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The Radiolysis of Anthraquinone Dye in Aqueous Solutions

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The decoloration yields of an Acid Blue 40 neutral aqueous solution, G(-Dye), obtained from the optical density at 610 nm for the nitrogen-, oxygen-, and N_2O-saturated solutions, equaled 0.18, 0.29, and 0.51 in the respective early stages. In view of the effects of NCS^- and NO_3^- on the G(-Dye), the decoloration is attributable to the attacks of the OH radicals and hydrated electrons on the dye. The rate constants for the reactions of the OH radical and the hydrated electron with Acid Blue 40, obtained from competition reactions with various additives, were $(6.6\pm1.2)\times10^9\ M^{-1}s^{-1}$ and $1.5\times10^{10}\ M^{-1}s^{-1}$ respectively. In the nitrogen-saturated solutions, the G(-Dye) increased markedly upon the addition of alcohols–for example, up to 1.25 upon the addition of 2 mM butyl alcohol. In this case, at the same time, a new absorption band which is attributable to the formation of the reduction products by the attacks of the hydrated electrons and alcohol radicals on the dye appeared at 460—490 nm. This new absorption band disappeared slowly in the presence of oxygen; the rate of this disappearance was $2.8\times10^{-5}\ s^{-1}$. On the other hand, in the oxygen-saturated solutions, the G(-Dye) decreased markeld upon the addition of even a small amount of alcohol.

In a preceding paper,[1)] we studied the radiation-induced decoloration of azo dye (Acid Red 265) in aqueous solutions and found that the decoloration is attributable to the attack of OH radicals and is promoted markedly by the addition of alcohols in the nitrogen-saturated solutions. On the other hand, it is known that quinones react easily with hydrated electrons as well as with OH radicals.[2,3)] The radiolysis of quinones in aqueous solutions is also interesting from the point of view of biochemistry.[4–6)]

In this paper, a study of anthraquinone dye (Acid Blue 40) was carried out as part of a series of radiolysis of dyes in aqueous solutions. This dye was not only decolored at 610 nm, but also gave a new absorption band at 460—490 nm as a result of the reduction reactions with the hydrated electrons and alcohol radicals. The behavior of the new absorption band will be clarified in this study.

Experimental

The experimental procedures were the same as in the preceding work[1)] except for those described below.

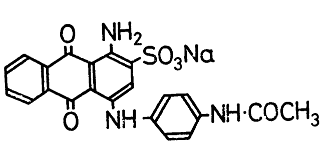

Fig. 1. Schematic diagram of the sodium salt of Acid Blue 40.

The Acid Blue 40 (Kayacyl Blue AGG, see Fig. 1), obtained from the Nippon Kayaku Co., Ltd., was further purified by recrystallization from a methyl alcohol–ethyl alcohol mixture.

When the irradiation was continued over 1 hr without any bubbling of oxygen, the dye solution began to lack oxygen. Therefore, in the case of an irradiation for over 1 hr, oxygen was bubbled in during the irradiation through a porous plate at the bottom of a Pyrex reaction vessel (5 cm in diameter and 16 cm in height).

The absorption spectra were measured with a Shimadzu spectrophotometer, UV-200. The decoloration yield was determined by the measurement of the optical density at 610 nm.

Results

Decoloration of Acid Blue 40 in Aqueous Solutions. The absorption spectra, shown in Fig. 2 as measured for the oxygen-saturated 0.1 mM Acid Blue 40 solution, indicate that the absorption bands at 250, 285, and 610 nm disappeared with the dose, and that these bands almost disappeared at 1.1×10^6 rad (Curve 7). The number of the curves is in common in Figs. 2 and 3 for the same dose.

