The Effect of NCS^- 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 NCS^-. In the N_2O-saturated solutions, the decoloration yield, G(–Dye), increased markedly upon the addition of NCS^-, which is an efficient scavenger of the OH radical—that is, from 1.46 up to 2.10 for Acid Red 265 and from 0.51 up to 1.51 for Acid Blue 40 upon the addition of 1 mM NCS^-. In the nitrogen-saturated solutions, however, the G(–Dye) decreased upon the addition of NCS^-. It is concluded that the increase in the G(–Dye) upon the addition of NCS^- in the N_2O-saturated solutions is mainly attributable to the attack of the radical anion $(NCS)_2^-$ on the ring structure of the dyes. This radical anion is formed through the following path: $NCS^- + OH \rightarrow NCS + OH^-$ and $NCS + NCS^- \rightleftarrows (NCS)_2^-$. At low NCS^- concentrations, the G(–Dye) decreased for Acid Red 265 and increased for Acid Blue 40. This may be attributable to the larger reactivity of $(NCS)_2^-$ on Acid Blue 40 than on Acid Red 265.

As has been described in preceding papers,[1,2] the radiation-induced decoloration of Acid Red 265 (azo dye) in aqueous solutions is mainly attributable to the attack of the OH radicals on the aromatic rings connected directly to the azo group, while that of Acid Blue 40 (anthraquinone dye) is attributable to the attack of the hydrated electrons on the carbonyl group in the anthraquinone ring, in addition to the attack of the OH radicals on the anthraquinone ring. In both cases, the decoloration is promoted in the N_2O-saturated solutions; that is, this increase in the G(–Dye) is due to the conversion of the hydrated electrons into the OH radicals by means of the following reaction;[3)]

$$N_2O + e^-_{aq} \longrightarrow OH + OH^- + N_2. \qquad (1)$$

The yield of the OH radical in the N_2O-saturated aqueous solution ($G(OH)+G(e^-_{aq})=5.5$)[4)] becomes about twice as large as that in the nitrogen-saturated aqueous solution ($G(OH)=2.74$).[4)]

In such systems, the rate constants of the reactions of the hydrated electron with N_2O and Acid Blue 40 are $8.7\times10^9\ M^{-1}\,s^{-1}$ at pH 7[5)] and $1.5\times10^{10}\ M^{-1}\,s^{-1}$ at pH 6.3—5.1[2)] 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 OH radicals because $(8.7\times10^9\ M^{-1}\,s^{-1})\times(3\times10^{-2}\ M)\gg(1.5\times10^{10}\ M^{-1}\,s^{-1})\times(1\times10^{-4}\ M)$. Therefore, in the N_2O-saturated solution, the OH radical is considered to be the only active species. In the present study, the effect of NCS^-, which is an efficient scavenger of the OH radical, on the radiation-induced decoloration of azo and anthraquinone dyes was investigated in order to demonstrate the above scheme more clearly.

Experimental

The experimental procedures were the same as in the preceding works.[1,2)] The dye solutions were prepared by dissolving recrystallized Acid Red 265[1)] or Acid Blue 40[2)] in triply distilled water. The solutions were bubbled with N_2O for 20 min prior to irradiation and were then irradiated with cobalt-60 gamma rays at room temperature.

The absorption spectra were measured with a Shimadzu UV-200 spectrophotometer. The decoloration yield was determined by measuring the optical density at 542 nm for Acid Red 265 and at 610 nm for Acid Blue 40. The NCS^- concentration was determined by the iron-thiocyanate method.[6)]

Results and Discussion

N_2O-saturated NCS^- Solutions without Dye. In order to study the effect of NCS^- on the radiation-induced decoloration of the dyes in N_2O-saturated solutions, it is necessary first to elucidate the behavior of the consumption of NCS^- in a solution without the dye. Thus, the NCS^- concentration in N_2O- and nitrogen-saturated solutions without the dye was measured after irradiation.

