Note

The Mode of Action of Sodium Hypochlorite in the Decolorization of Azo Dye Orange II in Aqueous Solution

HIROMI URANO, AND SATOSHI FUKUZAKI*

*Industrial Technology Center of Okayama Prefecture,
5301 Haga, Kita-ku, Okayama 701-1296, Japan*

Received 16 September, 2010/Accepted 21 May, 2011

The effect of sodium hypochlorite (NaOCl) on the decolorization of azo dye orange II (4-[(2-hydroxy-1-naphthalenyl) azo]-benzenesulfonic acid, monosodium salt) in aqueous solution was studied as a function of pH. The first-order rate constant of color reduction (k) was evaluated from the curve of color reduction in the initial stage of decolorization. The k values increased with increasing the pH from 5.4 to 9.3 and the NaOCl concentration from 2.82×10^{-4} M to 1.13×10^{-3} M. It was found that k depended on the concentration of OCl^- , but not on HOCl . On the other hand, k decreased markedly at pHs more than 10, depending on pH. This suggested that the reactivity of the orange II molecule with OCl^- decreased probably due to the competitive action of the hydroxide ion under alkaline conditions. It could be concluded that controlling the solution pH and the OCl^- concentration was indeed a key factor determining the rate of decolorization of orange II in aqueous solution.

Key words : Decolorization of azo dye/Orange II/Sodium hypochlorite/Dissociated hypochlorite ion/Hydroxide ion.

Sodium hypochlorite (NaOCl) has been widely used in disinfection, cleaning, decolorizing (or bleaching), and deodorizing operations in the food industry. In a diluted NaOCl solution, over the pH range of 5 to 10, there is an equilibrium between two free available chlorine (FAC) forms, i.e., undissociated hypochlorous acid (HOCl) and the dissociated hypochlorite ion (OCl^-). It is generally recognized that HOCl is the active species in the antimicrobial action (Fair et al., 1948; Brazis et al., 1958), whereas the concentration of OCl^- is a key factor determining the cleaning efficiency (Urano and Fukuzaki, 2005; Fukuzaki et al., 2007). These findings imply that the efficacy of NaOCl depends on the ratio of concentrations of HOCl and OCl^- , i.e., the pH of NaOCl solution. On the other hand, in the decolorization or bleaching of pigmented equipment, towels, clothing, and wastewater, NaOCl has been used without controlling the pH of the NaOCl solution although the ap-

plication of NaOCl began approximately 100 years ago. As to the decolorization property of NaOCl, the mechanism (Gregory and Stead, 1978; Kanazawa and Onami, 2001) and kinetics (Bredereck and Schumacher, 1993; Kanazawa and Onami, 1995; Sudoh and Iijima, 1989) of the degradation of azo dyes by NaOCl in aqueous solution have been investigated with the design for chlorine-fast dyes and wastewater treatment in mind. However, the effect of pH on the decolorization of azo dyes by NaOCl in aqueous solution is not fully understood. Azo dyes account for up to 70% of all textile dyestuffs produced (Zollinger, 1987). It is important to know the ability of HOCl and OCl^- to decolorize azo dyes in order to understand the decolorization properties of NaOCl.

The objective of this study was to investigate the mode of action of NaOCl in the decolorization of azo dye solution. We used orange II (4-[(2-Hydroxy-1-naphthalenyl)azo]-benzenesulfonic acid, monosodium salt) as a model pigment. Orange II contains a hydroxyl group conjugated with the azo-linkage (-N

* Corresponding author. Tel: +81-86-286-9600, Fax: +81-86-286-9631, E-mail: satoshi_fukuzaki(a)pref.okayama.lg.jp

=N- or -NH-N=), and it exists as an equilibrium mixture of two tautomeric forms, azo (Fig. 1A) and hydrazone (Fig. 1B), in aqueous solution (Gordon and Gregory; 1983; Koukouraki and Diamadopoulos; 2003). Orange II is also a weak acid with a dissociation constant of $pK_a = 11.4$ (Oakes and Gratton, 1998). Thus, dissociation occurs in the alkaline pH region to form a common dissociated form (Fig. 1C). In this study, the effect of NaOCl on the decolorization of the orange II solution was studied as a function of pH.

