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Studies on the Radical Species in Solid Methylene Blue as Revealed from the ESR Spectra

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The ESR signals of polycrystalline methylene blue (MB) salts have been investigated in respect to a) temperature effect, b) anion effect, c) influence of the addition of donor and acceptor and d) response to visible light irradiation. a) The signal intensity in general increases with the rising temperature, but a sharp difference in the ESR behavior has been found above and below room temperature. Response to the temperature change at low temperature is reversible and the apparent activation energy is *ca.* 0.03 eV (L-type behavior) whereas the high temperature behavior has a marked tendency of irreversibility and the activation energy is at least one order larger (H-type behavior). b) No essential anion effect has been observed on *g*-value, line shape and spin concentration for chloride, iodide and phosphate. c) The addition of trinitrobenzene and para-phenylenediamine in 10 : 1 to MB chloride also had no essential effect. d) Corresponding to the L-type and H-type behavior observed in a), visible light irradiation has been found to cause a decrease or an increase in signal intensity respectively at low and high temperature. From these findings it has been concluded that there are at least two kinds of defect (L-type and H-type) and that the formation of radical species occurs only on such defect sites. Some suggestions have been made on the nature of these two types of defects and on the molecular processes occurring at or near these defect sites. The radical formation reaction is most likely to be connected with dye-dye interaction, $D^+ + D^+ \rightleftharpoons D^{++} + D$.

The past work has shown that some kinds of dye give ESR signals in the solid state; various mechanisms have been proposed for their appearance, but they are not always amply established. Terenin *et al.*¹⁾ have proposed a conduction electron theory for xanthene and triphenylmethan dyes, on the basis of the similar dependence of conductivity and of the ESR signal intensity upon the addition of water or oxygen. Nelson *et al.*²⁾ has claimed for the case of crystal violet, the occurrence of electron transfer between dye cation and its paired anion, because of great dependence of the features of the signal on the paired anion. Other mechanisms conceivable from relevant work are the biradical theory which has been mentioned by Simpson *et al.*,³⁾ and the defect theory suggested by Lagercrantz *et al.*⁴⁾ for methylene blue.

In the present paper attention is focused on the possibility of electron transfer between two dye cations. Since the occurrence of the analogous process has been well established by our group⁵⁾ and by Lindqvist⁶⁾ in the case of the photoreaction of some dyes in solution, it is quite natural to expect its occurrence also in the solid state where dye ions exist close with each other.

Choosing methylene blue, we have investigated the effect of temperature, of paired anions, of the addition of typical electron donor or acceptor and of the visible light illumination on the ESR signal of the polycrystalline sample. ESR in methylene blue was studied previously by Lagercrantz *et al.*⁴⁾ and by Simpson *et al.*³⁾ in the solid state but there is disagreement in many respects. On the other hand, ESR signals of methylene blue radical have been reported by Heineken *et al.*⁷⁾ and by Tuck *et al.*⁸⁾ in the acidic or alkaline solution.

Experimental

Materials. Methylene blue chloride, Merck G. R. grade was purified by two methods, by recrystallization from *n*-buthanol and by the method reported by Bergmann *et al.*⁹⁾ The latter is particularly effective

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1) V. Holmogorov and S. Terenin, *Naturwiss.*, **50**, 299 (1963).

2) R. C. Nelson and L. C. Brown, *J. Chem. Phys.*, **39**, 499 (1963).

3) L. P. Simpson, J. S. Kirby-Smith and M. L. Randolph, *Nature*, **199**, 243 (1963).

4) C. Lagercrantz and M. Yjheland, *Acta Chem. Scand.*, **15**, 1204 (1961).

5) S. Kato, M. Morita and M. Koizumi, This Bulletin, **37**, 117 (1964); Y. Usui, K. Itoh and M. Koizumi, *ibid.*, **38**, 1015 (1965).

6) L. Lindqvist, *Arkiv. Kemi*, **16**, 79 (1960); J. Kaoshe and L. Lindqvist, *J. Phys. Chem.*, **68**, 817 (1964).

7) F. W. Heineken, M. Bruin and F. Bruin, *J. Chem. Phys.*, **37**, 1479 (1962).

8) L. D. Tuck and D. W. Schiesor, *J. Phys. Chem.*, **66**, 937 (1962).