The reduction of NCS^-, $G(-NCS^-)$, for the N_2O- and nitrogen-saturated solutions without the dye (initial pH 7.2) is shown as a function of the NCS^- concentration in Fig. 1. The $G(-NCS^-)$ for the N_2O-saturated solution increased steeply with an increase in the NCS^- concentration up to about 0.4 mM, and then it increased gradually above about 0.4 mM. The $G(-NCS^-)$ increased up to 1.72 from 0.96 in the NCS^- concentration

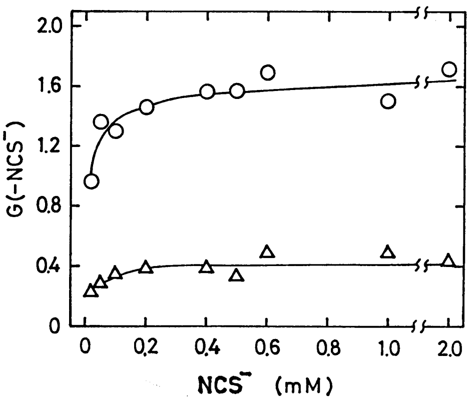

Fig. 1. $G(-NCS^-)$ as a function of NCS^- concentration in the N_2O- and nitrogen-saturated NCS^- solutions without the dye.
Dose: 1.8×10^4 rad. N_2O saturation (○) and N_2 saturation (△).

range from 0.02 to 2 mM. On the other hand, the G(–NCS$^-$) for the nitrogen-saturated solution increased with an increase in the NCS$^-$ concentration up to about 0.2 mM, and then it was kept nearly constant above about 0.2 mM. The G(–NCS$^-$) increased up to 0.43 from 0.22 in the NCS$^-$ concentration range from 0.02 to 2 mM. The ratio of $G(\text{–NCS}^-)_{N_2O}/G(\text{–NCS}^-)_{N_2}$ is about 4±1 in this NCS$^-$ concentration range.

In the irradiated N$_2$O-saturated solution, the hydrated electrons are converted into the OH radicals as Reaction 1. The OH radical reacts rapidly with NCS$^-$ to form the NCS radical, following the formation of the radical anion $(NCS)_2^-$;[7,8]

$$NCS^- + OH \xrightarrow{k_2} NCS + OH^-, \tag{2}$$

$$NCS + NCS^- \xrightleftharpoons[k_{3b}]{k_{3a}} (NCS)_2^-. \tag{3}$$

Then;[7,9]

$$2(NCS)_2^- \longrightarrow (NCS)_2 + 2NCS^-, \tag{4}$$

$$NCS + NCS \longrightarrow (NCS)_2. \tag{5}$$

Baxendale *et al.* determined the value of k_2 (2.8×10^{10} M^{-1} s^{-1}) from a kinetic study of the equilibrium of Reaction 3 at pH 7 by pulse radiolysis ($k_{3a}=7.0\times10^9$ M^{-1} s^{-1} and $k_{3b}=3.4\times10^4$ s^{-1}).[7] On the other hand, Willson *et al.* concluded that the most reasonable value of k_2 was 1.03×10^{10} M^{-1} s^{-1}, since the above value was significantly higher than the values obtained by other methods.[10]

Since the ratio of $G(OH)_{N_2O}/G(OH)_{N_2}$ equals about 2, as has been described already, the ratio of $G(\text{–NCS}^-)_{N_2O}/G(\text{–NCS}^-)_{N_2}$ should equal about 2. However, the ratio of $G(\text{–NCS}^-)_{N_2O}/G(\text{–NCS}^-)_{N_2}$ (about 4±1) obtained from Fig. 1 is larger than the above ratio. This may be mainly attributable to the consumption of the NCS radical by the hydrated electron in the nitrogen-saturated solution as Reaction 6:[9]

$$NCS + e_{aq}^- \longrightarrow NCS^- \tag{6}$$

N$_2$O-saturated Acid Blue 40 Solutions. The G(–Dye) for the N$_2$O-saturated 0.1 mM Acid Blue 40 solutions containing NCS$^-$ (initial pH 6.3) is shown as a function of the NCS$^-$ concentration in Fig. 2. The G(–Dye) increased steeply with an increase in the NCS$^-$ concentration up to about 0.4 mM, and then it increased gradually above about 0.4 mM. The G(–Dye) increased up to 1.51 upon the addition of 1 mM NCS$^-$ from 0.51 for the N$_2$O-saturated solution without NCS$^-$. It is noteworthy that the tendency of the G(–Dye)-NCS$^-$ concentration curve is similar to that of the G(–NCS$^-$)-NCS$^-$ concentration curve for the N$_2$O-saturated NCS$^-$ solution without the dye in Fig. 1. In the case of an unirradiated N$_2$O-saturated solution, the absorption spectrum was not changed upon the addition of NCS$^-$. On the other hand, in a nitrogen-saturated solution, the G(–Dye) decreased to 0.06 upon the addition of 1 mM NCS$^-$ from 0.18 for the solution without NCS$^-$.[2]