Orange II was obtained from Wako Pure Chemical Industries, Ltd. (Osaka) and used as received. The concentration of orange II solution was determined by measuring its absorbance at 484 nm (Abs_{484nm}) that gives an absorption maximum with a molar extinction coefficient of $1.896 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$. Sodium hypochlorite (NaOCl) was of extra pure grade and purchased from Kanto Chemical, Co., Inc. (Tokyo) in the form of a 6% FAC solution. The concentration of NaOCl was determined as FAC by the *N,N*-diethylphenylene-diamine (DPD) method. The concentration of OCl^- in NaOCl solution was calculated using an acid dissociation constant (pK_a) of 7.53 (Morris, 1966). Potassium di-hydrogen phosphate (KH_2PO_4) and di-potassium hydrogen phosphate (K_2HPO_4) were special grade reagents and purchased from Nacalai Tesque, Inc. (Kyoto). Stock solutions of orange II, NaOCl, and phosphate buffer were prepared by dilution with deionized water. All other chemicals were special grade reagents and purchased from commercial sources.

Batchwise decolorization experiments were conducted at 25°C in a 3-ml quartz cell (optical path length of 1 cm), which was installed in a cell folder, equipped with a temperature controller and magnetic

stirrer, of a spectrophotometer (UV-3100PC; Shimadzu, Kyoto). Before the experiment, the quartz cell and cell folder were kept at 25°C, and then 0.75 ml of NaOCl solution and 0.75 ml of 0.4 M phosphate buffer solution, pHs of which were adjusted from 5.4 to 11.7, were poured into the cell and stirred for 10 min, as the pre-heating treatment. After this was allowed to stand for 10 min, to initiate the decolorizing reaction, 1.5 ml of orange II solution pre-heated at 25°C was added into the cell, and spectroscopic measurement of Abs_{484nm} of the mixed solution was immediately started. The decrease in Abs_{484nm} was monitored at intervals of 5, 15, and 30 s depending on the degree of color reduction. There was no pH change throughout the decolorization reaction in all experiments.

To analyze the decolorization of orange II, the concept that a first-order reaction occurs during decolorization process was used. The curve of decolorization was obtained by plotting the natural logarithm of the concentration of orange II against the reaction time. The rate constant of the color reduction, k , was estimated by evaluating the slope of the best-fit straight line, using the linear regression method (correlation coefficient ≥ 0.99), for the first portion of the decrease of orange II in the initial stage of decolorization.

$$\ln [\text{Orange II}] = \ln [\text{Orange II}_0] - kt \quad (1)$$

where $[\text{Orange II}_0]$ and $[\text{Orange II}]$ are the concentrations of orange II at zero time and any given time, t , respectively.

To examine the effect of pH on the decolorization, experiments were conducted at an initial orange II concentration of $8.70 \times 10^{-5} \text{ M}$ ($Abs_{484nm} = 1.65$) over the pH range from 5.4 to 11.7, using 2.82×10^{-4} , 5.64×10^{-4} , and $1.13 \times 10^{-3} \text{ M}$ NaOCl. Figure 2 shows typical curves of decrease in orange II during decolorization by NaOCl at different pHs. The straight lines (solid lines) reflect the initial rate of color reduction. It was found that the rate of color reduction was markedly affected by both pH and the NaOCl concentration. At $2.82 \times 10^{-4} \text{ M}$ NaOCl, the rate of color reduction was slower at the weak acidic and neutral pH regions (pH 6 to 7) and it increased gradually with increasing pHs up to 9.3 (Fig. 2A). These features were more pronounced when using NaOCl concentrations of 5.64×10^{-4} to $1.13 \times 10^{-3} \text{ M}$ (Figs. 2B and 2C). More rapid decolorization was achieved at pH 9.3 at all NaOCl concentrations. On the contrary, it was found that the decreases in the rate of color reduction were observed at pHs more than 10.

Figure 3A shows the k values obtained from the graphs in Fig. 2, as a function of pH. Over the pH range from 5.4 to 9.3, k increased markedly with

FIG. 1. Structures of orange II in aqueous solution. (A) Azo; (B) hydrazone; (C) common ion.

