The Effects of Halide Ions on the Radiation-induced Decoloration of Azo and Anthraquinone Dyes in N_2O-saturated Aqueous Solutions

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The radiation-induced decoloration of azo and anthraquinone dyes was studied in N_2O-saturated aqueous solutions containing halide ions. In the N_2O-saturated solutions, the decoloration yield, $G(-\text{Dye})$, increased markedly upon the addition of Br^- and I^-, which are efficient scavengers of the OH radical. In the nitrogen-saturated solutions, however, the $G(-\text{Dye})$ decreased upon the addition of Br^- and I^-. Such an increase in the $G(-\text{Dye})$ upon the addition of Br^- and I^- in the N_2O-saturated solutions is mainly attributable to the attacks of the halide radical anions, Br_2^- and I_2^-, on the ring structure of the dyes. On the other hand, the $G(-\text{Dye})$ was not changed upon the addition of Cl^- in the N_2O-saturated solution. This may be attributable to the very slow rate of the formation of Cl_2^- in a neutral solution.

In a preceding paper,[1] we studied the effect of NCS^- on the radiation-induced decoloration of Acid Red 265 (azo dye) and Acid Blue 40 (anthraquinone dye) in N_2O-saturated aqueous solutions and found that the $G(-\text{Dye})$ increased markedly upon the addition of NCS^-, which is an efficient scavenger of the OH radical; we concluded that such an increase in the $G(-\text{Dye})$ was mainly attributable to the attack of the radical anion $(NCS)_2^-$, which is formed through Reactions 1 and 2, on the ring structure of the dyes;

$$NCS^- + OH \longrightarrow NCS + OH^-, \tag{1}$$

$$NCS + NCS^- \rightleftarrows (NCS)_2^-. \tag{2}$$

It is known that, in analogy with NCS^-,[2,3] in pulse-irradiated N_2O-saturated solutions halide ions, X^-, react rapidly and quantitatively with the OH radicals to form halide radicals, following the formation of halide radical anions, X_2^-:[3-7]

$$X^- + OH \xrightarrow{k_3} X + OH^-, \tag{3}$$

$$X + X^- \rightleftarrows X_2^-. \tag{4}$$

An effect similar to that of NCS^- on the radiation-induced decoloration of dyes may, therefore, be expected in the N_2O-saturated solutions containing halide ions. In this paper, the effects of Cl^-, Br^-, and I^- on the radiation-induced decoloration of azo and anthraquinone dyes were investigated in order to demonstrate the reaction scheme of inorganic radical anions with the dyes more clearly.

Experimental

The experimental procedures were the same as in the preceding work.[1,8,9] The dye solutions were prepared by dissolving recrystallized Acid Red 265 (C. I. 18129)[8] or Acid Blue 40 (C. I. 62125)[9] in triply distilled water. The dye solutions were bubbled with N_2O for 20 min prior to irradiation and were then irradiated with cobalt-60 gamma rays at room temperature. In some experiments, nitrogen was bubbled in for 30 min prior to irradiation.

The absorption spectra were measured with a Shimadzu UV-200 spectrophotometer. The decoloration yield, $G(-\text{Dye})$, was determined by measuring the optical density at 542 nm for Acid Red 265 and at 610 nm for Acid Blue 40.