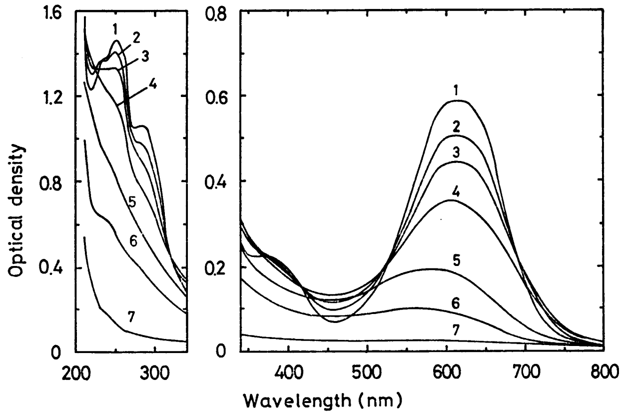

Fig. 2. Absorption spectra of irradiated oxygen-saturated Acid Blue 40 aqueous solutions.
Dye concentration: 0.1 mM. Dose (rad): 0 (Curve 1), 3.7×10^4 (Curve 2), 7.4×10^4 (Curve 3), 1.7×10^5 (Curve 4), 3.9×10^5 (Curve 5), 5.5×10^5 (Curve 6), and 1.1×10^6 (Curve 7).

The absorption spectra for the nitrogen-saturated solution are shown in Fig. 3. The absorption bands at 250 and 285 nm did not disappear with the dose so much as that at 610 nm. An interesting fact is that a new absorption band appears at 460—490 nm at 5.5×10^5 rad (Curve 6). This new absorption band hardly appeared for the N_2O-saturated solution, and the optical density at 250 and 285 nm decreased more efficiently for the N_2O-saturated solution than for the nitrogen-saturated solution.

Since the Acid Blue 40 solutions have a strong absorption band at 610 nm (Figs. 2 and 3), the degrees

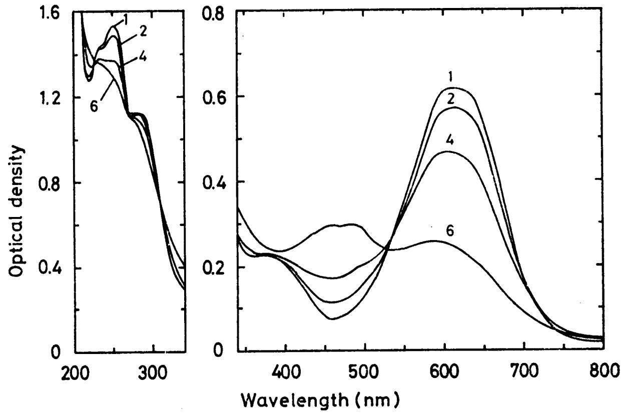

Fig. 3. Absorption spectra of irradiated nitrogen-saturated Acid Blue 40 aqueous solutions.
Dye concentration: 0.1 mM. The number of the curves is the same with Fig. 2.

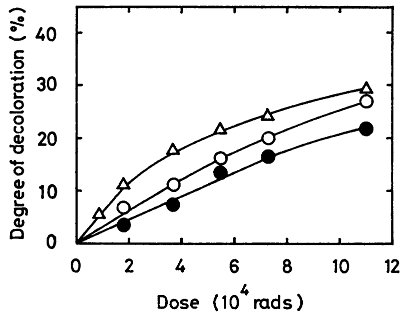

Fig. 4. Effects of inorganic gases on degree of decoloration.
Dye concentration: 0.1 mM. ●: N_2 saturation, ○: O_2 saturation, and △: N_2O saturation.

of decoloration were estimated from the reduction of the optical density. As may be seen in Fig. 4, the degrees of decoloration for the nitrogen-, oxygen-, and N_2O-saturated 0.1 mM Acid Blue 40 solutions increased with the dose. The decoloration yields, G(-Dye), obtained from the linear part in the early stage, are 0.18, 0.29, and 0.51 for the nitrogen-, oxygen-, and N_2O-saturated solutions respectively. These values were independent of the dose rate in the range from 5.3×10^4 to 1.9×10^5 rad/hr and of the initial dye concentration from 0.05 to 0.4 mM.

