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The Radiation-induced Decoloration of Azo Dye in Aqueous Solutions

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The decoloration yield of an Acid Red 265 neutral aqueous solution, G(-Dye), equaled 1.00 ± 0.04, regardless of the dose rate and the initial dye concentration in the early stage. The G(-Dye) increased to 1.46 in the presence of nitrous oxide, but was independent of the presence of oxygen and acetone. In nitrogen-saturated solutions, the G(–Dye) increased markedly upon the addition of alcohols—for example, up to 1.83 upon the addition of 2 mM n-butyl alcohol. On the other hand, in oxygen-saturated solutions, the G(-Dye) decreased markedly upon the addition of even a small amount of alcohols. The effects of alcohols, namely, the G(-Dye) in both the solutions were in the order of their reactivity with OH radicals. The decoloration is attributable to the attack of the OH radicals formed by the radiolysis of water to the dye. The increase in the G(-Dye) for the nitrogen-saturated solutions containing alcohols is attributable to the attack of the alcohol radicals ($R\dot{C}HOH$) formed by the reactions of alcohols with OH radicals. In the oxygen-saturated solutions, the $R\dot{C}HOH$ radicals are converted to the peroxides, which do not react with the dye. The rate constant for the reaction of the OH radical with Acid Red 265, obtained by using various additives from the competition reaction method, is $9.3 \pm 1.4 \times 10^9$ $M^{-1}\,s^{-1}$. The effects of CNS^-, glucose, and phenol were also examined.

The decoloration of organic dyes in aqueous solutions induced by ionizing radiation has recently been reviewed by Grossweiner.[1] However, the radiation chemistry of azo dyes in aqueous solutions has not been extensively studied. A few authors[2,3] have, though, reported on its radiation-induced decoloration of azo dye in aqueous solutions. Korgaonkar *et al.*[2] discussed the possibility that the color changes of azo dye solution induced by ionizing radiation might serve as convenient radiation dosimeters. Mytelka *et al.*[3] have studied the radiation-induced decoloration of azo dye waste water.

In this paper, the effects of alcohols and other additives on the radiation-induced decoloration of Acid Red 265 in aqueous solutions will mainly be discussed, and the rate of its decoloration reaction will be estimated.

Experimental

Reagents. The Acid Red 265 (Kayaku Acid Brilliant Red BL; see Fig. 1), obtained from the Nippon Kayaku Co., Ltd., was further purified by recrystallization from a methyl alcohol–ethyl alcohol mixture. The recrystallized Acid Red 265 was then dried overnight in a vacuum desiccator containing silica gel. A test by thin-layer chromatography showed only a single component in the sample. The nitrous oxide (99.0%) was used without further purification. The other reagents used were of a reagent grade.

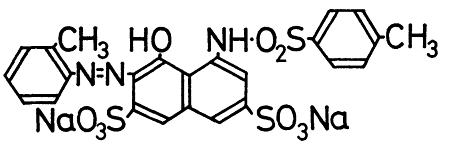

Fig. 1. Schematic of the sodium salt of Acid Red 265.

Irradiation Procedure and Analysis. The dye solution was prepared by dissolving recrystallized Acid Red 265 in triply distilled water. The solution was bubbled with nitrogen for 40 min or with oxygen for 15 min prior to irradiation. In some experiments, a nitrous oxide-saturated solution was prepared by bubbling for about 20 min. The solutions were placed in Pyrex glass tubes (30 ml) with a stopper and then irradiated with cobalt-60 gamma rays at room temperature. The dose rate (1.1×10^5 rad/hr) was determined by Fricke dosimetry ($G(Fe^{3+}) = 15.6$).

The degree of decoloration was determined by the measurement of the optical density at 542 nm with a Shimadzu spectrophotometer UV-200.

Results

Decoloration of Acid Red 265 in Aqueous Solutions. The degrees of decoloration for the nitrogen- and oxygen-saturated 0.1 mM Acid Red 265 aqueous solutions are shown as a function of the dose in Fig. 2. The degree of decoloration increased linearly with the dose below 4.8×10^4 rad, following the first-order kinetics. The degree of decoloration was independent of the presence of oxygen, at least below 6.4×10^4 rad. The pH of the solution changed from 6.4 to 4.7 at 4.8×10^4 rad. When the initial pH of the solution was changed by the addition of sulfuric acid, the degree of decoloration was independent of the initial pH between 4.3 and 6.4.