Results and Discussion

N_2O-saturated Acid Blue 40 Solutions. The $G(-\text{Dye})$ for the N_2O-saturated 0.1 mM Acid Blue 40 solutions containing halide ions (Cl^-, Br^-, and I^-) (initial pH 6.1—6.8) is shown as a function of the halide ion concentrations in Fig. 1. In the solutions containing Br^- and I^-, the $G(-\text{Dye})$ increased steeply with an increase in the Br^- and I^- concentrations up to about 4 mM Br^- and 0.4 mM I^-; then it increased gradually above about 4 mM Br^- and 0.4 mM I^-. The $G(-\text{Dye})$ increased up to 2.07 (at 10 mM Br^-) and 1.84 (at 1 mM I^-) upon the addition of halide ions from 0.51 for the N_2O-saturated solution without halide ions. In the N_2O-saturated solution containing Cl^-, however, the $G(-\text{Dye})$ was almost equal to that (0.51) for the N_2O-saturated solution without halide ions, even upon the addition of 20 mM Cl^-. It is noteworthy that the tendency of the $G(-\text{Dye})$—Br^- and I^--concentration curves is similar to that of the $G(-\text{Dye})$—NCS^--concentration curve, shown in Fig. 2 in our preceding paper.[1] The increase in the G-

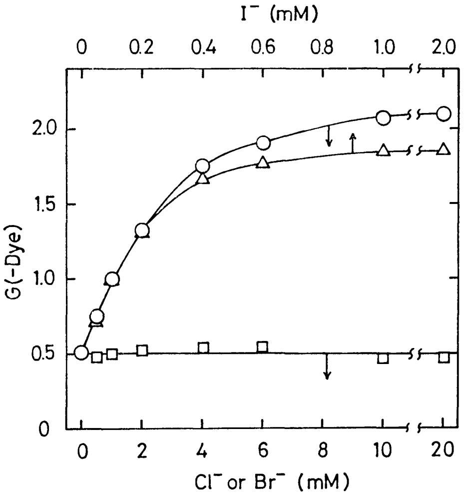

Fig. 1. Effect of halide ions on $G(-\text{Dye})$ in the N_2O-saturated Acid Blue 40 solutions.
Dye concentration: 0.1 mM. Dose: 1.8×10^4 rad.
Cl^- (□), Br^- (○), and I^- (△).

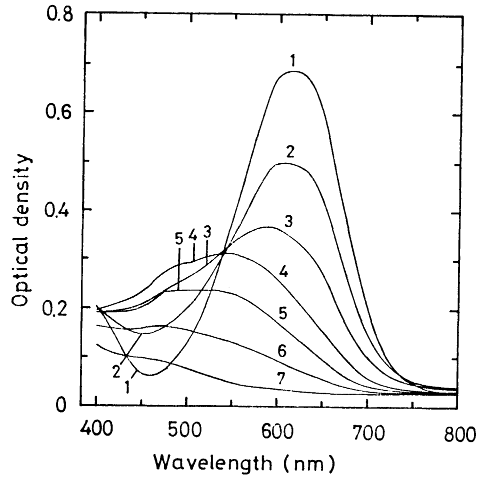

Fig. 2. Absorption spectra of unirradiated and irradiated N_2O-saturated Acid Blue 40 solutions containing 10 mM Br^-.
Dye concentration: 0.1 mM. Doses (rad): 0 (Curve 1), 1.8×10^4 (Curve 2), 3.7×10^4 (Curve 3), 5.5×10^4 (Curve 4), 1.1×10^5 (Curve 5), 2.2×10^5 (Curve 6), and 3.9×10^5 (Curve 7).

(—Dye) upon the addition of halide ions was in the order of $I^->Br^->Cl^-$ at the same concentrations. This order almost corresponds to the order of the rate constants for the reactions of halide ions with OH radicals in neutral solutions[10,11] (the rate constant for Cl^- was referred to the value at pH 9). The absorption spectrum of an unirradiated N_2O-saturated solution did not change upon the addition of halide ions. Also, scarcely no new absorption bands appeared in the wavelength range of 400 to 800 nm upon the irradiation of the N_2O-saturated Cl^-, Br^-, and I^- solutions without the dye. On the other hand, the G(—Dye) in the nitrogen-saturated solutions decreased to 0.10 (at 10 mM Br^-) and 0.07 (at 1 mM I^-) upon the addition of halide ions from 0.18 for the nitrogen-saturated solution without halide ions. In the nitrogen-saturated solution containing Cl^-, the G(—Dye) was almost equal to that (0.18) for the nitrogen-saturated solution without halide ions, even upon the addition of 20 mM Cl^-.