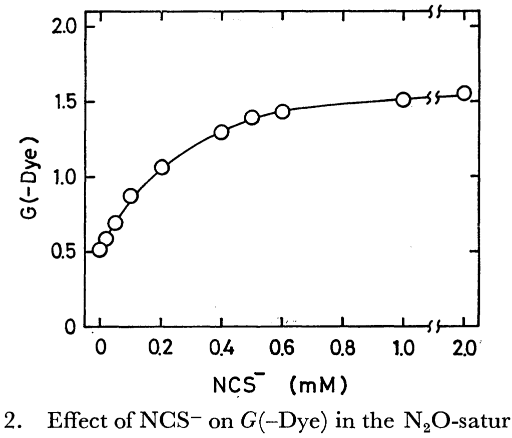

Fig. 2. Effect of NCS$^-$ on G(–Dye) in the N$_2$O-saturated Acid Blue 40 solutions.
Dye concentration: 0.1 mM. Dose: 1.8×10^4 rad.

The radiation-induced decoloration scheme of Acid Blue 40 in the nitrogen-saturated solution has been represented in a preceding paper[2] as follows:

$$AB + OH \xrightarrow{k_7} ABOH \text{ (decolored product)}, \tag{7}$$

$$AB + OH \longrightarrow ABOH' \text{ (colored product)}, \tag{8}$$

$$AB + e_{aq}^- \longrightarrow AB_{red} \text{ (decolored product)}, \tag{9}$$

$$AB + e_{aq}^- \longrightarrow AB_{red}' \text{ (colored product)}, \tag{10}$$

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$_2$O-saturated solution, however, since the hydrated electrons are converted into the OH radicals as Reaction 1, Acid Blue 40 is decolored only by Reaction 7.

According to the earlier studies of the radiation-induced inactivation of lysozyme in the N$_2$O-saturated solution containing NCS$^-$,[8,11] the inactivation was caused by a reaction between lysozyme and $(NCS)_2^-$:

$$\text{lysozyme} + (NCS)_2^- \longrightarrow \text{inactive product} \tag{11}$$

The site of the $(NCS)_2^-$ attack is the ring structure of tryptophan in lysozyme; that is, the reaction with $(NCS)_2^-$ is a direct addition to the ring structure of tryptophan (T);

$$T + (NCS)_2^- \longrightarrow (T(NCS)_2)^-. \tag{12}$$

In the Acid Blue 40 solution containing NCS$^-$, most of the OH radicals react rapidly with NCS$^-$ to form the NCS radical at NCS$^-$ concentrations above about 0.2 mM, because k_2 is larger than k_7 (6.6×10^9 M^{-1} s^{-1} at pH 6.3–5.1).[2] Therefore, it may be concluded from these facts that the increase in the G(–Dye) upon the addition of NCS$^-$ in the N$_2$O-saturated solution is mainly attributable to the attack of the radical anion $(NCS)_2^-$ formed through Reactions 2 and 3 on the Acid Blue 40 molecule as follows:

$$AB + (NCS)_2^- \longrightarrow (AB(NCS)_2)^- \text{ (decolored product)}, \tag{13}$$

$$AB + (NCS)_2^- \longrightarrow (AB(NCS)_2)^{-\prime} \text{ (colored product)}. \tag{14}$$

The Acid Blue 40 molecule has two kinds of reaction sites for Reactions 13 and 14; (a) the anthraquinone ring and (b) the substituted benzene ring, not conjugated to the carbonyl group in the anthraquinone ring. The attack of the radical anion $(NCS)_2^-$ on Site b is independent of the decoloration reaction. The increase in the G(–Dye) in Fig. 2 indicates that the radical anion

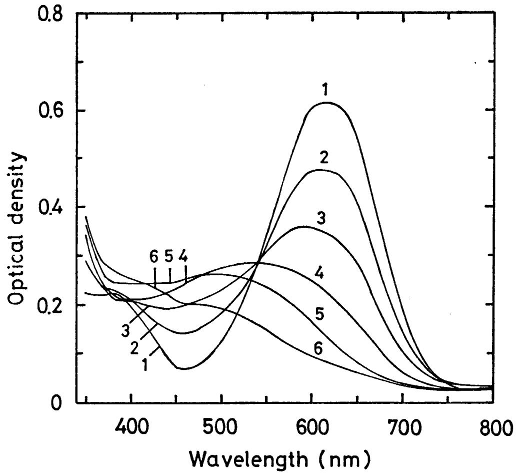

Fig. 3. Absorption spectra of unirradiated and irradiated N_2O-saturated Acid Blue 40 solutions containing 1 mM NCS^-.
Dye concentration: 0.1 mM. Doses (rad): 0 (Curve 1), 1.8×10^4 (Curve 2), 3.7×10^4 (Curve 3), 5.5×10^4 (Curve 4), 1.1×10^5 (Curve 5), and 3.9×10^5 (Curve 6).