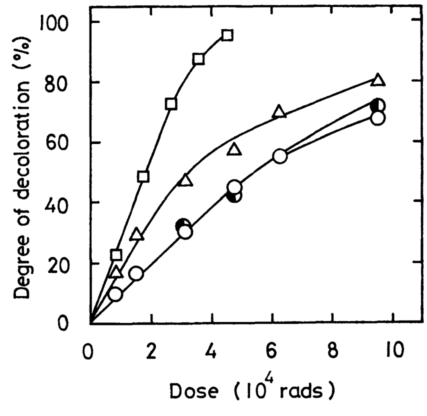

Fig. 2. Effects of additives on degree of decoloration. Dye concentration: 0.1 mM; ○: N_2 saturation, ◐: O_2 saturation, △: N_2O saturation, □: 2 mM n-butyl alcohol + N_2O.

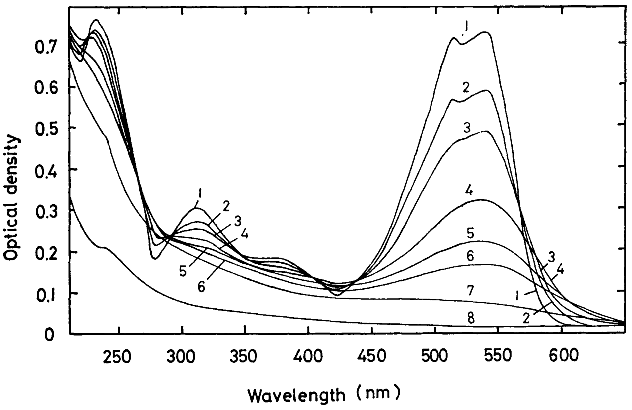

Fig. 3. Absorption spectra of unirradiated and irradiated oxygen-saturated Acid Red 265 aqueous solutions. Dye concentration: 0.1 mM; Curve 1 corresponds to the unirradiated sample. Curves 2—8 represented the spectra of solutions irradiated at the total doses of 1.6 × 10^4, 3.2 × 10^4, 6.4 × 10^4, 9.5 × 10^4, 1.3 × 10^5, 1.9 × 10^5, 2.8 × 10^5 rad, respectively.

The absorption spectra, shown in Fig. 3 as measured for the oxygen-saturated aqueous solution, indicate that the absorption band at 542 nm decreases with the dose, and that, below 6.4 × 10^4 rad (Curve 4), the isosbestic points appear at six different wavelengths, namely, 564, 439, 403, 290, 263, and 224 nm. Above 9.5 × 10^4 rad (Curve 5), the absorption band of the Acid Red 265 aqueous solution at 542 nm practically disappears and the isosbestic points disappear completely.

The results for the nitrous oxide-saturated similar solution are shown by open triangles in Fig. 2. The degree of decoloration for the nitrous oxide-saturated solution was higher than that for the nitrogen- and oxygen-saturated solutions. This suggests that nitrous oxide promotes the decoloration reaction.

When the decoloration yield, G(-Dye), was estimated as the number of dye molecules decolored per 100 eV of energy absorbed, from the concentration of the dye decolored, the G(-Dye) in the early stage equaled 1.00±0.04, regardless of the dose rate in the range from 1 × 10^4 to 1.9 × 10^5 rad/hr and regardless of the initial dye concentration from 0.05 to 0.4 mM.

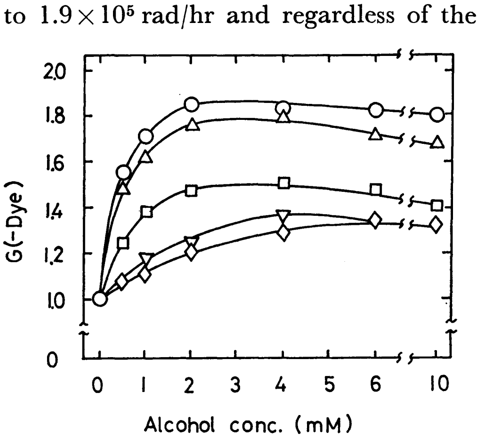

Fig. 4. Effect of alcohols on the G(-Dye) in the nitrogen-saturated solutions. Dose: 4.8 × 10^4 rad, Dye concentration: 0.1 mM, ◇: methyl alcohol, □: ethyl alcohol, △: *n*-propyl alcohol, ○: *n*-butyl alcohol, ▽: *tert*-butyl alcohol.