The radiation-induced decoloration scheme of Acid Blue 40 in the nitrogen-saturated solution has been presented in a preceding paper[9] as follows:

$$\mathrm{AB + OH \xrightarrow{k_5} ABOH \longrightarrow decolored\ product,} \quad (5)$$

$$\mathrm{AB + OH \longrightarrow ABOH' \longrightarrow colored\ product,} \quad (6)$$

$$\mathrm{AB} + e_{aq}^- \longrightarrow \mathrm{AB_{red}\ (decolored\ product),} \quad (7)$$

$$\mathrm{AB} + e_{aq}^- \longrightarrow \mathrm{AB'_{red}\ (colored\ product),} \quad (8)$$

where AB, ABOH, and AB_{red} are Acid Blue 40, its OH adduct, and its reduction product by the attack of the hydrated electron respectively. In the N_2O-saturated solution, however, the hydrated electrons are converted into the OH radicals by Reaction 9:[12]

$$\mathrm{N_2O} + e_{aq}^- \longrightarrow \mathrm{OH + OH^- + N_2}. \quad (9)$$

In such systems, the rate constants of the hydrated electron with N_2O and Acid Blue 40 are $8.7\times10^9\ M^{-1}\ s^{-1}$ at pH 7[13] and $1.5\times10^{10}\ M^{-1}\ s^{-1}$ at pH 5.1—6.3[9] respectively. In the N_2O-saturated 0.1 mM Acid Blue 40 solution, since the N_2O concentration (about 3×10^{-2} M) is about 300 times larger than the dye concentration, a large portion of the hydrated electrons are converted into the OH radicals, because $(8.7\times10^9\ M^{-1}\ s^{-1})\times(3\times10^{-2}\ M)\gg(1.5\times10^{10}\ M^{-1}\ s^{-1})\times(1\times10^{-4}\ M)$. In the N_2O-saturated solution, therefore, Acid Blue 40 is decolored only by Reaction 5.

In the N_2O-saturated 0.1 mM Acid Blue 40 solutions containing Br^- and I^-, most of the OH radicals react rapidly with Br^- and I^- to form the Br and I radicals above about 2 mM Br^- and 0.2 mM I^-, because k_3 ($1.2\times10^9\ M^{-1}\ s^{-1}$ at pH 7 for Br^-[10])$\times[Br^-]$ and k_3 ($1.02\times10^{10}\ M^{-1}\ s^{-1}$ at neutral for I^-[10])$\times[I^-]$ are larger than k_5 ($6.6\times10^9\ M^{-1}\ s^{-1}$ at pH 5.1—6.3[9])$\times$[Dye], following the formation of the halide radical anions, Br_2^- and I_2^-, by Reactions 3 and 4.[3,5-7] In a neutral solution containing Cl^-, however, the rate of the formation of Cl_2^- by Reactions 3 and 4 is very slow.[4,10,14]

In our preceding paper,[1] we concluded that the increase in the G(—Dye) upon the addition of NCS^- in the N_2O-saturated solution was mainly attributable to the attack of the radical anion $(NCS)_2^-$ formed through Reactions 1 and 2 on the ring structure of the dye as follows:

$$\mathrm{AB + (NCS)_2^- \longrightarrow (AB(NCS)_2)^- \longrightarrow decolored\ product,} \quad (10)$$

$$\mathrm{AB + (NCS)_2^- \longrightarrow (AB(NCS)_2)^{-\prime} \longrightarrow colored\ product.} \quad (11)$$