When the initial pH of the solutions was changed by the addition of sulfuric acid, the G(-Dye) was independent of the initial pH between 6.3 and 5.1; it increased from 0.29 to 0.35 for the oxygen-saturated solution and from 0.18 to 0.24 for the nitrogen-saturated solution at initial pH values between 5.1 and 2.4. This tendency may be attributable to the pH dependence of the yields of the primary species formed from the radiolysis of water.[7] The pH of the nitrogen- and oxygen-saturated solutions used in the present study changed from 6.3 to 6.0 and to 5.1 at 6.7×10^4 rad respectively. Therefore, the G(-Dye) is hardly affected by this pH change during irradiation.

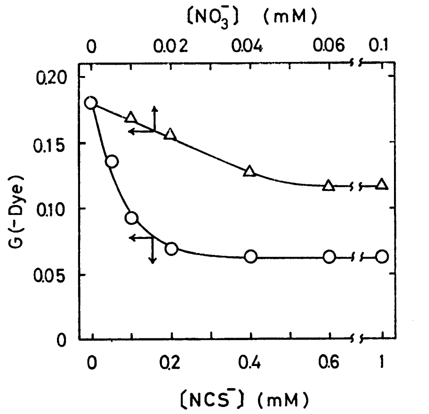

Fig. 5. Effects of NCS^- and NO_3^- on G(-Dye).
Dye concentration: 0.1 mM. Dose: 5.5×10^4 rad.
Additives: NCS^-(○) and NO_3^-(△).

Effects of NCS^- and NO_3^-. The G(-Dye) for the nitrogen-saturated 0.1 mM Acid Blue 40 solution containing NCS^- at 5.5×10^4 rad is shown as a function of the NCS^- concentration in Fig. 5. The G(-Dye) decreased to 0.06 upon the addition of NCS^- and became constant above 0.4 mM. The reduction upon the addition of NCS^- was G(-Dye)$=0.12$ above 0.4 mM. On the other hand, the G(-Dye) decreased to 0.12 upon the addition of NO_3^- and became constant above 0.06 mM. The reduction upon the addition of NO_3^- was G(-Dye)$=0.06$ above 0.06 mM. The sum of the two reductions equals the original G(-Dye)$=0.18$ without these solutes.

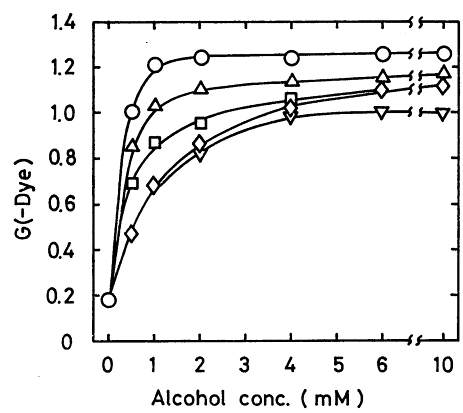

Fig. 6. Effects of alcohols on G(-Dye) in the nitrogen-saturated solutions.
Dye concentration: 0.1 mM. Dose: 5.5×10^4 rad.
◇: methyl alcohol, □: ethyl alcohol, △: propyl alcohol, ○: butyl alcohol, and ▽: *t*-butyl alcohol.

Effects of Alcohols. The G(-Dye) for the nitrogen-saturated 0.1 mM Acid Blue 40 solutions containing normal alcohols (C_1—C_4) and *t*-butyl alcohol at 5.5×10^4 rad is shown as a function of the alcohol concentration in Fig. 6. The G(-Dye) increased steeply with an increase in the alcohol concentration to 2 mM. The G(-Dye) at 2 mM alcohols is shown in Table 1. The increase in the G(-Dye) upon the addition of alcohols was in the order of:

$$\text{butyl alcohol} > \text{propyl alcohol} > \text{ethyl alcohol} > \text{methyl alcohol} > t\text{-butyl alcohol} \quad (1)$$

