1-e^{-i\,2\sqrt{R^2-y^2}(b-x)}\right\}h.\,dy \quad \text{and}$$
$$I_0\left\{1-e^{-i\{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}(b-x)}\right\}h.\,dy \quad \ldots\ldots\ldots\ldots(6)$$



Horizontal section of the apparatus.
T : Thermostat vessel.
V : Reaction vessel. (Radius R.)
A : Agitator. (Radius r.)

Fig. 1.

Where b is the initial concentration of the substance, x the concentration of the substance formed, h the height of the part of the vessel exposed to the light, R and r the radii of the vessel and the agitator.

The equation (3) can be then, put as follows :

$$\frac{dM}{dt}=\frac{d\,V(b-x)}{dt}=K_0\left[2\int_r^R I_0\left\{1-e^{-i\,2\sqrt{R^2-y^2}(b-x)}\right\}h.\,dy\right.$$
$$\left.+\,2\int_0^r I_0\left\{1-e^{-i\{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}(b-x)}\right\}h.\,dy\right]\ldots\ldots\ldots\ldots(7)$$

where $$e^{-i\,2\sqrt{R^2-y}\,(b-x)}=1-i\,2\sqrt{R^2-y^2}(b-x)+\frac{[i\,2\sqrt{R^2-y^2}(b-x)]^2}{1\cdot2}-\ \ldots(8)$$

$$e^{-i\{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}(b-x)}=1-i\{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}(b-x)$$
$$+\frac{[i\{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}(b-x)]^2}{1\cdot2}-\ \ldots\ldots\ldots\ldots(9)$$

and if i or b is very small, we can neglect higher terms and consequently the equation (7) becomes

$$\frac{d(b-x)}{dt}=\frac{K_0}{V}\,2I_0h\left[\int_r^R i\,2\sqrt{R^2-y^2}.dy+\int_0^r i\{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}dy\right](b-x)$$
$$=a\ \text{constant}\times(b-x)=K(b-x)\ \ldots\ldots\ldots\ldots(10)$$

and finally the equation of the velocity constant can be put as

$$K=\frac{1}{t}\,[\log b-\log(b-x)]\ldots\ldots\ldots\ldots(11)$$

where b and x can be expressed in terms of $\log \cos\alpha$ as in Experiment 1.

Although the extinction coefficient of the solution could not yet been determined, it is evident, however, that the concentration of the light sensitive substance is very small in this experiment and higher terms of the equations (8) and (9) may be neglected.

Velocity constants were thus calculated according to the equation (11) and pretty constant values were obtained as will be seen in Table 3, etc, giving rather smaller values at the beginning of the reaction.

It must be noted here that, the thermostat vessel used being cylindrical, the refraction of light beams at the wall of the vessel must be taken into consideration in the above calculations, but this was neglected for the sake of simplification, incident rays being assumed to be parallel.

TABLE 3.

Time (min)	2	4	6	8	10	12	14	16	18
$K \times 10^3$ (A)	35	44	51	53	51	51	50	—	—
$K \times 10^3$ (B)	35	43	43	51	51	53	59	—	53
$K \times 10^3$ (C)	39	41	45	52	58	61	59	54	—

In order to study the effect of the concentration of alkali, 5 c.c. of 0.03 and 0.02 N. NaOH were respectively added to each 250 c.c. of the solution A and the same experiment as mentioned above was done. It was, however found that in these cases there was good accordance of the observed values with those of Table 3, that is to say, the light reaction is independent of the concentrations of alkali present.

TABLE 4.

Time (min)	1	2	4	6	8	10	12	16
$K \times 10^3$ (0.02)	34	37	43	47	51	56	58	56
$K \times 10^3$ (0.03)	34	35	36	39	45	51	57	56

The temperature coefficient was then determined at 25° and 35° in using the solution A added with 0.01 N. NaOH and it was proved that the light reaction is practically not effected by the raise of temperature, at this interval, although more accurate experiment on this account will be necessary for its support.

TABLE 5.

Time (min)	2	4	6	8
$K \times 10^3$ (25°)	34	51	49	49
$K \times 10^3$ (35°)	32	42	49	49

Finally the effect of light intensity on the light reaction was also examined. The light of three different intensities of 1/2, 1/4 and 1/8 were applied to the solution C added with 0.01 N. NaOH, and it was found that the velocity of the light reaction is exactly proportional to the light intensity as will be expected.

Experiment 3. Five c.c. of 0.01 N. NaOH was added to each 50 c.c. of the solution A and C and these mixtures which show moderate reaction velocities were transferred into absorption tubes, after having exposed to the light of the mercury lamp until the green colour of these solutions took maximum intensity, and then the light absorption was measured in definite time interval in exactly the same manner as in Experiment 1. (Table 6)

TABLE 6.

Time (min.)	10	20	30	40	60	90	100	120	150	170	180
$K \times 10^3$ (sol. A)	76	62	—	58	56	—	57	—	56	—	55
$K \times 10^3$ (sol. C.)	53	58	59	55	59	59	—	55	52	52	—

The reaction velocity increases linearly with the concentrations of NaOH added as was proved in Experiment 1, only slightly differing in the angle of inclination. (Table 7)

TABLE 7.

