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Ozone Fading of 2,2′-Dihydro Azo Copper Complex Dyes

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The reactivities of dyes with ozone were in the following order, Acid Blue 74>disodium 1-(2-hydroxyphenylazo)-2-naphthol-3,6-disulfonate>Direct Yellow 12>Acid Orange 7>disodium 1-phenylazonaphthalene-3,6-disulfonate-2,2′-diolatocopper(II)>Mordant Red 3>Basic Green 4. The reaction of disodium 1-phenylazonaphthalene-3,6-disulfonate-2,2′-diolatocopper(II) with ozone was retarded by the introduction of electron-withdrawing groups and 8-sulfonato group. The potassium sulfonate dye was less reactive than the sodium one. Ozonization of 1-phenylazonaphthalene-2,2′-diolatocopper(II) gave phenol, 2-naphthol, and phthalic anhydride.

Reaction of dyes with ozone is of interest from the viewpoint of ozone fading of coloring matter and ozone treatment of dye wastewater.[1] It is important to evaluate the factors which affect the ozone fading of dyes. In our continuing series of studies on the reaction of ozone with dyes, ozone fading mechanism of several dyes have been proposed.[2–6] This report describes the reactivity and products in ozone fading of 2,2′-dihydro azo copper complex dyes.

Results and Discussion

Figure 1 shows dyes used in this study. 2-Hydroxybenzenediazonium chloride, prepared from 2-aminophenol, sodium nitrite, and hydrochloric acid, was reacted with 1- and 2-naphthol derivatives to afford metal free **1** and **2**, which were treated with copper sulfate to give **1** and **2**.

It is of interest to compare the reactivity of metal complex dyes with those of the other dyes whose ozone fading mechanisms have been reported.[2–6] In order to estimate the reactivity, the reaction in the initial stage was applied to first-order rate kinetics. For example, Fig. 2 shows the plots of logarism of A_0/A_t vs. time, where A_0 and A_t are absorbance at 0 and t sec at maximum wavelength, respectively. The plots of **1a** were linear and the rate constant (k) was calculated to be $0.0057\ \mathrm{s}^{-1}$.