The G(-Dye) increased to 1.25 upon the addition of

Table 1. G(-Dye) for the aqueous solutions containing alcohols

Alcohols	Alcohol conc. (mM)	G(-Dye)
a) Nitrogen-saturated solutions.		
None	0	0.18
Methyl alcohol	2	0.86
Ethyl alcohol	2	0.95
Propyl alcohol	2	1.10
Butyl alcohol	2	1.25
t-Butyl alcohol	2	0.82
b) Oxygen-saturated solutions.		
None	0	0.29
Methyl alcohol	2	0.10
Ethyl alcohol	2	0.07
Propyl alcohol	2	0.06
Butyl alcohol	2	0.04
t-Butyl alcohol	2	0.14

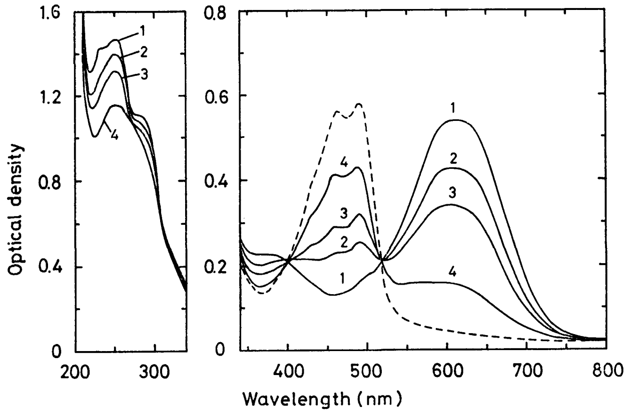

Fig. 7. Absorption spectra of irradiated nitrogen-saturated Acid Blue 40 aqueous solution containing methyl alcohol.
Dye concentration: 0.1 mM. Dose: 5.5×10^4 rad. Methyl alcohol concentration (mM): 0 (Curve 1), 0.5 (Curve 2), 1 (Curve 3), and 10 (Curve 4). Dotted curve represents the spectrum of the irradiated solution containing 10 mM butyl alcohol.

2 mM butyl alcohol from 0.18 for the non-alcoholic solution.

The absorption spectra, shown in Fig. 7 as measured for the nitrogen-saturated solution containing methyl alcohol, indicate that the absorption band at 610 nm disappears with an increase in the alcohol concentration, while, at the same time, the new absorption band at 460—490 nm appears more clearly than that for the non-alcoholic solution (Fig. 3). Similar results were obtained for the solutions containing other alcohols. In Fig. 7, the spectrum of the irradiated solution containing 10 mM butyl alcohol is shown by the dotted curve as a typical result. The intensity in the new absorption bands at 490 nm was in the same order (1) as the increase in the G(-Dye) for the nitrogen-saturated solutions for the same dose.

On the other hand, the G(-Dye) for the oxygen-saturated solutions containing normal alcohols (C_1—C_4) and *t*-butyl alcohol at 5.5×10^4 rad decreased with an increase in the alcohol concentration, in contrast with that for the nitrogen-saturated solutions, much like the curves in Fig. 5 in the preceding paper.[1] The decrease in the G(-Dye) upon the addition of 2 mM alcohol, as is shown in Table 1, was in the same order (1) as the increase in the G(-Dye) for the nitrogen-saturated solutions.

Discussion

The Nitrogen-saturated Solutions. As may be seen in Fig. 5, the G(-Dye) in the nitrogen-saturated solution decreased from 0.18 to 0.06 upon the addition of NCS^-, which is an efficient scavenger of OH radicals.[8] This means that the reduction (0.12) in the G(-Dye) is due to the contribution of the OH radical to the decoloration. On the other hand, the G(-Dye) decreased from 0.18 to 0.12 upon the addition of NO_3^-, which is an efficient scavenger of hydrated electrons.[9,10]

$$e_{aq}^- + NO_3^- \xrightarrow{k_2} NO_2 + 2OH^- \qquad (2)$$

This means that the reduction (0.06) in the G(-Dye) is due to the contribution of the hydrated electron to the decoloration. The sum of the two contributions equals the original G(-Dye) (0.18) without these solutes. It may be concluded from these results that the decoloration reaction of Acid Blue 40 in the nitrogen-saturated solution is mainly attributable to the attacks of the OH radicals and hydrated electrons, and that the contribution of the H atom to the decoloration reaction is minor.