9) K. Bergmann and C. T. O'Konski, *ibid.*, **67**, 2169 (1963).

for removing a trace of trimethylthionine, which can be preferentially extracted from the aqueous 0.01 N ammonia-alkaline solution of methylene blue (0.1 g 100c) with benzene layer. Ten to twenty times extraction was necessary for the disappearance of the purple color of trimethylthionine in benzene layer. The solution of methylene blue purified, was concentrated under reduced pressure at room temperature and the obtained sample was dried below 40°C for 7 hr in an ampule at 10^{-5} mmHg.

s-Trinitrobenzene of Wakō G. R. grade was recrystallized from benzene at least three times. Paraphenylenediamine was purified by sublimation *in vacuo*.

The mixture of methylene blue with trinitrobenzene or paraphenylenediamine was prepared in the following way. The mixture at a desired composition was milled in a mortar and pressed at 4000 kg/cm^2 after degassing. The pressed sample was crashed to the size less than 1.5 mm and then desiccated in an ampule similarly as in the case of polycrystalline sample.

Procedure. All the samples dried in ampules were transferred to ESR sample tubes (5 mm in diameter) *in vacuo* and then sealed off. All the above procedures were performed in the dark. The ESR spectra were measured by a JEOL JESP-10 type ESR spectrometer (X-band, 100KC field modulation). The temperature was controlled over the range from 137°K to 373°K by passing a cold gas from liquid nitrogen or hot air through the inside of the cavity. The constancy was ±0.5°C. A light source was usually a projector incandescent lamp (Kondo 100V-500W, operated at 90V). Y2 cut off filter ($\lambda > 470$ nm) and a $CuSO_4$ aq. solution filter were employed. For the investigation of the wavelength effect, Xe-arc lamp (Ushio UXL 500W) was used with a set of suitable interference filters. The light was focused on the sample tube with a condenser lens ($f \simeq 1.8$). Intensity was not controlled in particular but was ascertained to be nearly the same.

Results and Discussion

To examine the possible effect of impurity, the samples purified by different methods have been compared at first. The samples recrystallized five times and eight times from *n*-buthanol showed the ESR signal of nearly equal intensity; it was always a single line of Lorentzian type with $\Delta H_{msl}=9.6$ and $g=2.0049$. Figure 1 shows one example. The spin concentration was respectively 1.3×10^{18} and 1.4×10^{18} per unit gram. The sample purified by Bergmann's method also gave the spin concentration of $\sim1\times10^{18}$ spins/g. These values are of the same order as the one reported by Simpson, 1.2×10^{18} spin/g and also are not very different from 10^{15}—10^{18} spin/g of Lagercrantz. On the basis of the above agreement irrespective of the different procedures in making samples, one may safely conclude that the signal is intrinsic for methylene blue.

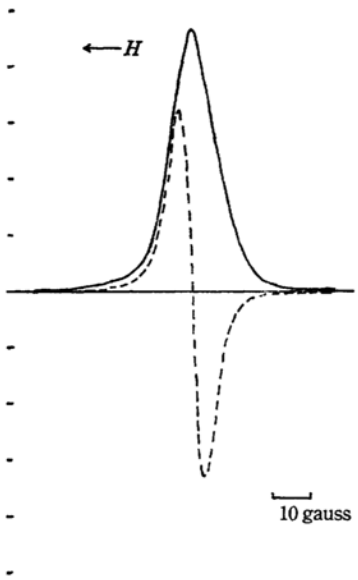

Fig. 1. ESR line shape of methylene blue chloride in the solid state.
Solid line: Integrated curve
Dotted line: Differential curve

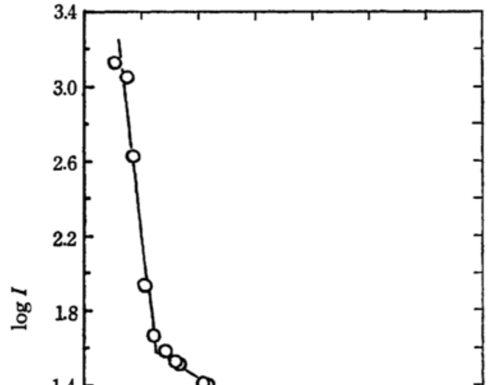

Fig. 2. Temperature dependence of the signal intensity of polycrystalline MB.

Temperature Effect. As the first attempt to elucidate the origin of ESR signal, measurements were made at different temperatures from 143 to 343°K. Such studies are expected to be helpful to distinguish the defect theory, the conduction electron theory and the biradical theory.