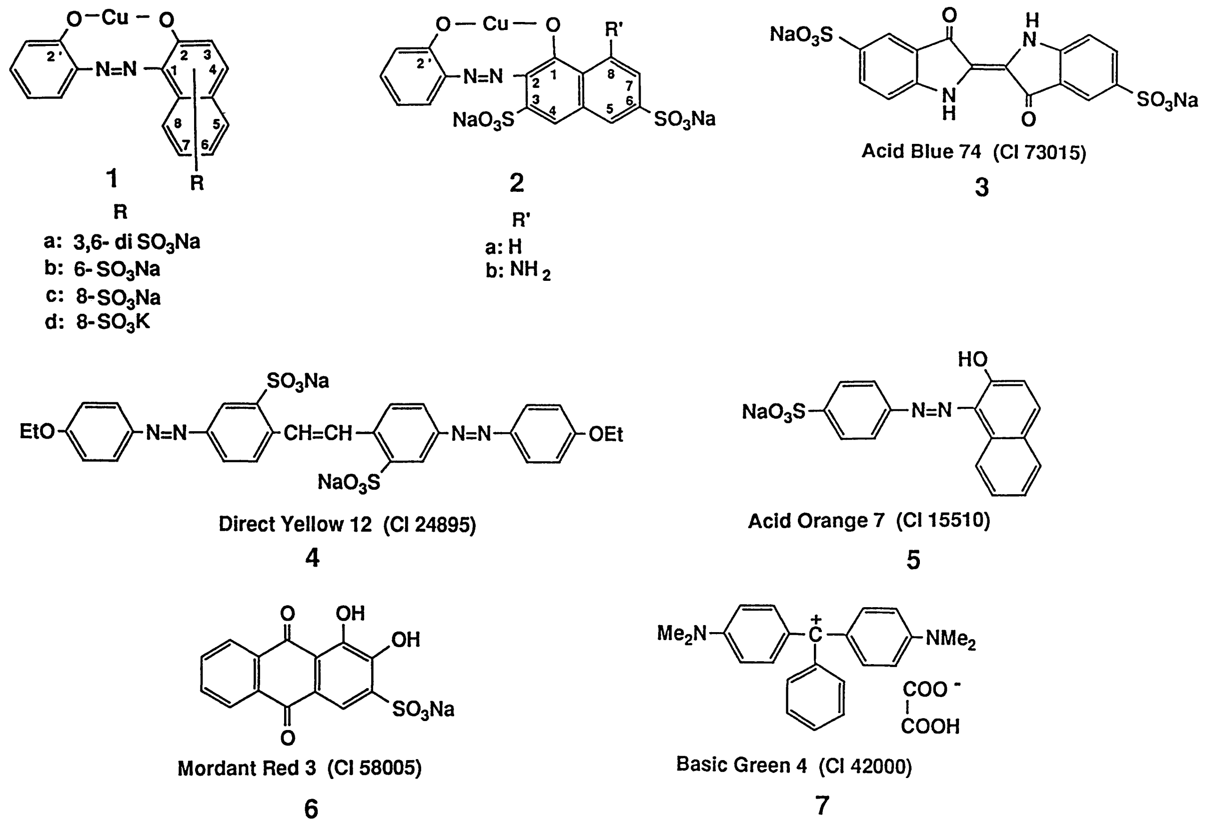

Fig. 1. Materials.

Table 1. Reactivities of Dyes with Ozone

Run	Dyes	$k\times10^3$ (s^{-1})
1	**3**	13.0±0.3
2	Metal free **1a**	12.3±0.3
3	**4**	9.6±0.0
4	**5**	6.6±0.1
5	**1a**	5.7±0.1
6	**6**	5.2±0.6
7	**7**	4.6±0.4
8	**1b**	6.8±0.1
9	**1c**	5.5±0.3
10	**1d**	4.0±0.2
11	**2a**	4.9±0.1
12	**2b**	6.0±0.1

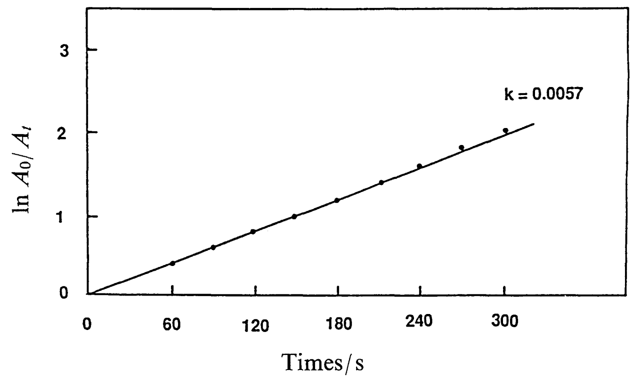

Fig. 2. Reactivity of disodium 1-phenylazonaphthalene-3,6-disulfonate-2,2′-diolatocopper(II) with ozone.

Table 1 shows the reactivities of dyes with ozone. The rate constants of dyes were in the following order, Acid Blue 74 (**3**)>metal free **1a**>Direct Yellow 12 (**4**) >Acid Orange 7 (**5**)>**1a**>Mordant Red 3 (**6**)>Basic Green 4 (**7**) (Runs 1—7). Ozone reacts easily with double bonds such as C=C and C=N. Ozonolyses of central olefinic bonds of 2-(1,3-dihydro-3-oxo-2*H*-indol-2-ylidene)-1,2-dihydro-3*H*-indol-3-one (Vat Blue 1, CI 73000) and Direct Yellow 12 (**4**) have been reported to give carbonyl compounds.[2,3] Ozone fading of 2-hydroxyazo dyes have been reported to proceed via the hydrazone isomers on the basis of substituent and solvent effects.[4] It has been reported that 1,2-dihydroxyanthraquinone (Pigment Red 83, CI 58000) was ozonized to give phthalic anhydride.[5] Although ozone attacked both the dimethylamino and olefinic moieties of aminotriphenylmethane dyes, it attacked mainly the dimethylamino moiety in the case of Basic Green 4 to give the formylmethylamino derivative.[6] Since the product is still colored, the rate constant of ozone fading is apparentely small. Aromatic azo compounds are fairly stable for ozone.[7,8] Since **1a** has bulky and electron-withdrawing copper atom in a molecule, the rate constant was smaller than the metal free **1a**.

Figure 3 shows the substituent effect on ozone fading of **1a**. The plots of logarism (k_R/k_H) vs. Hammett's σ constants, where k_R and k_H are rate constants of substituted and unsubstituted dyes respectively, were linear, whose slope (ρ) was calculated to be -0.22 (r=0.95). This result suggested that ozone attacked electrophilically the substrate and that introduction of electron-withdrawing groups into diazo component improved stability of dyes for ozone.