Effect of Alcohols. The degrees of decoloration for the nitrogen-saturated 0.1 mM Acid Red 265 aqueous solutions containing 4 mM alcohols increased linearly with the dose up to 4.8 × 10^4 rad in all cases. The values of the G(-Dye) for the nitrogen-saturated solutions containing *n*-alcohols and *tert*-butyl alcohol at 4.8 × 10^4 rad are shown as a function of the alcohol concentration in Fig. 4. Similar results for other isomers of butyl alcohol were also obtained. The G(-Dye) increased steeply with an increase in the concentration of alcohols up to 2 mM; then it decreased gradually except in the cases of methyl alcohol and *tert*-butyl alcohol.

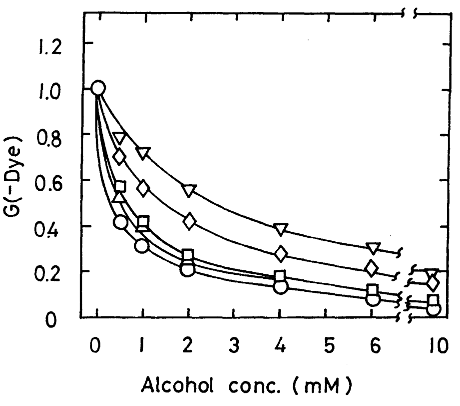

Fig. 5. Effect of alcohols on the G(-Dye) in the oxygen-saturated solutions. Dose: 4.8 × 10^4 rad, Dye concentration: 0.1 mM, ◇: methyl alcohol, □: ethyl alcohol, △: *n*-propyl alcohol, ○: *n*-butyl alcohol, ▽: *tert*-butyl alcohol.

On the other hand, the values of the G(-Dye) for the oxygen-saturated solutions containing *n*-alcohols and *tert*-butyl alcohol at 4.8 × 10^4 rad are shown as a function of the alcohol concentration in Fig. 5. Similar results for other isomers of butyl alcohol were also obtained. The G(-Dye) decreased with an increase in the concentration of alcohols.

Effect of Other Organic Additives. The values of the G(-Dye) for the nitrogen-saturated 0.1 mM Acid Red 265 aqueous solutions containing glucose and phenol are shown in Fig. 6 as a function of the organic additive concentration by open triangles and open squares respectively. The G(-Dye) increased up to 2 mM glucose, and thereafter decreased gradually with an increase in the concentration of glucose above 2 mM. The effect of phenol was in contrast to that of alcohols and glucose; that is, the G(-Dye) decreased upon the addition of phenol.

The results for the oxygen-saturated solutions containing glucose and phenol are shown in Fig. 7 as a function of the organic additive concentration by open triangles and open squares respectively. The G(-Dye) decreased steeply up to 2 mM glucose and phenol, and then decreased gradually above 2 mM. This tendency was almost the same as that for the solution containing alcohols.

The values of the G(-Dye) for the nitrogen- and oxygen-saturated solutions containing acetone are shown

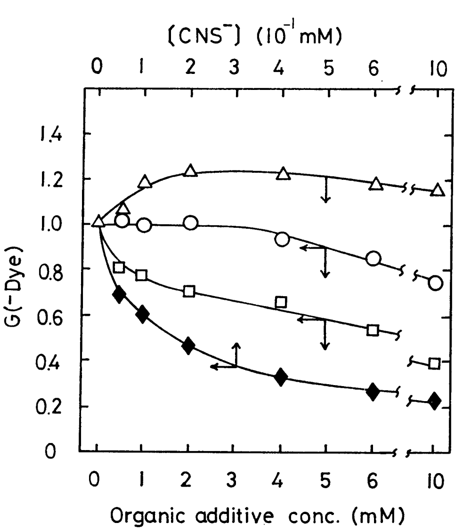

Fig. 6. Effect of organic additives and CNS^- on the G(–Dye) in the nitrogen-saturated solutions.
Dose: 4.8×10^4 rad, Dye concentration: 0.1 mM, △: glucose, □: phenol, ○: acetone, ◆: CNS^-.