According to the earlier studies of the radiation-induced inactivation of lysozyme in the N_2O-saturated solutions containing halide ions,[14,15] the inactivation was caused by a reaction between lysozyme and the halide radical anion:

$$\mathrm{lysozyme + X_2^- \longrightarrow inactive\ product.} \quad (12)$$

Adams *et al.*[14,15] suggested the possibility that the site of the X_2^- attack is the ring structure of tryptophan in lysozyme; that is, the reaction with X_2^- is a direct addition to the ring structure of tryptophan (T):

$$\mathrm{T + X_2^- \longrightarrow (TX_2)^-}. \quad (13)$$

Consequently, it may be concluded from these facts that the increase in the G(—Dye) upon the addition of Br^- and I^- in the N_2O-saturated solutions is mainly attributable to the attacks of the halide radical anions, Br_2^- and I_2^-, formed through Reactions 3 and 4 on the Acid Blue 40 molecule as follows:

$$\mathrm{AB + Br_2^-\ (or\ I_2^-) \longrightarrow (ABBr_2)^-\ (or\ (ABI_2)^-) \longrightarrow decolored\ product,} \quad (14)$$

$$\mathrm{AB + Br_2^-\ (or\ I_2^-) \longrightarrow (ABBr_2)^{-\prime}\ (or\ (ABI_2)^{-\prime}) \longrightarrow colored\ product.} \quad (15)$$

The Acid Blue 40 molecule has two kinds of reaction sites for Reactions 14 and 15: (a) the anthraquinone ring, and (b) the substituted benzene ring, not conjugated to the carbonyl group in the anthraquinone ring. The attack of the halide radical anions, Br_2^- and I_2^-, on Site b is independent of the decoloration reaction. The increase in the $G(-\text{Dye})$ in Fig. 1 indicates that the halide radical anions, Br_2^- and I_2^-, destroy the dye chromophore more efficiently than does the OH radical. As has already been described, the $G(-\text{Dye})$ was not changed upon the addition of Cl^- in the N_2O-saturated solution. This may be attributable to the very slow rate of the formation of Cl_2^- in a neutral solution.[4,10,14]

The absorption spectra for the unirradiated and irradiated N_2O-saturated solutions containing 10 mM Br^- and 1 mM I^- are shown in Figs. 2 and 3 respectively. The absorption band at 610 nm in both the solutions disappear with an increase in the dose; at the same time, a new absorption band near 460—490 nm seems to appear slightly at a higher dose (Curves 4—7 in Figs. 2 and 3). This new absorption band scarcely appeared at all in the N_2O-saturated solutions without halide ions, however, as may be seen in Fig. 4 in the preceding paper.[1] The absorption band near 460—490 nm coincides approximately with that for the reduction products of Acid Blue 40 formed by the attacks of the hydrated electron and the alcohol radical on the carbonyl group in the anthraquinone ring.[9] The new absorption band which appeared in the solutions containing Br^- and I^- was also similar to that which appeared in the solution containing NCS^-, as may be seen in Fig. 3 in our preceding paper.[1] Consequently, it may be assumed that a part of the Acid Blue 40 is reduced by the attack of the halide radical anions, Br_2^- and I_2^-, on the carbonyl group in the anthraquinone ring, thus forming the reduction product as follows:

$$AB + Br_2^- \text{ (or } I_2^-) \longrightarrow AB_{red} \text{ (decolored product at 610 nm)}. \qquad (16)$$

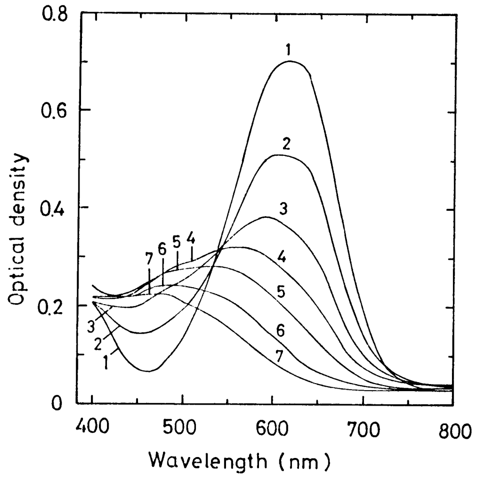

Fig. 3. Absorption spectra of unirradiated and irradiated N_2O-saturated Acid Blue 40 solutions containing 1 mM I^-.
Dye concentration: 0.1 mM. The number of the curves is the same with Fig. 2.