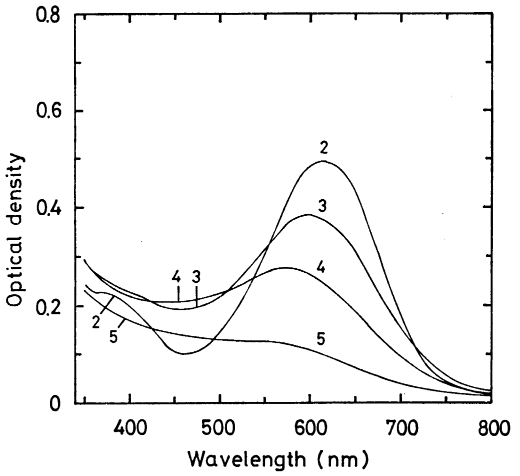

Fig. 4. Absorption spectra of irradiated N_2O-saturated Acid Blue 40 solutions without NCS^-.
Dye concentration: 0.1 mM. Doses (rad): 3.7×10^4 (Curve 2), 1.7×10^5 (Curve 3), 3.9×10^5 (Curve 4), and 5.5×10^5 (Curve 5).

$(NCS)_2^-$ destroys the dye chromophore more efficiently than the OH radical does.

The absorption spectra for the unirradiated and irradiated N_2O-saturated solution containing 1 mM NCS^- are shown in Fig. 3. The absorption band at 610 nm disappeared with an increase in the dose, and at the same time, the new absorption band near 460—490 nm seems to appear at a slightly higher dose (Curves 5 and 6 in Fig. 3). This new absorption band hardly appeared at all in the N_2O-saturated solution without NCS^-, as is shown in Fig. 4. 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.[2)] It is known that quinones are easily reduced by such reducing species as alcohol radicals.[12,13)] Therefore, it is assumed that a part of the Acid Blue 40 is reduced by the attack of the radical anion $(NCS)_2^-$ on the carbonyl group in the anthraquinone ring, thus forming the reduction product as follows:

$$AB + (NCS)_2^- \longrightarrow AB_{red}\ (\text{decolored product}) + (NCS)_2 \qquad (15)$$

On the other hand, the G(–Dye) for the nitrogen-saturated solution decreased upon the addition of NCS^-,[2)] in contrast to that for the N_2O-saturated solution. The decrease in the G(–Dye) upon the addition of NCS^- in the nitrogen-saturated solution may be mainly attributable to the consumption of the NCS radical by Reaction 6, without forming $(NCS)_2^-$.

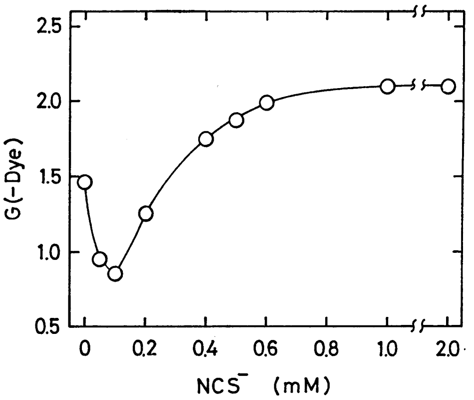

Fig. 5. Effect of NCS^- on G(–Dye) in the N_2O-saturated Acid Red 265 solutions.
Dye concentration: 0.1 mM. Dose: 1.8×10^4 rad.

N_2O-saturated Acid Red 265 Solutions. The G(–Dye) for the N_2O-saturated 0.1 mM Acid Red 265 solutions containing NCS^- (initial pH 6.4) is shown as a function of the NCS^- concentration in Fig. 5. The G(–Dye) decreased at first to 0.85 upon the addition of 0.1 mM NCS^-, and then it increased steeply with an increase in the NCS^- concentration up to about 0.6 mM NCS^-, in contrast to the result for the Acid Blue 40 solution in Fig. 2. The G(–Dye) increased up to 2.10 upon the addition of 1 mM NCS^- from 1.46 for the N_2O-saturated solution without NCS^-. In the case of the unirradiated N_2O-saturated solution, the absorption spectrum was also unchanged upon the addition of NCS^-. On the other hand, in the nitrogen-saturated solution the G(–Dye) decreased to 0.22 upon the addition of 1 mM NCS^- from 1.00 for the solution without NCS^-.[1)]