The essential features of the signal remain the same throughout the entire temperature region. The intensity increases monotonously with the rise of temperature. This agrees with Lagercrantz at least qualtitatively, but not with Simpson. A notable finding is that in the response to temperature change, a clear difference exists above and below room temperature. Thus in the lower temperature region, the response is rather rapid and the change is reversible. At higher temperature, on the other hand, the response is very slow, requiring as long as several hours to get the final state at ∼340°K. Around this temperature the equilibrium intensity is difficult to determine; the behavior appeared often to be even irreversible. The temperature dependence of the signal intensity (I) in the high and low temperature regions was found to be different in the order of magnitude. Figure 2 gives the plot of $\log I$ (corrected for Curie Law) against $1/T$. In the higher temperature region, the I-value at one to two hours after fixing temperature in heating experiments, was conventionally adopted. It is evident that the plot consists of two linear parts; from the slopes of the two linear lines, the energy difference between the two states with and without unpaired electron, was evaluated as 0.036 eV (ΔE^L) and 0.28 eV (ΔE^H) respectively for low and high temperature regions.

Although there is some ambiguity in the latter value, yet it is quite definite that ΔE^L is of the order of van der Waals energy and ΔE^H is more than one order larger.

If the electrons raised to the conduction band were the origin of the signal, as in the case of triphenylmethane and xanthene dyes,(1) the values of ΔE should be of the same order as the one evaluated from the temperature dependence of the electric conductivity. The latter value of Meier(10) is 1.36 eV and the value of Matsumoto is 1.6 eV(11) in the room temperature region; these values differ from the above ΔE values in the order of magnitude. Hence the conductive electron theory in a simple form may be rejected for the present sample. The biradical theory may also be ruled out from the similar reasoning, since the triplet level is expected to be located much higher than ΔE^H and ΔE^L.

On the other hand, the defect theory proposed by Lagercrantz(4) seems to be satisfactory if it is complemented by the following two assumptions. The first is that at low temperature, the radical formation reaction is in equilibrium only at certain defect sites, and the second is that at higher temperature, other type(s) of defect gradually come to play a dominant role. The first assumption is necessary, because the number of unpaired spins is less than 1% of the entire dye ions and yet the ΔE^L value is so small that quite an appreciable quantity of unpaired spin should exists in the equilibrium. Provided several % of the entire lattice sites exist as defects, the present result may be satisfactorily interpreted. The second assumption is less compulsive, but it is reasonable because an alternative assumption that two kinds of reaction occur at a single type of defect depending upon temperature, seems unlikely from the general theory of defect in solid state.

In the further investigations, emphasis was placed on the clarification of the process occurring at lower temperature, because the phenomena at lower temperature were thought to be more simple than at higher temperature.

Anion Effect and Donor, Acceptor Effect. Provided the electron transfer were occurring between dye cation and its paired anion, as has been established by Nelson *et al.*(2) for crystal violet, other salts than chloride would display quite different features in their ESR signals. Hence iodide and phosphate of methylene blue were investigated. Further, the effect of the addition of some inorganic salts and of a typical electron donor and acceptor was examined in a pressed form. The effect of pressing was also examined using polycrystalline methylene blue chloride.

ESR spectra of iodide and phosphate of methylene blue were measured at various temperatures from 143 to 293°K, quite similarly as in the case of chloride. The shapes of ESR spectra were essentially the same as the one of chloride. The data for the line width (ΔH_{msl}), the g-value, spin concentration at ordinary temperature and the values of ΔE^L are given in Table 1. It is seen that there is no significant difference in the three salts. Slight differences in the spin concentration and in

TABLE 1. ESR PARAMETERS OF THE VARIOUS SAMPLES

	ΔH_{msl} (G)	g-Value	Spin concn.**	ΔE^L (eV)
MB^+Cl^-	9.6	2.0049	1×10^{18}	0.036
MB^+I^-	13.6	2.004	$\sim10^{17}$	0.041
$(MB^+)_2HPO_4^{2-}$	6.3	2.0056	3×10^{18}	0.051
MB^+Cl^- pressed	9.2	2.0041	$\sim10^{19}$	0.026
MB : TNB (1 : 10)	9.0_6	2.0040	2×10^{18}	0.017*
MB : PPD (1 : 10)	—	2.004	2.5×10^{18}	0.011

* for the sample MB : TNB=1 : 50

** per g of MB

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10) H. Meier, *Z. physik. Chem.*, **208**, 325 (1958).