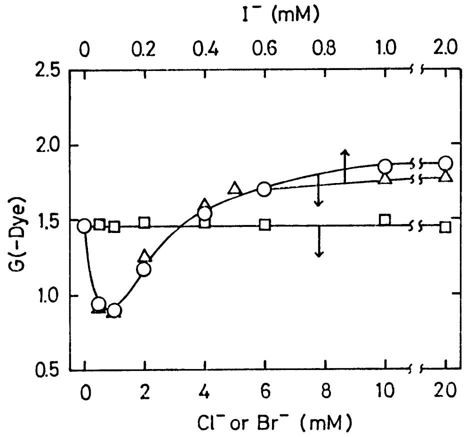

Fig. 4. Effect of halide ions on $G(-\text{Dye})$ in the N_2O-saturated Acid Red 265 solutions.
Dye concentration: 0.1 mM. Dose: 1.8×10^4 rad. Cl^- (□), Br^- (○), and I^- (△).

On the other hand, the $G(-\text{Dye})$ for the nitrogen-saturated solutions decreased upon the addition of Br^- and I^-, as has already been described, in contrast to that for the N_2O-saturated solutions. This phenomenon was similar to that for the nitrogen-saturated solution containing NCS^-.[1] Reactions 17 and 18 may be considered as the reactions responsible for the decrease in the $G(-\text{Dye})$ upon the addition of Br^- and I^- in the nitrogen-saturated solution,[5,13] that is, the reactions of the hydrated electron with the halide radical anions, X_2^-, and the halide radicals, X, decreasing the X_2^- concentration:

$$X_2^- + e_{aq}^- \longrightarrow 2X^-, \qquad (17)$$

$$X + e_{aq}^- \longrightarrow X^-. \qquad (18)$$

Under the conditions of this study, the contribution of Reaction 17 to the decrease in the $G(-\text{Dye})$ is very large and that of Reaction 18 is very small, because the X and hydrated electron concentrations are negligibly small compared with the X^- concentration and the rate constants of the reactions of X with X^- [3,5] and of the hydrated electron with X_2^- [13] are very large.

N_2O-saturated Acid Red 265 Solutions. The $G(-\text{Dye})$ for the N_2O-saturated 0.1 mM Acid Red 265 solutions containing halide ions (Cl^-, Br^-, and I^-) (initial pH 6.4—6.9) is shown as a function of the halide ion concentrations in Fig. 4. In the solutions containing Br^- and I^-, the $G(-\text{Dye})$ decreased at first to 0.90 (at 1 mM Br^-) and 0.88 (at 0.1 mM I^-) upon the addition of halide ions, and then it increased with an increase in the Br^- and I^- concentrations up to about 10 mM Br^- and 1 mM I^-, in contrast to the results for the Acid Blue 40 solution in Fig. 1. The $G(-\text{Dye})$ increased up to 1.85 (at 10 mM Br^-) and 1.76 (at 1 mM I^-) upon the addition of halide ions from 1.46 for the N_2O-saturated solution without halide ions. In the N_2O-saturated solution containing Cl^-, however, the $G(-\text{Dye})$ was almost equal to that (1.46) for the N_2O-saturated solution without halide ions, even upon the addition of 20 mM Cl^-, analogous with the results for the Acid Blue 40 solution in Fig. 1. It is noteworthy that the tendency of the $G(-\text{Dye})$ —Br^- and I^- concentrations curves is similar to that of the $G(-\text{Dye})$—NCS^- concentration curve, shown in Fig. 5 in our preceding paper[1]. The absorption spectrum of an unirradiated N_2O-saturated solution was not changed upon the addition of halide ions. On the other hand,