The primary yields[11] of the OH radical and the hydrated electron formed from the radiolysis of water are 2.74 and 2.76 respectively for neutral water. These primary yields are much larger than the above G(-Dye) value. This fact indicates that the most of the primary species are consumed by reactions other than the decoloration reaction.

On the basis of these results, as postulated previously for azo dye,[1] the radiation-induced decoloration reaction of Acid Blue 40 at 610 nm in the nitrogen-saturated solutions may be represented as follows:

$$AB + OH \xrightarrow{k_3} ABOH \text{ (decolored product)} \qquad (3)$$

$$AB + OH \longrightarrow ABOH' \text{ (colored product)} \qquad (4)$$

$$AB + e_{aq}^- \xrightarrow{k_5} AB_{red} \text{ (decolored product)} \qquad (5)$$

$$AB + e_{aq}^- \longrightarrow AB'_{red} \text{ (colored product)} \qquad (6)$$

where AB, ABOH, and AB_{red} are Acid Blue 40, its OH adduct, and its reduction product by the hydrated electron respectively.

The dye molecule has three kinds of reaction sites for Reactions 3—6: (a) the anthraquinone ring, (b) the carbonyl group in the anthraquinone ring, and (c) the substituted benzene ring, not conjugated to the carbonyl group in the anthraquinone ring. The attacks of the OH radical and hydrated electron on Site c are independent of the decoloration reaction and cause little change in the absorption spectrum at 610 nm. This is represented by Reactions 4 and 6.

In Fig. 3, the absorption band at 285 nm is attributable to the carbonyl group, and that at 610 nm, to an auxochromic effect on the anthraquinone.[12,13] The absorption band near 250 nm is attributable to substituted aromatic rings.[12,13] The optical density at 250 nm does not decrease with the dose so much as does that at 610 nm. This suggests that the decoloration reaction is not necessarily accompanied by the destruction of the skeleton of the dye molecule.

According to Broadbent and Newton,[14] the reaction of sodium 9,10-anthraquinone-2-sulfonate with Fenton's reagent gives the hydroxylation products. In this case, the OH radical does not react with the carbonyl group, but with the anthraquinone ring. This rate constant is $5.6\times10^9\ \mathrm{M^{-1}s^{-1}}$.[3] On the other hand, according to Hulme *et al.*,[3] the pulse radiolysis of sodium 9,10-anthraquinone-2-sulfonate in an aqueous solution gives its radical anion. This means that the hydrated electron reacts with the carbonyl group. The rate constant of the reduction is $2.8\times10^{10}\ \mathrm{M^{-1}s^{-1}}$.[3]

Therefore, it may be concluded that Site a is attacked by the OH radical, and Site b, by the hydrated electron. These processes reduce the absorption band at 610 nm. The OH radical and the hydrated electron also react with the part (Site c) not conjugated to Site b. Furthermore, since the ABOH and the $\mathrm{AB_{red}}$ from Reaction 3 and 5 can react with the OH radicals and hydrated electrons, the dye molecule is degraded to the lower molecular weight compounds by consuming many primary species formed from the radiolysis of water. Therefore, the *G*(-Dye) is much less than the primary yields of the OH radical and the hydrated electron.

The absorption band at 460—490 nm is attributable to the reaction of the dye with the hydrated electron (Reaction 5), which will be interpreted in detail after discussing Reaction 3.

The Oxygen-saturated Solutions. As may be seen in Fig. 2, the absorption bands at 250, 285, and 610 nm in the oxygen-saturated solution decrease more efficiently than in the nitrogen-saturated solution. Curve 7 in Fig. 2 suggests that the skeleton of the dye molecule in the oxygen-saturated solution is almost destroyed at 1.1×10^6 rad. The *G*(-Dye) (0.29) in the oxygen-saturated solution is higher than that (0.18) in the nitrogen-saturated solution. This may be attributable to the contribution of the $\mathrm{HO_2}$ radical, which is formed from the reaction of oxygen with the hydrogen atom. Peroxides formed by the degradation of the dye molecule may also accelerate the decoloration reaction.