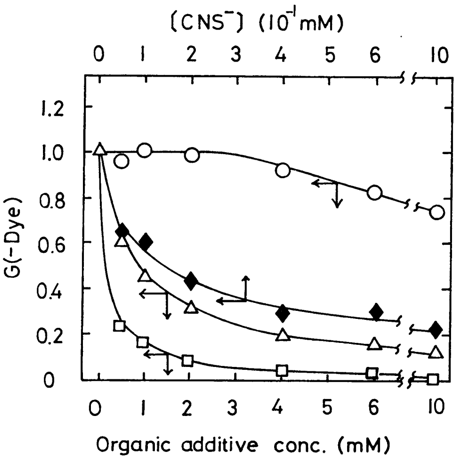

Fig. 7. Effect of organic additives and CNS^- on the G(–Dye) in the oxygen-saturated solutions.
Dose: 4.8×10^4 rad, Dye concentration: 0.1 mM, △: glucose, □: phenol, ○: acetone, ◆: CNS^-.

by open circles in Figs. 6 and 7 respectively. The G(-Dye) for neither solution was affected by the addition of acetone, at least not in the range from 0.5 to 2 mM. The effect of acetone for both the solutions is very different from those for the solutions containing alcohols and other organic additives.

Effect of CNS^-. The G(-Dye) for the nitrogen- and oxygen-saturated 0.1 mM Acid Red 265 aqueous solutions containing CNS^- at 4.8×10^4 rad decreased markedly with an increase in the CNS^- concentration, as is shown in Figs. 6 and 7 respectively by solid lozenges. The two curves are almost the same. The effect of CNS^- for the nitrogen-saturated solution is, though, different from those for the solutions containing alcohols and other organic additives.

Effect of n*-Butyl Alcohol in* N_2O*-saturated System.* The degree of decoloration for the nitrous oxide-saturated 0.1 mM Acid Red 265 aqueous solution containing 2 mM *n*-butyl alcohol is shown by open squares in Fig. 2 as a function of the dose. The degree of decoloration increased linearly in the early stage. The G(-Dye) for the nitrous oxide-saturated aqueous solution containing 2 mM *n*-butyl alcohol was 2.56; this value was the highest of all the values for the nitrogen-saturated solutions.

Discussion

When a neutral aqueous solution is irradiated with cobalt-60 gamma rays, radicals and molecular products are formed from water:

$$H_2O \rightsquigarrow OH,\ H,\ e_{aq}^-,\ H_2O_2,\ H_2, \qquad (1)$$

and in the presence of oxygen:

$$H + O_2 \longrightarrow HO_2 \qquad (2)$$

$$e_{aq}^- + O_2 \longrightarrow O_2^- \qquad (3)$$

As may be seen in Figs. 2, 6, and 7, the G(-Dye) was independent of the presence of oxygen; it was not even affected by the addition of 2 mM acetone. Acetone effectively scavenges hydrated electrons:[4,5]

$$e_{aq}^- + (CH_3)_2CO \longrightarrow (CH_3)_2CO^- \qquad (4)$$

and the rate of the reaction of acetone with the OH radical is slow.[6] This indicates that hydrated electrons do not contribute to the decoloration reaction. On the other hand, the G(-Dye) decreased markedly in the nitrogen- and oxygen-saturated solutions upon the addition of CNS^-, which is an efficient scavenger of OH radicals:[7]

$$OH + CNS^- \longrightarrow OH^- + CNS\cdot \qquad (5)$$

It is concluded from these findings that the decoloration of Acid Red 265 aqueous solutions is attributable to the attack of OH radicals formed from the radiolysis of water, and the species formed from water other than the OH radical contribute little to the decoloration reaction.

The G(-Dye) equals 1.00 ± 0.04 for the neutral aqueous solution. The primary yield of the OH radical, G(OH), formed from the radiolysis of water is 2.74 for neutral water.[8] This fact indicates that more than a half of the primary OH radicals are consumed by reactions other than the decoloration reaction.

On the basis of the results described above, the radiation-induced decoloration reaction of Acid Red 265 in aqueous solutions may be represented as follows:

$$A + OH \xrightarrow{k_6} AOH \text{ (decolored product)} \qquad (6)$$

$$A + OH \longrightarrow AOH' \text{ (colored product)} \qquad (7)$$

where A is Acid Red 265. The dye molecule has three kinds of sites for Reactions 6 and 7: (a) the azo group, (b) aromatic rings connecting directly to the azo group, (c) the benzene ring, not conjugated to the azo group. The attack of the OH radical on Site c would be independent of the decoloration reaction and would cause little change in the absorption spectra. This is represented as Reaction 7.