$K \times 10^3$	76	65	40	30	19	7.8	5.6
Conc. of alkali	0.03	0.025	0.02	0.015	0.01	0.005	0.003

Discussion of Experimental Results. In Experiment 1, the decolourisation velocity of malachite green in presence of alkali was proved to be proportional to the concentration of sodium hydroxide added and the reaction may be taken as of first order, on the contrary to the results obtained by Mueller(1) and by Gerlinger,(2) who calculated the velocity constant by electrochemical method. But it must be taken in mind that my experiment has been carried out in excess of alkali in comparison with that of light sensitive substance. If this photochemical reversible reaction of malachite green, however, is considered to be a tautomeric change of colour-base as was indicated by Hantzsch and Osswald,(3) it seems more probable that the reaction is of first order, alkali acting itself catalyticaly.

Experiment 3 may be discussed exactly the same way as in Fxperiment

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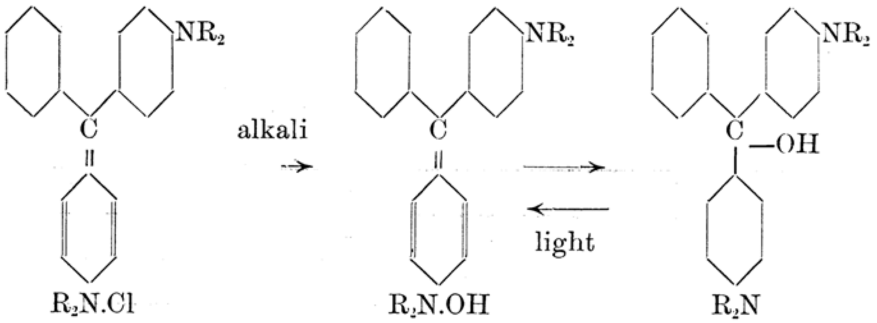
(1) W. J. Mueller, *Ber.*, **43** (1910), 2609.

(2) P. Gelinger, *Ber.*, **37** (1904), 3958.

(3) A. Hantzsch u. G. Osswald, *Ber.*, **33** (1900), 278.

1, if we consider that the coloured substance produced by light (Exp. 2) is a ammoniumbase, its decolourising velocity in the dark increasing linearly with the concentration of alkali added.

Hantzsch and Osswald have proved that in malachite green as well as in triphenylmethane dyes two kinds of modification are possible, one being in coloured and unstable ammonium-base and the other colourless and stable pseudo-ammonium-base type (carbinol type):



Salt of dye | Coloured ammonium base | Colourless pseudo ammonium base

If it is allowed to adopt these formulae, the coloured substance which is produced by the action of light can be considered to be this unstable coloured ammonium-base, and the other formed by the decolourisation in the dark will then be the stable colourless pseudo-ammonium-base.

In Experiment 2 it was observed that the linear relation holds between the intensity of the light and the reaction velocity. I have carried out the further experiments with the intention of finding out the limit at which the equation of zero order would be satisfied when factors such as thickness of liquid layer and the light intensity were changed. But sufficient data for this purpose have not yet been obtained.

The temperature coefficient of the velocity constant of the light reaction per ten degrees has been shown to be unity in the interval between 25° and 35°C, and this fact can be taken as a strong support that the reaction which we are now dealing with, is of pure photochemical one. The velocity of the dark reaction, which is quite insignificant as long as the concentration of alkali is small, increases rapidly in raising its concentration as well as temperature, while the light reaction is neither influenced by the temperature nor by the concentration of alkali.

So far as the visible part of the spectrum concerned, the absorptions are quite same in both cases of original colouring matter solution and the photo-product. Absorption spectrum of ultraviolet region was also studied in using the quartz spectrograph (Adam Hilger), and iron arc as the light source. But I failed to obtain a good photography of the absorption spectrum; the concentration of the substance having been very small, no distinct absorption band was to be detected on the plates.

As for the wave lengths of the most effective light, it will require further studies. Only it may be said that the optimum part lies in the ultraviolet region of spectrum, because the solution contained in an ordinary glass tube is not effected by illuminating with the light of iron arc, while it is easily coloured if a quartz glass vessel is used. Intense direct sunshine or the light from a mercury lamp of high intensity has shown, however, the colouring effect even in an ordinary glass vessel.

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Summary.

1. The photochemical reversible reaction of the alkaline solution of malachite green was studied with the quartz-mercury-lamp, and its nature was discussed.

2. The reaction velocities were determined both in the light and the dark reaction, using Nutting's spectro-photometer. The former is proportional to the intensity of light and the latter to the concentration of the alkali added.

3. The temperature coefficient of the reaction velocity of the light reaction was found to be unity at the interval between 25° and 35° C.

4. Equation of the reaction of first order was derived with approximation for the light reaction.

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