FIG. 2. Curves characterizing decrease in orange II during the decolorization with NaOCl at 2.82×10^{-4} (A), 5.64×10^{-4} (B) and 1.13×10^{-3} M (C). The initial orange II concentration was 8.70×10^{-5} M ($Abs_{.484nm} = 1.65$). The solid lines denote the slopes given by linear curve fitting for the portion of rapid decrease of orange II in the initial stage of decolorization. Symbols (pH) : (A) $\circ$ 6.0, $\square$ 7.0, $\diamond$ 8.1, $\triangle$ 9.3, $\bullet$ 10.4, $\blacksquare$ 10.9; (B) $\circ$ 5.4, $\square$ 6.3, $\diamond$ 6.8, $\triangle$ 9.3, $\bullet$ 10.4, $\blacksquare$ 10.9; (C) $\circ$ 5.4, $\square$ 6.2, $\diamond$ 7.1, $\triangle$ 9.3, $\bullet$ 10.4, $\blacksquare$ 10.9.

FIG. 3. Effect of pH and the NaOCl concentration on the k value for the decolorization of orange II by NaOCl. (A) Plotted as a function of pH; (B) plotted as a function of the initial concentration of dissociated OCl^- at pHs below 10. Experimental conditions are given in the legend to Figure 2. The solid line was derived by curve-fitting using the linear regression method. Symbols (initial NaOCl concentration; M): $\diamond$ 2.82×10^{-4} , $\circ$ 5.64×10^{-4} , $\square$ 1.13×10^{-3} .

increasing the solution pHs and it reached an maximum value at pH 9.3. Under weak acidic conditions (pH 5.5 to 6.5), where undissociated HOCl is prevalent, NaOCl exerted little action in the decolorization of orange II in spite of its high concentration (2.82×10^{-4} to 1.13×10^{-3} M). It seemed that k increased with the increase in the OCl^- concentration over the pH range from 5.4 to 9.3. To clarify the action of OCl^- , we put aside the data obtained at pHs more than 10 and plotted the k values against the initial OCl^- concentrations (Fig. 3B). It was clearly noted that the k values increased in an OCl^- -dependent manner. The graph of the OCl^- concentration versus the k value gave the following relationship (correlation coefficient = 0.985):

$$k = 231 \times [OCl^-]^{0.736} \quad (2)$$

These data demonstrated that OCl^- , as a dissociated form of FAC, was the active species in the decolorization of orange II in aqueous solution. It has been reported that the rate-determining step in the oxidative degradation of azo dyes was the cleavage of azo-linkage moiety (Kanazawa and Onami, 2001). The Cl atom in OCl^- behaves as Cl^+ , a strong electrophile, and combined with a pair of electrons in parts of the substrate that have high electron densities (Fukuzaki, 2006). The azo-linkage on orange II has a high electron density and hence it is readily chlorinated by OCl^- having the high polarity. The electrophilic action of OCl^- toward nucleophilic N atoms on orange II molecules is responsible for the decolorization of the orange II solution. On the other hand, undissociated HOCl is electrically neutral and has a lower polarity

than OCl^- . These might result in the lower reactivity of orange II with HOCl . This phenomenon is similar to that of the low reactivity of ammonia and *N*-organo compounds with HOCl (Koukouraki and Diamadopoulos, 2003; Takehara and Fukuzaki, 2006).

In this study, the maximum k values were found to occur at pH 9.3 at different NaOCl concentrations, whereas they decreased markedly at pHs more than 10 (Fig. 2). It is thought that no structural change occurs in the azo-linkage moiety, a target of Cl^+ attack, on orange II even though orange II dissociates to a common anion under alkaline conditions (Fig. 1C). These findings suggest that the decrease in the k value at higher pHs was due to the interfering action of coexisting OH^- . At pHs lower than 9.3, the concentrations of OH^- were lower by at least one to two orders of magnitude than those of OCl^- (2.82×10^{-4} to 1.13×10^{-3} M). Under these conditions, k was proportional to $[\text{OCl}^-]^{0.736}$ (eq. 2). The low value of the exponent of 0.736 implies the existence of rate-determining factors. It is likely that low concentrations of OH^- might somewhat inhibit the action of OCl^- even at pHs below 9.3. On the other hand, at pHs above 10, the concentrations of OH^- become the same order of magnitude as those of OCl^- . Both OH^- and OCl^- show electrostatically similar behavior in aqueous solution. The accessibility of OCl^- to reactive sites such as the azo-linkage on orange II would go down by concentrated OH^- . It is reasonable that the attack of OCl^- on orange II is competitively inhibited by OH^- at the alkaline pH region (pH > 10).