11) Private communication from S. Matsumoto.

ΔE^{L} are not compatible with the hypothesis of electron transfer between cation and anion. The pressed sample of methylene blue mixed with trinitrobenzene or paraphenylenediamine (TNB, PPD) (at the mole ratio, MB : TNB=1 : 10) as well as the similarly pressed sample of methylene blue alone gave essentially the similar signals. The ESR parameters such as line width, *g*-value and the ΔE^{L} value of these samples are given in Table 1. All of them are not different significantly from the values of the polycrystalline methylene blue unpressed. Furthermore it was found that the addition of sodium chloride, potassium bromide and pottassium iodide to chloride of methylene blue in the mole ratio of 2 : 1, do not essentially affect the characteristics of the signal.

All these findings support the afore-mentioned view that the formation of unpaired electron occurs at some defect points; because it is reasonable to consider that the added substances do not affect the nature of the defect so much as they may affect the average properties of the sample. Although the nature of the reaction related to the formation of unpaired electron is still unknown at this stage, it seems natural to consider the occurrence of reaction $D^+ + D^+ \rightleftharpoons D^{++} + D\cdot$ at defect sites, because the electron transfer between paired anion and cation has been ruled out and further because it is well-known that an analogous reaction, $D^{+*} + D^+ \rightarrow D^{++} + D\cdot$ occurs photochemically in solutions.

Irradiation Effect. The investigation of the effect of light will give information on the nature of the molecular processes which may occur at normal and defect sites.

The effect of illuminating the polycrystalline methylene blue chloride by the visible light, has proved to be very unique in that it occurrs in the opposite direction at high and low temperature regions. At very low temperatures ($<$223°K) the signal intensity decreases upon irradiation, quite rapidly and reaches the steady value within a few minutes. When the illumination is stopped, the intensity recovers its initial value also in a few minutes. At higher temperatures ($\gtrsim$293°K) the intensity increases, upon irradiation, but more slowly. When the light is off, the increase still continues for a few minutes and then begins to decrease. At an extremely high temperature of 373°K, this increase after the light being off, is not observable. At high temperatures, the recovery of the original intensity is very slow and in some cases seems to be even irreversible. Some examples of the intensity *vs.* time plot are shown in Fig. 3. It is evident that at 291°K and at 273°K, *i. e.*, in the medium temperature region, the plot can be interpreted as a superposition of the high and low temperature behaviors. Thus the slight increase observed when the light is off, is due to the existence of the low temperature type process. Although the intensity change upon irradiation is quite remarkable, as stated above, there is no essential change in the signal shape as well as in

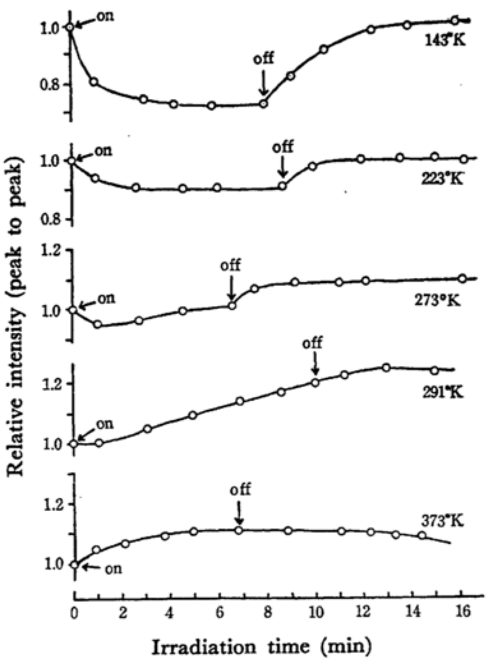


Fig. 3. Effect of photo-irradiation on the signal intensity of polycrystalline MB (measured by peak to peak distance of differential curve of ESR spectra).