In Fig. 3, the absorption bands near 310 and 542 nm are attributable to the azo group and its auxochromic effect.[9,10] The absorption band near 230 nm is attributable to substituted aromatic rings.[9,10] The optical density at 230 nm does not decrease with the dose so much as do those at 310 and 542 nm, and the isosbestic points at 224 and 263 nm appear below 6.4×10^4 rad (Curve 4). This suggests that the decoloration reaction is not necessarily accompanied by the destruction of substituted aromatic rings.

Azo group (Site a) is stabilized by hydrogen bonding with an adjacent OH group in a naphthalene ring.[11] Furthermore, the masking of the azo group can be expected because of the steric effect of the adjacent SO_3Na and CH_3 groups. Therefore, the direct attack on Site a would be minor. On the other hand, the attack of the OH radical on Site b clearly makes the dye decolor. This attack is, then, the main process for Reaction 6, as will be described later. Since the skeleton of the dye molecule is not necessarily destroyed by this reaction, the decrease in the optical density at 230 nm is small, as may be seen in Fig. 3.

When the attack of the OH radical on Site a occurs, this reaction may follow to scissor the C–N–N–C bridge. As aromatic rings after this scission may give a spectrum near 230 nm similar to that of the attack on Site b, the two attacks can not be distinguished by means of these spectra.

Nitrogen-saturated Solutions Containing Alcohols. Alcohols are also efficient scavengers of OH radicals.[12,13]

$$RCH_2OH + OH \xrightarrow{k_8} RCHOH + H_2O \qquad (8)$$

However, the addition of alcohols makes the G(-Dye) increase in the nitrogen-saturated solutions. This means that alcohol radicals ($R\dot{C}HOH$) contribute to the decoloration reaction in the nitrogen-saturated solutions, while some of alcohol radicals as well as OH radicals may be consumed by a reaction other than the decoloration reaction, like Reaction 7.

$$A + RCHOH \longrightarrow ARCHOH \text{ (decolored product)} \qquad (9)$$

$$A + RCHOH \longrightarrow ARCHOH' \text{ (colored product)} \qquad (10)$$

Ekstrom and Garnett have reported that, in the radiolysis of air-free binary mixture, that is, benzene–methyl alcohol[14] and polycyclic aromatic compounds–methyl alcohol,[15] $\cdot CH_2OH$ radicals add to benzene and the polycyclic aromatic compound. This supports the addition of alcohol radicals on aromatic rings (Reactions 9 and 10).

As may be seen in Fig. 4, the G(-Dye) increases steeply up to 2 mM alcohols and decreases gradually with an increase in the concentration of alcohols above 2 mM. The maximum values of the G(-Dye) and the concentration of alcohols for them are shown in Table 1. The increase in the G(-Dye) upon the addition of alcohols was in the order of *n*-butyl alcohol>*n*-propyl alcohol> *iso*-butyl alcohol, *sec*-butyl alcohol>ethyl alcohol>*tert*-butyl alcohol>methyl alcohol. The G(-Dye) increased up to 1.83 upon the addition of 2 mM *n*-butyl alcohol from 1.00 for the non-alcoholic aqueous solution. The order of the G(-Dye) in Table 1 almost corresponds 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.[6,7] The concentrations for the maximum G(-Dye) are high for methyl alcohol and *tert*-butyl alcohol, whose rate constants are low in comparison with others. The present findings indicate that the $R\dot{C}HOH$ radical destroys the dye chromophore more effectively than does the OH radical.

Table 1. G(-dye) for the aqueous solutions containing various additives

Additives	Additive concn. (mM)	G(-Dye)
a) Nitrogen-saturated solutions.		
None	0	1.00
Methyl alcohol	6	1.34
Ethyl alcohol	2	1.47
n-Propyl alcohol	2	1.75
n-Butyl alcohol	2	1.83
iso-Butyl alcohol	2	1.64
sec-Butyl alcohol	2	1.64
tert-Butyl alcohol	4	1.37
Glucose	2	1.23
Phenol	2	0.71
Acetone	2	1.00
CNS^-	1	0.22
b) Oxygen-saturated solutions.		
None	0	1.00
Methyl alcohol	2	0.42
Ethyl alcohol	2	0.27
n-Propyl alcohol	2	0.25
n-Butyl alcohol	2	0.20
iso-Butyl alcohol	2	0.22
sec-Butyl alcohol	2	0.23
tert-Butyl alcohol	2	0.56
Glucose	2	0.31
Phenol	2	0.08
Acetone	2	0.98
CNS^-	1	0.22
c) Nitrous oxide-saturated solutions.		
None	0	1.46
n-Butyl alcohol	2	2.56