The N_2O-saturated Solutions. The $G(\text{-Dye})_{\mathrm{N_2O}}$ (0.51) for the $\mathrm{N_2O}$-saturated solution is larger than that (0.18) for the nitrogen-saturated solution. $\mathrm{N_2O}$ reacts rapidly with the hydrated electron to form the OH radical:[10]

$$e_{aq}^- + \mathrm{N_2O} \longrightarrow \mathrm{OH} + \mathrm{OH^-} + \mathrm{N_2} \qquad (7)$$

Therefore, such a large *G*(-Dye) is attributable to an increase in the OH radical.

As has been already described, the absorption band at 250 nm in the $\mathrm{N_2O}$-saturated solution disappears more efficiently than in the nitrogen-saturated solution. This suggests that the skeleton of the dye molecule is mainly destroyed by the attack of the OH radical.

The Solutions Containing Alcohols. The increase in the *G*(-Dye) upon the addition of alcohols in the nitrogen-saturated solution (Fig. 6) means that the alcohol radical ($\mathrm{R\dot{C}HOH}$) destroys the dye chromophore more efficiently than the OH radical does.[1]

$$\mathrm{RCH_2OH} + \mathrm{OH} \xrightarrow{k_8} \mathrm{R\dot{C}HOH} + \mathrm{H_2O} \qquad (8)$$

The values of the *G*(-Dye) in Table 1 correspond to the order of the rate constants for the reaction of alcohols with OH radicals, as measured by the pulse-radiolysis technique; these rate constants are listed in Table 2.[8,15]

TABLE 2. RATE CONSTANTS FOR REACTIONS 3 AND 8

Additives	k_3[a)] $(\mathrm{M^{-1}s^{-1}})$	k_8[b)] $(\mathrm{M^{-1}s^{-1}})$
Methyl alcohol	5.5×10^9	4.8×10^8
Ethyl alcohol	6.6×10^9	1.1×10^9
Propyl alcohol	6.7×10^9	1.5×10^9
Butyl alcohol	7.4×10^9	2.2×10^9
t-Butyl alcohol	5.3×10^9	2.5×10^8
NCS-	7.8×10^9	6.6×10^9

a) Initial pH 6.3. b) Rate constants for reaction of OH radical with additives from Ref. 8 and 15.

On the basis of these results, the radiation-induced decoloration reaction of Acid Blue 40 at 610 nm in the nitrogen-saturated solution containing alcohols may be represented as follows:

$$\mathrm{AB} + \mathrm{R\dot{C}HOH} \longrightarrow \mathrm{ABH\ (decolored\ product)} + \mathrm{RCHO} \qquad (9)$$

where AB and ABH are Acid Blue 40 and its reduction product respectively. It is known that quinones are reduced by alcohol radicals, leading to the formation of reduction products.[6,16]

On the other hand, in the oxygen-saturated solution, the alcohol radicals react rapidly with oxygen prior to Reaction 9 and are degraded to lower molecular weight compounds.[1] Therefore, the *G*(-Dye) for the oxygen-saturated solution decreased upon the addition of alcohols, in contrast with that for the nitrogen-saturated solution.

Rate Constant for Reaction 3. The rate constant for Reaction 3 can be determined by using a competition reaction method with additives from the following equation:[1]

$$\frac{1}{G(\text{-Dye})} = \frac{1}{G_r}\left(1+\frac{k_8[\mathrm{RCH_2OH}]}{k_3[\mathrm{AB}]}\right) \qquad (10)$$

where G_r is the yield of the OH radicals consumed by Reactions 3 and 8, and where [AB] and [$\mathrm{RCH_2OH}$] are the initial concentrations of Acid Blue 40 and alcohols respectively.