The radiation-induced decoloration scheme of Acid Red 265 in the nitrogen-saturated solution has been represented in a preceding paper[1)] as follows:

$$AR + OH \longrightarrow AROH\ (\text{decolored product}) \qquad (16)$$

$$AR + OH \longrightarrow AROH'\ (\text{colored product}) \qquad (17)$$

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

In the N_2O-saturated solution containing NCS^-, the increase in the G(–Dye) is also mainly attributable to the attack of the radical anion $(NCS)_2^-$ formed through Reactions 2 and 3 on the Acid Red 265 molecule as follows:

$$\mathrm{AR} + (\mathrm{NCS})_2^- \longrightarrow (\mathrm{AR}(\mathrm{NCS})_2)^- \text{ (decolored product)}, \quad (18)$$

$$\mathrm{AR} + (\mathrm{NCS})_2^- \longrightarrow (\mathrm{AR}(\mathrm{NCS})_2)^{-\prime} \text{ (colored product)}. \quad (19)$$

The Acid Red 265 molecule has two kinds of reaction sites for Reactions 18 and 19; (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 radical anion $(\mathrm{NCS})_2^-$ on Site b is independent of the decoloration reaction. It is difficult for the direct attack of the radical anion $(\mathrm{NCS})_2^-$ 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.1) Furthermore, the masking of the azo group can be expected because of the steric effect of the adjacent $\mathrm{SO_3Na}$ and $\mathrm{CH_3}$ groups.1)

The decrease in the G(–Dye) upon the addition of $\mathrm{NCS^-}$ up to 0.1 mM in Fig. 5 may be explained as follows. At low $\mathrm{NCS^-}$ concentrations, since the equilibrium of Reaction 3 may be rather shifted to the left side, a part of the NCS radical is consumed by Reaction 5, thus decreasing the G(–Dye). As the $\mathrm{NCS^-}$ concentration increases, the OH radicals are scavenged efficiently by $\mathrm{NCS^-}$ and the equilibrium of Reaction 3 is shifted to the right side. Therefore, the G(–Dye) increases at high $\mathrm{NCS^-}$ concentrations, as has previously been described.

The decrease in the G(–Dye) upon the addition of $\mathrm{NCS^-}$ was not observed in the $\mathrm{N_2O}$-saturated Acid Blue 40 solution. This may be attributable to the larger reactivity of the radical anion $(\mathrm{NCS})_2^-$ on Acid Blue 40 than on Acid Red 265, because the increase in the G(–Dye) upon the addition of $\mathrm{NCS^-}$ is larger for Acid Blue 40 than for Acid Red 265 in spite of the smaller G(–Dye) value for the Acid Blue 40 solution without $\mathrm{NCS^-}$ than for the Acid Red 265 one.

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References

1) N. Suzuki, T. Nagai, H. Hotta, and M. Washino, *Bull. Chem. Soc. Jpn.*, **48**, 2158 (1975).

2) N. Suzuki, T. Nagai, H. Hotta, and M. Washino, *Bull. Chem. Soc. Jpn.*, **49**, 600 (1976).

3) F. S. Dainton and S. R. Logan, *Trans. Faraday Soc.*, **61**, 715 (1965).

4) B. H. J. Bielski and A. O. Allen, *Int. J. Radiat. Phys. Chem.*, **1**, 153 (1969).

5) M. Anbar, M. Bambenek, and A. B. Ross, NSRDS-NBS 43 (1973).

6) I. Iwasaki, S. Utsumi, T. Ozawa, and R. Hasegawa, *Nippon Kagaku Zasshi*, **78**, 468 (1957).

7) J. H. Baxendale, P. L. T. Bevan, and D. A. Stott, *Trans. Faraday Soc.*, **64**, 2389 (1968).

8) G. E. Adams, J. E. Aldrich, R. H. Bisby, R. B. Cundal, J. L. Redpath, and R. L. Willson, *Radiat. Res.*, **49**, 278 (1972).

9) G. E. Adams, J. W. Boag, J. Currant, and B. D. Michael, "Pulse Radiolysis," Proceedings of the International Symposium held at Manchester, April 1965, Academic Press, London (1965), pp. 117—129.

10) R. L. Willson, C. L. Greenstock, G. E. Adams, R. Wageman, and L. M. Dorfman, *Int. J. Radiat. Phys. Chem.*, **3**, 211 (1971).

11) G. E. Adams, *Adv. Radiat. Chem.*, **3**, 125 (1972).

12) G. O. Phillips, N. W. Worthington, J. F. McKellar, and R. R. Sharpe, *J. Chem. Soc., A*, **1969**, 767.

13) E. Hayon and M. Simic, *J. Am. Chem. Soc.*, **95**, 1029 (1973).