The results presented here provide useful information concerning the decolorization of azo dyes by NaOCl . The concentration of OCl^- , but not of HOCl , is indeed the key factor determining the efficacy of NaOCl in the decolorization of orange II. The rate constant of decolorization increased with increasing pHs up to 9.3. However, an excess OH^- behaves as a competitive inhibitor for OCl^- , thereby interfering with the decolorization by OCl^- . For optimizing the decolorization process by NaOCl , therefore, it is very important to control the pH of the NaOCl solution or pigmented solution by considering both the OCl^- and OH^- concentrations.

REFERENCES

- Brazis, A. R., Leslie, J. E., Kabler, P. W., and Woodward, R. L. (1958) The inactivation of spores of *Bacillus globigii*

- and *Bacillus anthracis* by free available chlorine. *Appl. Microbiol.*, **6**, 338-342.
- Bredereck, K., and Schumacher, C. (1993) Structure reactivity correlations of azo reactive dyes based on H-acid. I. NMR chemical shift values, pK_a values, dyestuff aggregation and dyeing behavior. *Dyes and Pigments*, **21**, 23-43.
- Bredereck, K., and Schumacher, C. (1993) Structure reactivity correlations of azo reactive dyes based on H-acid. II. Dye degradation by hypochlorite. *Dyes and Pigments*, **21**, 45-66.
- Fair, G. M., Morris, J. C., Chan, S. L., Weil, I., and Burden, R. P. (1948) The behavior of chlorine as a water disinfectant. *J. Am. Water Assoc.*, **40**, 1051-1061.
- Fukuzaki, S. (2006) Mechanisms of actions of sodium hypochlorite in cleaning and disinfection processes. *Biocontrol Sci.*, **11**, 147-157.
- Fukuzaki, S., Urano, H., and Yamada, S. (2007) Effect of pH on the efficacy of sodium hypochlorite solution as cleaning and bactericidal agents. *J. Surface Finish Soc. Jpn.*, **58**, 465-469.
- Gordon, P. F., and Gregory, P. (1983) *Organic Chemistry in Color*, Springer-Verlag, New York.
- Gregory, P., and Stead, C. V. (1978) The degradation of water-soluble azo compounds by dilute sodium hypochlorite solution. *J. Soc. Dyers Colour*, **94**, 402-407.
- Kanazawa, H., and Onami, T. (1995) Degradation of Azo dyes by sodium hypochlorite 3. estimation of the rate equation for degradation of orange G and benzopurpurine. *Bull. Chem. Soc. Jpn.*, **68**, 2483-2489.
- Kanazawa, H., and Onami, T. (2001) Mechanism of the degradation of orange G by sodium hypochlorite. *Color. Technol.*, **117**, 323-327.
- Koukouraki, E., and Diamadopoulos, E. (2003) Modelling the formation of THM (trihalomethanes) during chlorination of treated municipal wastewater. *Water Sci. Technol.*, **3**, 277-284.
- Morris, J. C. (1966) The acid ionization constant of HOCl from 5 to 35°. *J. Phys. Chem.*, **70**, 3798-3805.
- Oakes, J., and Gratton, P. (1998) Kinetic investigations of azo dye oxidation in aqueous media. *J. Chem. Soc. Perkin Trans.*, **2**, 1857-1864.
- Sudoh, Y., and Iijima, T. (1989) Oxidative fading reaction of azo dye in aqueous solution with sodium hypochlorite. *Sen-i Gakkaishi*, **45**, 332-334.
- Takehara, A., and Fukuzaki, S. (2006) Relationship between the pH and decrease in available chlorine of sodium hypochlorite in the presence of organic compounds or during freezing treatment. *Report of Ind. Technol. Ctr. Okayama*, **32**, 10-13 (in Japanese).
- Urano, H., and Fukuzaki, S. (2005) The mode of action of sodium hypochlorite in the cleaning process. *Biocontrol Sci.*, **10**, 21-29.
- Zollinger, H. (1987) *Colour Chemistry: Syntheses, Properties and Applications of Organic Dyes and Pigments*. VCH Publishers, Inc., New York.