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Reactions of Ozone with 1-(*m*-Substituted phenylazo)-2-naphthol-6-sulfonic Acids in Aqueous Solutions

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(Received March 15, 1985)

The substituent effect on the ozone decoloration reactions of 1-(*m*-substituted phenylazo)-2-naphthol-6-sulfonic acids (PANSA) in aqueous solutions was investigated. Both the acidities of PANSA and the variation of the ozone decoloration rates of them increased compared to those of the corresponding 1-(*m*-substituted phenylazo)-2-naphthol-3,6-disulfonic acids (PANDSA). The relationships between the decoloration rates and the indexes(pK_{OH} and σ_m values) of the basicities of the dyes, however, indicated nearly the same characteristics between the data of these two series of dyes, and the ozone decoloration reactions of PANSA appeared to proceed by nearly the same mechanism as those of PANDSA. The changes of the keto–enol ratios of the dyes with their ozone decolorations suggested that the decoloration rates might rise as the reduction rates of their keto–enol ratios increased. It seems likely that the chief organic product that was finally produced in these reactions is oxalic acid.

Because of the toxicity of dye waste, the biological treatment of it is very difficult. Ozone decoloration reactions of dyes have already been applied for the removal of the organic color of the waste water from dyeing industries. However, little is known about the ozonation mechanism of dyes and about the ozone reactivities of them in aqueous media. Ikehata and co-workers[1] have investigated the ozone oxidation products of some azo dyes in water. Matsui *et al.*[2] reported on the ozonation of *p*-aminoazobenzene in aqueous solution. In the previous papers,[3,4] some phenylazonaphthols and naphthylazonaphthols were taken up, and the ozone decoloration reactions of them were investigated. The ozone decoloration rates of these dyes showed the tendency to increase with increasing the electron-withdrawing powers of their substituents. It was also proved that the ozone decolorations of the dyes were accelerated with their substituent sulfo groups. On the basis of these results, the selectivity of the ozone decoloration reactions of a series of phenylazonaphthol dyes was expected to increase with decreasing the number of sulfo groups in their naphthol moieties. Therefore, a series of dyes bearing only one sulfo substituent on each of their naphthol moieties was desired to be taken up for the purpose of the further investigations on the mechanism of the ozone decoloration reactions of azo dyes. The ozone reactivities of seven 1-(*m*-substituted phenylazo)-2-naphthol-6-sulfonic acids(PANSA) were previously investigated using ^{1}H-NMR spectra.[5] In the present work, eight PANSA were examined similarly to eight 1-(*m*-substituted phenylazo)-2-naphthol-3,6-disulfonic acids(PANDSA)[4] so as to throw light mainly on the polar effect of the ozone decoloration rates of them in aqueous media. These observations induce us to know the reaction mechanism more precisely and to see what the difference in the reactivity is between the ozone decoloration of PANSA and that of the corresponding PANDSA.

Experimental

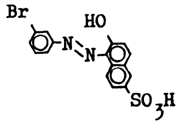
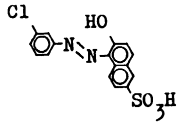
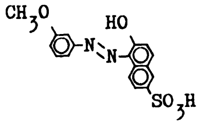
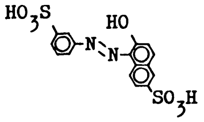
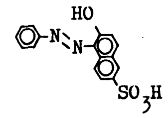
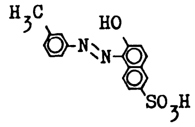
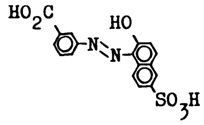
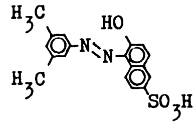
Preparations of the Dyes. The dyes were prepared by the diazotizated-coupling reactions of *m*-substituted anilines with Schaeffer's acid(2-naphthol-6-sulfonic acid) in the ordinary way. They were extracted with 1-butanol from the resulting reaction mixtures followed by purification on a cellulose column using a 2 mol dm^{-3} NH_3 solution saturated with 1-butanol as eluent. And then they were recrystallized from suitable organic solvents for a few times. The properties of the dyes are shown in Table 1.