The plots of $1/G$(-Dye) are linear against the alcohol concentration, in good agreement with Eq. (10). From Eq. (10), the slope of the curve gives the k_8/k_3 ratio and the intercept gives the G_r value by means of the least-squares method. The k_3 values listed in Table 2 were obtained from the observed k_8/k_3 ratio by using the corresponding k_8 values in Table 2. The average k_3 value is $(6.6\pm1.2)\times10^9\ \mathrm{M^{-1}s^{-1}}$. This value is in good agreement with the rate constant of the additional reaction of the OH radical with sodium 9,10-anthraquinone-2-sulfonate ($5.6\times10^9\ \mathrm{M^{-1}s^{-1}}$),[3] as obtained by the pulse-radiolysis technique. The k_3 value is also near to the rate constant of the similar reaction with Acid Red 265 (azo dye, $9.3\times10^9\ M^{-1}s^{-1}$).1) The rate constant, obtained by using a competition reaction with NCS^-, is listed in Table 2.

Rate Constant for Reaction 5. Similarly, the rate constant for Reaction 5 (k_5) can be determined from the results shown in Fig. 5.

The plots of $1/G$(-Dye) are linear against the NO_3^- concentration. The k_5 value can be obtained from the observed k_2/k_5 ratio by using the k_2 value ($1.1\times10^{10}\ M^{-1}s^{-1}$).9) The k_5 value is $1.5\times10^{10}\ M^{-1}s^{-1}$. This value is near to the rate constant of the reduction reaction of the hydrated electron with sodium 9,10-anthraquinone-2-sulfonate ($2.8\times10^{10}\ M^{-1}s^{-1}$).3)

Appearance of Absorption Band at 490 *nm*. As may be seen in Fig. 3, in the nitrogen-saturated solution a new absorption band appears clearly at 460—490 nm at 5.5×10^5 rad (Curve 6). This new absorption band appears hardly at all in the presence of oxygen and N_2O, which react rapidly with hydrated electrons, leading to the formation of the O_2^- and OH radicals (Reaction 7) respectively. Furthermore, as may be seen in Figs. 3 and 7, this new absorption band appears more clearly for the solution containing alcohols than for the non-alcoholic solution, while the absorption band at 610 nm disappears more efficiently in the presence of alcohols as a consequence of Reaction 9.

It may be concluded from these facts that the formation of the reduction product from Reactions 5 and 9 reduces the absorption band at 610 nm; at the same time, it causes new absorption bands with maxima at about 460 and 490 nm, and also with a shoulder at about 430 nm, to appear, as may be seen in Fig. 7.

The final reduction product through Reactions 5 and 9, whose half-life is about 7 hr, as will be discussed in the next section, is appreciably stable. Therefore, this product is considered to be a permanent product even if it is unstable chemically. Then, the final reduction product is assumed to be the hydroquinone of AB. In fact, the Acid Blue 40 solution was immediately reduced to the leuco-form with alkaline sodium dithionite, and then recovered by oxygen. The leuco-base solution at pH 8.2 had two bands with maxima at about 460 and 485 nm, while the solution at pH 13.2 had two bands with maxima at about 430 and 480 nm. These bands are in good agreement with those in Fig. 7.

According to Phillips *et al.*,16) the flash photolysis of the sodium 9,10-anthraquinone-2-sulfonate (A) alcoholic aqueous solution gives absorption bands at 275 and 385 nm for the semiquinone radical ($AH\cdot$), and at 395 and 505 nm for the semiquinone radical anion ($A\cdot^-$). Both transients are long-lived (several millisec.). On the other hand, sodium 9,10-anthrahydroquinone-2-sulfonate (AH_2), a permanent reduction product of A, has two bands with maxima at about 265 and 385 nm, and the corresponding dianion (A^{2-}) has two bands with maxima at about 435 and 505 nm. The AH_2 and A^{2-} are produced through the disproportionation reaction from the semiquinone radical ($AH\cdot$) and from the semiquinone radical anion ($A\cdot^-$) respectively.16)

The reduction product may be dissociated in the aqueous solution as follows:

$$ABH\cdot \rightleftharpoons AB\cdot^- + H^+ \qquad (11)$$

where $ABH\cdot$ is the semiquinone radical of AB. The p*K* values of the semiquinone radical are 4 for benzoquinone,2) 4.5 for menaquinone,6) and 3.25 for sodium 9,10-anthraquinone-2-sulfonate.16) Since the pH is about 5—6 for the present experiments, as has been already described, $ABH\cdot$ may be rather dissociated to the right side. Since the pH values of the above leuco-base solutions are higher than the pH of the solution shown in Fig. 7, the spectra at the high pH must correspond to the dianion, and the spectra in Fig. 7 must contain the spectra of the undissociated form.