The reaction rates of some 2,2′-dihydro azo copper complex dyes, whose couplers consisted of 1- and 2-naphthol derivatives are summarized in Table 1. The results indicated that 1) electron-withdrawing sulfonato group (σ: 0.09 (p), 0.05 (m)) inhibited the reaction (Runs 5, 8); 2) bulky sulfonato group at the 8 position retarded the reaction (Runs 8, 9); 3) greater potassium ion (ionic radius, K=1.38 Å, Na=1.02 Å) inhibited the reaction (Runs 9, 10); and 4) electron-releasing amino group of the coupler accelerated the reaction (Runs 11, 12).

Ozonization of 1-phenylazonaphthalene-2,2′-diolatocopper(II) (**8**) gave phenol (**9**), 2-naphthol (**10**), and

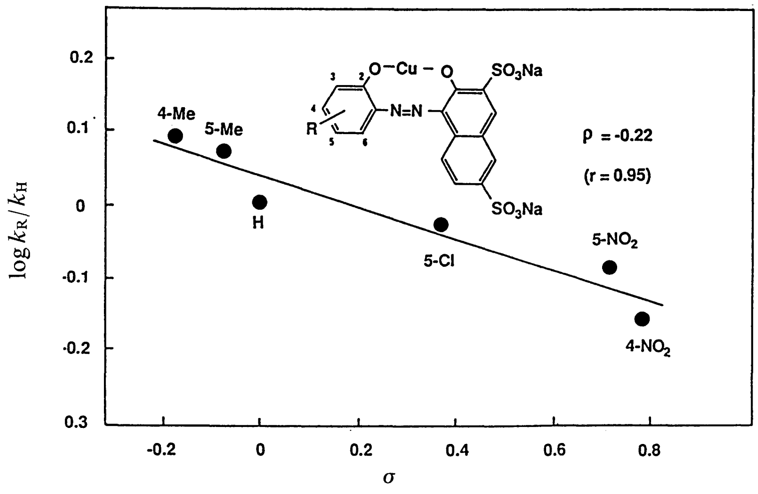

Fig. 3. Hammett's plots for the ozone fading of disodium 1-phenylazonaphthalene-3,6-disulfonate-2,2′-diolatocopper(II).

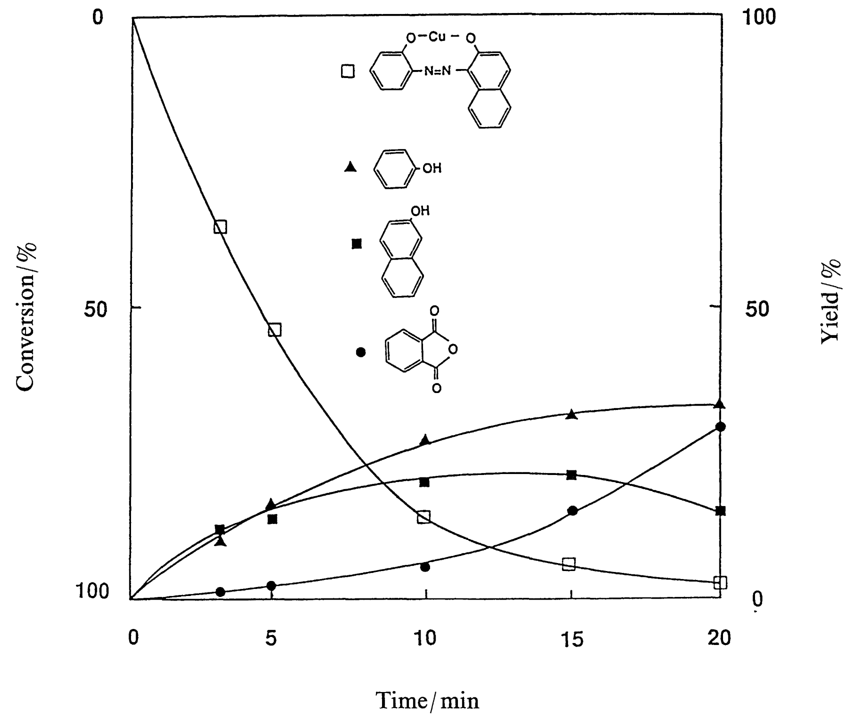

Fig. 4. Ozonization of 1-phenylazonaphthalene-2,2′-diolatocopper(II). Ozonization was carried out with an ozone–oxygen mixture (O_3: 0.068 mmol min^{-1}, O_2: 200 ml min^{-1}) on 1-phenylazonaphthalene-2,2′-diolatocopper(II) (1.6 mmol) in DMSO (2 ml) at 30 °C.