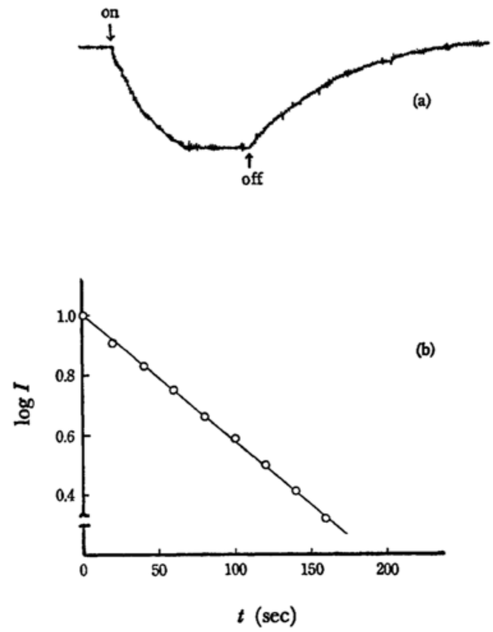


Fig. 4. Recovery processes of the signal intensity after the light is cut off. (at 183°K)
a: Recovery curve
d: Logarithmic plot of the amount of decrease of signal intensity *vs.* time.

the line width and the g-value. The kinetics of the recovery at low temperatures could be investigated accurately by measuring the peak to peak distance in the differential curve of ESR signal. The recovery is satisfactorily exponential as is shown in Fig. 4. From the measurements at different temperatures, the apparent activation energy of 0.5 kcal/mol (0.02 eV) was obtained (ΔE_R).

All the above findings are consistent with the view which has been proposed; there are apparently two kinds of defect playing a dominant role respectively at high and low temperatures. The value of the activation energy for the recovery process (0.02 eV) at low temperature, which approximates the ΔE^L value, strongly suggests that the similar process as in the thermal one is occurring for the recovery.

Figure 5 gives the comparison of chloride, iodide and phosphate when they are irradiated at low temperatures. It is seen that the anion effect is remarkable. Thus the L-type behavior is very prominent in chloride, less in iodide whereas in phosphate the H-type one is notable even at 243°K.

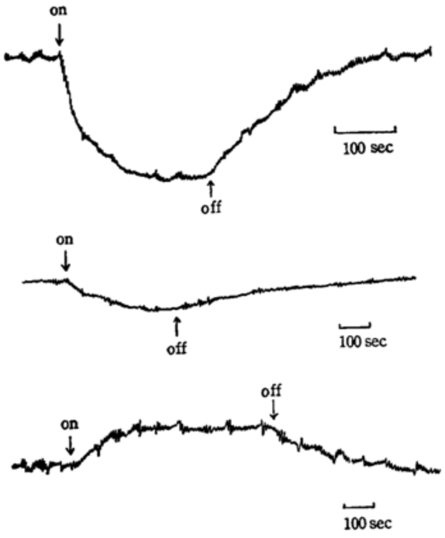
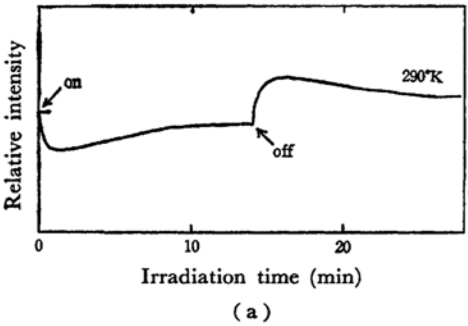
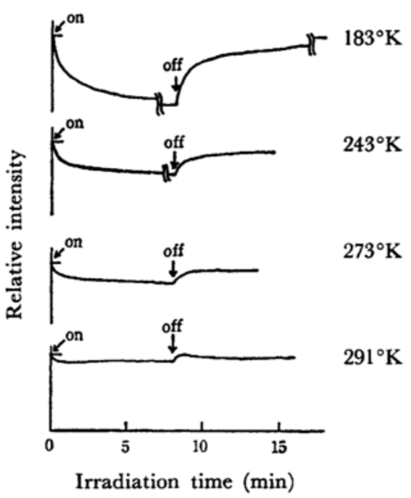