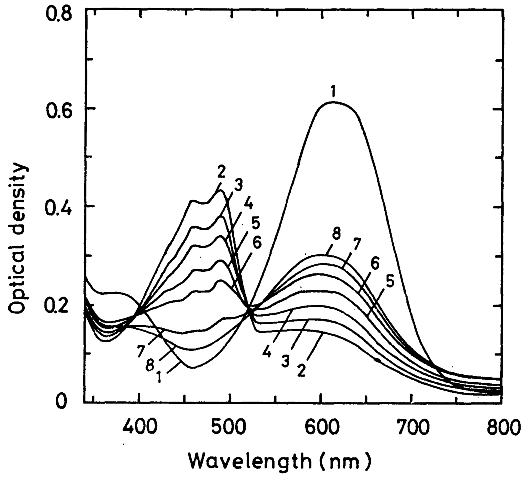

Fig. 8. Effect of oxygen on the spectra of the nitrogen-saturated Acid Blue 40 aqueous solution containing 10 mM methyl alcohol after irradiation of 5.5×10^4 rad. Dye concentration: 0.1 mM. Bubbling time of oxygen (hr): 0 (Curve 2), 1 (Curve 3), 2 (Curve 4), 4 (Curve 5), 7 (Curve 6), 24 (Curve 7), and 45 (Curve 8). Curve 1 represents the spectrum of the solution before irradiation.

Disappearance of Absorption Band at 490 *nm by Oxygen*. As may be seen in Fig. 8, the absorption spectra for the irradiated nitrogen-saturated solution containing methyl alcohol changed gradually upon the bubbling-in of oxygen after irradiation. The spectrum after 70 hr was almost identical with the curve after 45 hr. At the same time, about one-half of the intensity of the original absorption band at 610 nm was recovered finally. The other half of the intensity is attributable to the degradation of the dye by, for example, through Reaction 3. This recovery of the absorption band at 610 nm may be represented as follows:

$$AB_{red,f} + O_2 \xrightarrow{k_{12}} AB \text{ (colored product at 610 nm)} + O_2^- \text{ (or } HO_2) \qquad (12)$$

where $AB_{red,f}$ is the final reduction product.

Thus, the rate of Reaction 12 can be represented in terms of the rate constant, k_{12}, as follows:

$$-\frac{d[AB_{red,f}]}{dt} = k_{12}[O_2][AB_{red,f}] \qquad (13)$$

When the oxygen concentration dissolved is assumed to be constant, Eq. (13) can be rewritten by using the rate of the disappearance of the absorption band at 490 nm (k_{12}') as follows:

$$-\frac{dx}{dt} = k_{12}'(a-x) \tag{14}$$

that is;

$$-k_{12}'t = \ln\frac{(a-x)}{a} \tag{15}$$

where a is the initial intensity of the absorption band at 490 nm, and where x is the intensity of the absorption band which disappears in time t. The plots of $\ln(a-x)/a$ are linear against the time, in good agreement with Eq. (15). From the slope of the curve, the k_{12}' value is $2.8\times10^{-5}\,s^{-1}$. Then, the half-life of $AB_{red,f}$ is 6.8 hr. Similarly, the rate of the recovery of the absorption band at 610 nm, k_{12}'', can be estimated. When the intensity of the absorption band at 610 nm for the dye solution after 45 hr is assumed as the initial concentration, the k_{12}'' value is $2.6\times10^{-5}\,s^{-1}$. Since the value of $[O_2]$ is 1.2×10^{-3} M in the oxygen-saturated solution,17) the k_{12} value becomes $2.3\times10^{-2}\,M^{-1}\,s^{-1}$.

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