Table 2. Rate constants for reactions 6 and 8

Additives	k_6[a) ($M^{-1}s^{-1}$)	k_8[b) ($M^{-1}s^{-1}$)
Methyl alcohol	8.1×10^9	4.8×10^8
Ethyl alcohol	8.1×10^9	1.1×10^9
n-Propyl alcohol	1.03×10^{10}	1.5×10^9
n-Butyl alcohol	9.9×10^9	2.2×10^9
iso-Butyl alcohol	1.03×10^{10}	2.0×10^9
sec-Butyl alcohol	1.05×10^{10}	1.9×10^9
tert-Butyl alcohol	7.9×10^9	2.5×10^8
Glucose	8.7×10^9	1.0×10^9
Phenol[c)	7.2×10^9	4.2×10^9
	1.81×10^{10}	1.06×10^{10}
CNS^-	1.02×10^{10}	6.6×10^9

a) Initial pH 6.4. b) Rate constants for reaction of OH radical with additives from references 6) and 7).
c) See a text for the values of phenol.

The small decrease in the G(-Dye) at 10 mM alcohol in Fig. 4 may be explained in terms of the following spur effect. Since alcohol molecules exist inside the spur of gamma rays at such a high concentration, they react with a fraction of the OH radical larger than that predicted from the ratio of the concentration of alcohol to that of azo dye. The local concentration of the alcohol radicals produced is high in the spur or in the neighborhood of the spur, and the dye concentration is low. Therefore, some of the alcohol radicals are consumed through the following process,[16] that is, disproportionation or dimerization in advance of Reaction 9:

$$\begin{aligned} 2\mathrm{RCHOH} &\longrightarrow \mathrm{RCHO} + \mathrm{RCH_2OH} \qquad &(11\mathrm{a})\\ &\searrow (\mathrm{RCHOH})_2 \qquad &(11\mathrm{b})\end{aligned}$$

According to Taub and Dorfman, the rate of the bimolecular reaction of two α-ethyl alcohol radicals in water is very fast and the absolute rate constant is $1.1 \pm 0.3 \times 10^9\ \mathrm{M^{-1}s^{-1}}$.[17]

Oxygen-saturated Solutions Containing Alcohols. In the oxygen-saturated solutions, the alcohol radicals ($\mathrm{R\dot{C}HOH}$) react rapidly with oxygen, leading to the formation of peroxyradicals:

$$\mathrm{R\dot{C}HOH} + \mathrm{O_2} \longrightarrow \mathrm{RC(O_2\cdot)HOH} \qquad (12)$$

As may be seen in Table 1, the G(-Dye) for the oxygen-saturated solutions decrease upon the addition of alcohols. This means that the peroxyradicals from Reaction 12 do not react with the dye. These peroxyradicals are easily converted to aldehydes (or ketones), glycols, and peroxide.[18,19]

The decrease in the G(-Dye) upon the addition of 2 mM alcohols for the oxygen-saturated solutions, as is shown in Table 1, was in the order of *n*-butyl alcohol> *iso*-butyl alcohol>*sec*-butyl alcohol>*n*-propyl alcohol> ethyl alcohol>methyl alcohol>*tert*-butyl alcohol. The order of the decrease in the G(-Dye) corresponds exactly to that of the rate constants for the reaction of alcohols with OH radicals in Table 2, because the role of alcohols in the above reaction scheme is simpler in the oxygen-saturated solutions than in the nitrogen-saturated solutions.

N_2O-saturated Solutions. As may be seen in Table 1, the $G(\text{-Dye})_{\mathrm{N_2O}}$ for the nitrous oxide-saturated solution is 1.46; it increases to 2.56 upon the addition of 2 mM *n*-butyl alcohol. These values are remarkably larger than those for the nitrogen-saturated solutions. It is well known that nitrous oxide reacts rapidly with hydrated electrons, produced in an aqueous solution by ionizing radiations, thus leading to the formation of the OH radical:[20]

$$e_{\mathrm{aq}}^- + \mathrm{N_2O} \longrightarrow \mathrm{OH} + \mathrm{OH^-} + \mathrm{N_2} \qquad (13)$$

Therefore, such a large G(-Dye) is attributable to an increase in the OH radical through Reaction 13 in addition to the primary radical.