phthalic anhydride (**11**). Figure 4 shows the time-dependence of products. The ozonization of **8** gave **9** and **10**, which was further ozonized to afford **11**. Ozonization of phenol has been reported to give formic acid as a main product.[9] The reaction of 2-naphthol with ozone gave phthalic anhydride. Ozone attacked the azo linkage of **8** to give unstable azoxy intermediates which is followed by the hydrolysis of Cu–O bond to give **9** and **10**. Ozone could attack also the C=N bond of the hydrazone isomer of **8** to give the products.

Experimental

Instruments. Ozone was generated with a Nihon Ozon 0-1-2 type ozonizer. Melting points were measured with a Yanagimoto micro melting point apparatus and uncorrected. NMR, UV, and mass spectra were obtained with JEOL JUM GX 270, JASCO 410, and Shimadzu QP-1000 spectrometers, respectively. Gas chromatography was performed on a Shimadzu 4C-PF gas chromatograph.

Materials. Acid Blue 74 (**3**), Direct Yellow 12 (**4**), Acid Orange 7 (**5**), and Basic Green 4 (**7**) were purchased from Tokyo Kasei Co., Ltd. Mordant Red 3 (**6**) was obtained from Aldrich Chemical Co., Ltd. They were used without further purification.

2,2′-Dihydro azo compounds were prepared as follows; to 50% hydrochloric acid solution of 2-aminophenol (3.2 g, 29 mmol) was added 30% aqueous solution (8 ml) of sodium nitrite at 0 °C. The mixture was stirred for 1 h. To the diazotized solution was added 20% aqueous sodium hydroxide solution (35 ml) of a coupler (30 mmol). The mixture was stirred at 0 °C for 1 h. The product was obtained by salting-out techniques. Physical and spectral data of 1-(2-hydroxyphenylazo)-2-naphthol are shown below. Mp 194.0—195.0 °C (lit,[10] 193 °C); ^{1}H NMR ($CDCl_3$) δ=7.0—8.2 (m, 10H), 12.4 (s, 1H), and 14.5 (s, 1H); EIMS (70 eV) *m/z* (rel intensity) 264 (M^+, 100).

2,2′-Dihydro azo copper complex dyes were synthesized as follows; in the case of **1** and **2**, to an aqueous solution (150 ml) of 2,2′-dihydro azo compound (10 mmol) was added an aqueous solution of copper sulfate penta hydrate (10 mmol). The mixture was stirred at room temperature. In the case of **8**, the reaction was carried out in an acetone solution. The resulting precipitate was collected and washed with water or acetone. Found: C, 54.19; H, 3.26; N, 7.89%. Calcd for $C_{16}H_{10}N_2O_2Cu \cdot H_2O$: C, 55.89; H, 3.52; N, 8.15%.

Reactivity of Dyes with Ozone. Ozonization was carried out with an ozone–oxygen mixture (O_3: 0.068 mmol min^{-1}, O_2: 200 ml min^{-1}) on dye (0.1 mmol) in phosphate buffer solution (pH=6.8, 500 ml) at 30 °C. The rate constants were calculated on the basis of the changes of the absorbance at λ_{max} of the solution during the reaction.

Ozonization of 1-Phenylazonaphthalene-2,2′-diolatocopper(II). Ozonization was carried out with an ozone–oxygen mixture (O_3: 0.068 mmol min^{-1}, O_2: 200 ml min^{-1}) on 1-phenylazonaphthalene-2,2′-diolatocopper(II) (1.6 mmol) in DMSO (2.0 ml) at 30 °C. After the reaction, the mixture was allowed to stand overnight. The disappearance of peroxide activity was checked by a KI test. Products were identified by GC-mass analysis and determined by gas chromatography. The conditions of gas chromatography are shown below. GLC 1: column 2% OV-1 on Gaschrom Q (60—80 mesh), 3 mm×1 m; column temperature 80—240 °C (10 °C min^{-1});

injection temperature 250 °C; detector temperature 250 °C; detection FID. GLC 2: column 2% FFAP on Gaschrom Q (80—100 mesh), 3 mm×1 m; column temperature 80—210 °C (10 °C min^{-1}); injection temperature 220 °C; detector temperature 220 °C; detection FID.

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