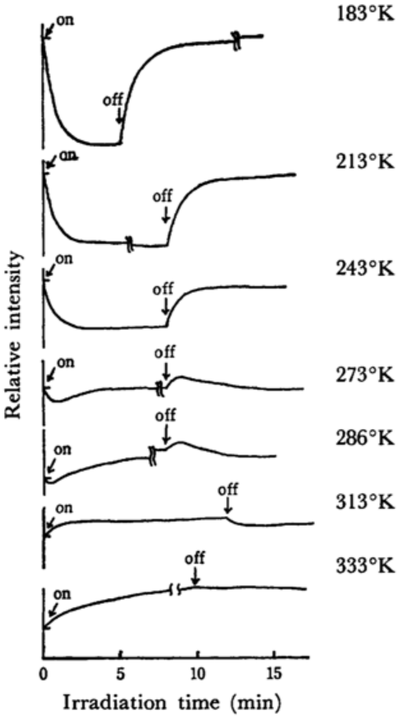
Fig. 5. Comparison of the effects of photo-irradiation on the signal intensity of different salts of MB. (from up to down)
a: MB^+Cl^- (at 215°K)
b: MB^+I^- (at 222°K)
c: $(MB^+)_2HPO_4^{2-}$ (at 243°K)



(a)



(b)



(c)

Fig. 6. Effect of photo-irradiation on the signal intensity of pressed MB alone and those dispersed into electron donor or acceptor media at several lower temperatures.
a: Pressed MB (at room temperature)
b: MB+PPD (1 : 10)
c: MB+TNB (1 : 10)

It is to be noted that the H-type behavior in this case appears quite reversible. Careful inspection

TABLE 2. KINETICS OF THE PHOTORESPONSE

Sample	1st order decay constant when the light is "ON" $\times 10^{-2}$sec^{-1} Temperature			Recovery process when the light is "OFF" (Half period several ten sec) Temperature		
	183°K	213°K	243°K	183°K	213°K	243°K
MB pressed						2nd order (room temp.)
MB+TNB (1 : 10)	2.7	3.0	3.6	1st order	1st order +2nd order	2nd order
MB+TNB (1 : 50)	2.4	2.8	3.5	1st order		2nd order
MB+PPD (1 : 10)	2.5		3.5	1st order		~2nd order

of the irradiation effect upon various samples leads to the suggestion that H-type defects in general consists of the reversible type and the other one(s) at which the ESR behavior is almost irreversible.

At any rate it seems plausible to attribute these differences in the three salts to the different contributions of the H-type defects in these salts, because the thermal behavior at L-type defects are so similar that it is difficult to attribute them to the L-type defect.

In the pressed methylene blue sample, the L-type behavior is quite prominent even at 290°K, as is shown in Fig. 6. The effect of the addition of donor or acceptor is not so pronounced but a general tendency is seen that the addition of TNB or PPD respectively enhances and suppresses the H-type behavior (when compared with the pressed methylene blue sample). This is clearly seen from Fig. 6(a)—(c). These results can be interpreted to be due to the opposite influence of a donor and an acceptor on the photochemical formation of radical species at H-type defects. Furthermore, the energy transfer by exciton mechanism is improbable, because if it really occurs, it would be greatly suppressed and consequently the photoeffect should be much reduced by the addition of donor and acceptor. Thus it may be concluded that most of the acts induced by illumination take place only in the close neighborhood of the defect sites.

Since the slow response when the light is on or off, suggests an appreciable structural change near defects, or mass transfer, some further kinetic studies were made in terms of the intensity change, when the light is on or off at low temperatures. The results are given in Table 2. It is seen that at low temperatures where the L-type defect plays a dominant role, the kinetic feature is essentially the same in all the samples. The second order process at 243°K suggests that the transient species produced by illumination, are two particles existing independently with each other. The activation energy for the disappearance reaction of radical species, as estimated from the data in Table 2 is 0.001—0.002 eV (ΔE_{D}).

Figure 7 shows the time dependence of the signal intensity when the pressed sample of methylene blue was irradiated by the light of narrow region at 18°C. The clear tendency is seen that the light of shorter wavelength enhances the H-type behavior. Since 660—670 nm and 625—630 nm correspond respectively to the main peak of methylene blue and the dimer absorption, it is tempting to consider that the dye ions at the H-type defects or in its close neighborhood take a dimer-like configuration.

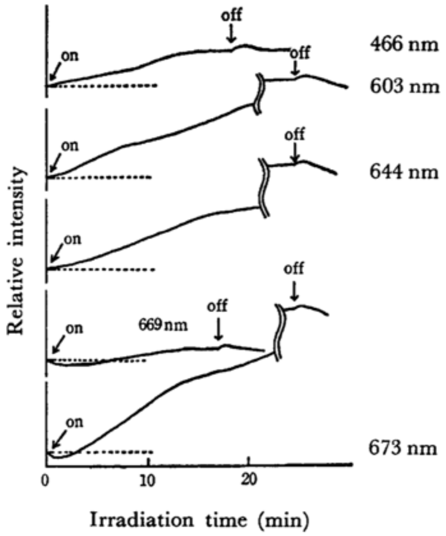


Fig. 7. Wavelength dependency of photo-irradiation effect on the signal intensity of pressed MB.