Since the G(-Dye) for the nitrogen- and oxygen-saturated solutions equals 1.0 for $G(\mathrm{OH}) = 2.7$, the $G(\text{-Dye})_{\mathrm{N_2O}}$ for the nitrous oxide-saturated solutions should be at least 2.0 for $G(\mathrm{OH})_{\mathrm{N_2O}} = G(\mathrm{OH}) + G(e_{\mathrm{aq}}^-) = 5.6$, according to the scheme proposed above. The observed value of the $G(\text{-Dye})_{\mathrm{N_2O}}$ indicates only a half of the expected increase, suggesting that OH radicals are consumed through another path, such as their recombination because of the high concentration.

Effects of Glucose and Phenol. The effect of glucose on the G(-Dye) is similar to that of alcohols in Table 1. The order of the decrease in the G(-Dye) for the oxygen-saturated solutions containing glucose in Table 1 corresponds exactly to that of the rate constant for the reactions of glucose with the OH radical shown in Table 2. However, in the nitrogen-saturated solution, glucose is less effective than methyl alcohol, even though the rate constant for glucose is larger than that for methyl alcohol (see Table 2). This may be due to the dependence of the rate constant of Reaction 9 on the structure of R- that is, a steric effect.

The effect of phenol on the G(-Dye) for the oxygen-saturated solution in Table 1 can be explained on the basis of the above reaction scheme; that is, phenol gives the smallest G(-Dye) in Table 1 and has the largest rate constants in Table 2. The G(-Dye) for the nitrogen-saturated solution also decreases upon the addition of phenol. This suggests that a $\mathrm{C_6H_5(OH)_2\cdot}$ radical formed by the addition reaction of the OH radical to phenol hardly contributes to the decoloration reaction. According to Land and Ebert,[21] the $\mathrm{C_6H_5(OH)_2\cdot}$radical subsequently undergoes either the unimolecular elimination of water to form a more resonance-stabilized phenoxy radical($\mathrm{C_6H_5O\cdot}$), or bimolecular radical-radical reactions.

Rate Constant for Reaction 6. The rate constant for Reaction 6 can be determined by using a competition reaction with additives. If G_r is the yield of the OH radicals consumed by Reactions 6 and 8, then:

$$\frac{1}{G(\text{-Dye})} = \frac{1}{G_r}\left(1 + \frac{k_8[\mathrm{RCH_2OH}]}{k_6[\mathrm{A}]}\right) \qquad (14)$$

where [A] and [$\mathrm{RCH_2OH}$] are initial concentrations of Acid Red 265 and additives respectively. Since Reaction 9 is also attributable to the decoloration in the nitrogen-saturated solutions, the experiment of the competition reaction was carried out in the oxygen-saturated solution. The plots of $1/G$(-Dye) are linear against the additive concentration, in good agreement with Eq. 14. From Eq. 14, the slope of the curve gives the k_8/k_6 ratio and the intercept gives the G_r value by means of the least-squares method. The k_6 values listed in Table 2 were obtained from the observed k_8/k_6 ratio by using the corresponding k_8 values in Table 2. These k_6 values are in good agreement with each other. The average k_6 value is $9.3 \pm 1.4 \times 10^9\ \mathrm{M^{-1}s^{-1}}$. This value is near to the rate constants of the reactions of the OH radical with benzene ($3.0 \times 10^9\ \mathrm{M^{-1}s^{-1}}$), toluene ($3.0 \times 10^9 \mathrm{M^{-1}s^{-1}}$), and phenol ($4.2 \times 10^9$ and $1.06 \times 10^{10}\ \mathrm{M^{-1}s^{-1}}$).[6] This fact supports the idea that the decoloration reaction is mainly attributable to the addition of the OH radical to aromatic rings adjacent to chromophore. The rate constants for the reactions of various dyes with the OH radical reported by some investigators are also of an order of about 10^9—$10^{10}\ \mathrm{M^{-1}s^{-1}}$.[1,22]

Since the k_8 values for phenol in the reference are scattered, the k_6 value for phenol in Table 2 is calculated by using the two k_8 values, excluding the above average value.

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