the $G(-\text{Dye})$ in the nitrogen-saturated solution decreased to 0.25 (at 10 mM Br^-) and 0.27 (at 1 mM I^-) upon the addition of halide ions from 1.00 for the nitrogen-saturated solution without halide ions. In the nitrogen-saturated solution containing Cl^-, the $G(-\text{Dye})$ was almost equal to that (1.00) for the nitrogen-saturated solution without halide ions, even upon the addition of 20 mM Cl^-.

The radiation-induced decoloration scheme of Acid Red 265 in the nitrogen-saturated solution has been presented in a preceding paper[8] as follows:

$$\text{AR} + \text{OH} \longrightarrow \text{AROH} \longrightarrow \text{decolored product}, \qquad (19)$$

$$\text{AR} + \text{OH} \longrightarrow \text{AROH}' \longrightarrow \text{colored product}, \qquad (20)$$

where AR and AROH are Acid Red 265 and its OH adduct respectively.

In the N_2O-saturated Acid Red 265 solutions containing Br^- and I^-, the increase in the $G(-\text{Dye})$ is also mainly attributable to the attack of the halide radical anions, Br_2^- and I_2^-, formed through Reactions 3 and 4 on the Acid Red 265 molecule as follows:

$$\text{AR} + Br_2^- \text{ (or } I_2^-) \longrightarrow (\text{ARBr}_2)^- \text{ (or } (\text{ARI}_2)^-) \longrightarrow \text{decolored product}, \qquad (21)$$

$$\text{AR} + Br_2^- \text{ (or } I_2^-) \longrightarrow (\text{ARBr}_2)^{-\prime} \text{ (or } (\text{ARI}_2)^{-\prime}) \longrightarrow \text{colored product}. \qquad (22)$$

The Acid Red 265 molecule has two kinds of reaction sites for Reactions 21 and 22: (a) the aromatic rings connected directly to the azo group, and (b) the substituted benzene ring, not conjugated to the azo group. The attack of the halide radical anions, Br_2^- and I_2^-, on Site b is independent of the decoloration reaction. It is difficult for the direct attack of the halide radical anions, Br_2^- and I_2^-, on the azo group to take place because the azo group is stabilized by the hydrogen bonding with an adjacent OH group in a naphthalene ring.[8] Furthermore, the masking of the azo group can be expected because of the steric effect of the adjacent SO_3Na and CH_3 groups.[8]

The decrease in the $G(-\text{Dye})$ upon the addition of Br^- (up to 1 mM) and I^- (up to 0.1 mM) in Fig. 4 may be explained as follows.[1] At low Br^- and I^- concentrations, the halide radicals formed by Reaction 3 react with Acid Red 265 rather than with the halide ions to form mainly the colored product as in Reaction 23:

$$\text{AR} + \text{X} \longrightarrow \text{ARX}' \longrightarrow \text{colored product}, \qquad (23)$$

thus decreasing the $G(-\text{Dye})$. As the Br^- and I^- concentrations increase, the halide radicals react with the halide ions rather than with Acid Red 265 to form the halide radical anions as in Reaction 4, thus increasing the $G(-\text{Dye})$. On the other hand, the decrease in the $G(-\text{Dye})$ upon the addition of Br^- and I^- was not observed in the N_2O-saturated Acid Blue 40 solution (Fig. 1). This may be attributable to the formation of both the decolored and colored products by the reaction of the halide radicals with Acid Blue 40 as in Reactions 24 and 25:

$$\text{AB} + \text{X} \longrightarrow \text{ABX} \longrightarrow \text{decolored product}, \qquad (24)$$

$$\text{AB} + \text{X} \longrightarrow \text{ABX}' \longrightarrow \text{colored product}. \qquad (25)$$

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