Summarized Discussion and a Possible Molecular Model

The existence of more than two types of defect, where unpaired electrons are located in the polycrystalline methylene blue chloride, have been verified from the temperature dependence of the signal intensity and the response to the irradiation. This has been further supported by the finding that the change from L-type to H-type behavior occurs at about the same temperature in both phenomena. The formation of radical species is considered to occur mainly on these defect sites in both the illuminated and unilluminated conditions, on the basis that electron donor and acceptor of the high concentration does not essentially affect the signal intensity. The process occurring at L-type defects is mild and reversible and the one occurring at H-type defects is drastic. From the values of ΔE^{L}, ΔE_{D} and ΔE_{R}, the energy levels for the two states wth and without unpaired spin at L-type defects are given as Fig. 8.

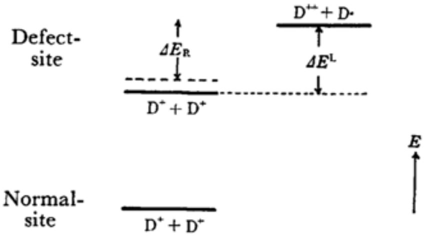


Fig. 8. Energy levels for the two states with and without unpaired spin at L-type defects.

It is particulary interesting that L-type defects show the decrease in signal intensity upon irradiation, while H-type defects show the increase. The magnitude of the contribution of L-type and H-type defects depends upon the kind of anion but at very low temperatures the L-type defect plays a dominant role irrespective of the salt type. Thus the characteristics of the signals in dark are not essentially affected by the anion. Sharp contrasts observed in the response to illumination in three salts, are concerned with the magnitude of the contribution of H-type defect, which is at most about 20% of the entire intensity at room temperature.

As to the molecular process occurring at L-type defects, the most plausible process is the electron transfer between two dye ions,

$$D^{+} + D^{+} \rightleftharpoons D^{++} + D\cdot \quad (\text{or } D^{++}\cdots D\cdot)$$

Although there is no strong evidence for this mechanism, all the other hypothesis cannot interpret the present results. Especially, the absence of a large anion effect on the features of the signal in dark, rules out the electron transfer between anion and cation.

The decrease in radical species upon irradiation may be due to the reaction of $(D^{++}\cdots D\cdot)$ with a near-by D^{+*} ion which may produce three ground state dye ions in a slightly different configuration, which is of course unstable. When the light is off, it returns to the original cofiguration and ultimately yield $D^{++}\cdots D\cdot$ to restore the equilibrium state. First order kinetics at very low temperatures justifies this view, in addition to the approximate agreement of ΔE^{L} and ΔE_{R}. However, with the rise of temperature, the process becomes more complicated as judged from the second order kinetics at 243°K. Further details of the process are quite unknown at the present stage.

Although detailed studies have not been attempted to elucidate the nature of the H-type defect, it is quite notable that the H-type response to illumination is brought about conspicuously by the wavelength corresponding to dimer absorption. This suggests the hypothesis that the dye ions exist as a dimer-like configuration at or around the H-type defects, and that the process occurring upon illumination is the reaction

$$(D^{+}\cdots D^{+}) \rightarrow D^{++} + D\cdot$$

In connection with this hypothesis, it is interesting that the phosphate of methylene blue displays the H-type behavior to a great extent, as has been shown in the H-type-response to illumination even at a low temperature of 243°K. This may be due to the circumstance that two dye ions attached to the bivalent anion are rather easy to take the dimer-like configuration. The results given in Table 1, seem to be interpreted along the similar reasoning. Thus a slightly higher spin concentration, narrowing of the linewidth and a slightly larger value of ΔE^{L} for the phosphate can be attributed to a larger contribution of the H-type defect in this salt.

The above discussion on the molecular process is of course still speculative. It will be interesting to extend the investigation to the salts involving other polyvalent anions and also to mixed dyes along the above picture.

The authors are grateful to Professor H. Kokubun for discussion.