Measurements. Equipments and measuring methods were the same as those shown in the previous paper.[3] All the chemicals employed for the experiment were special reagent grade. A solution of dye(4×10^{-5} mol dm^{-3}) in 0.5 dm^3 distilled water, the pH and the ionic strength (μ: 0.2) of which were controlled with the Sörensen buffer solution and KNO_3 respectively, was employed for the ozone decoloration reaction. The prepared solution was placed in a 0.5 dm^3 Pyrex gas-washing bottle having a G-2 sintered-glass filter at the bottom of it as a diffuser. Ozonized air(O_3 concn: 1.94 mg dm^{-3}) was continuously supplied into the bottle at a constant flow rate of 2.7 dm^3 min^{-1} through the sintered-glass filter. A part(3.5 cm^3) of the solution was circulated through micro flow-cell of the spectrophotometer with a micropump, and the ozone decoloration of the dye was continuously recorded. Ozonized air was obtained using a Nihon Ozon 0-3-3 electric discharge ozone generator. A Nihon Bunko UVIDEC-1 digital doublebeam spectrophotometer was used for the measurements of the decoloration rates. The visible absorption spectra and the acid dissociation constants of the dyes were obtained on a Hitachi 323 spectrophotometer. Elemental analysis was performed on a Yanaco MT-3 CHN Corder. Fatty acids were measured with a Nihon Bunko FLC 350 high-performance liquid chromatograph equipped with a UVIDEC-100 UV spectrometer as a detector.

Results and Discussion

Acid Dissociation Constants of the Dyes. The acid dissociation constants(pK_{OH}) of the dyes were

Table 1. Properties of the dyes

No.	Constitution	Anal (C/N) Found (Calcd)	λ_{max} (nm)(ε_{max})[a]	pK_{OH}[b]	Keto-enol[c] ratio
1		6.99 (6.86)	474 (1.58×10^4)	10.27	2.14
2		7.00 (6.86)	473 (1.59×10^4)	10.30	2.10
3		7.37 (7.29)	482 (1.50×10^4)	10.39	2.28
4		6.86 (6.86)	475 (1.54×10^4)	10.13	2.11
5		6.89 (6.86)	478 (1.43×10^4)	10.51	2.36
6		7.39 (7.29)	482 (1.53×10^4)	10.67	2.57
7		7.40 (7.29)	472 (1.47×10^4)	10.50	2.40
8		8.00 (7.72)	487 (1.54×10^4)	10.83	2.70

a) Measured in methanol at room temperature. b) Acid dissociation constant of the dye at 21 °C (μ: 0.2 (KNO_3)). c) A_{CO}/A_{OH} value of the dye in distilled water.

determined spectrophotometrically at 21 °C (μ: 0.2 (KNO_3)) in the same manner as that was shown in the previous report.[3] The result is shown in Fig. 1.

The relationship between the pK_{OH} values of PANSA and the Hammett's σ_m values of their substituent groups is shown in Fig. 2. The pK_{OH} values of the dyes showed the tendency to decrease with increasing σ_m values of their substituents, and the regression equation was calculated as follows: pK_{OH}=10.51−0.62 σ_m. The result indicated nearly the same tendency as that shown in the pK_{OH} values of PANDSA: pK_{OH}=10.80−0.91 σ_m. However, the pK_{OH} values of PANSA were smaller than those of the corresponding PANDSA in contrast to the expectation that was produced from the reduction of the inductive effect of the sulfo substituent in the *ortho*-position to OH. This seemed to be based on the disappearance of another influence (for example, the effect of the negative charge) of the substituent.

The pH Dependence of the Ozone Decoloration Rates of the Dyes. Because of the electrophilic nature of ozone, the ozone decoloration rates of PANSA can be estimated to be accelerated with their proton dissociations. The relationship between the logarithms of pseudo-first-order rate constants(log k_{obsd})

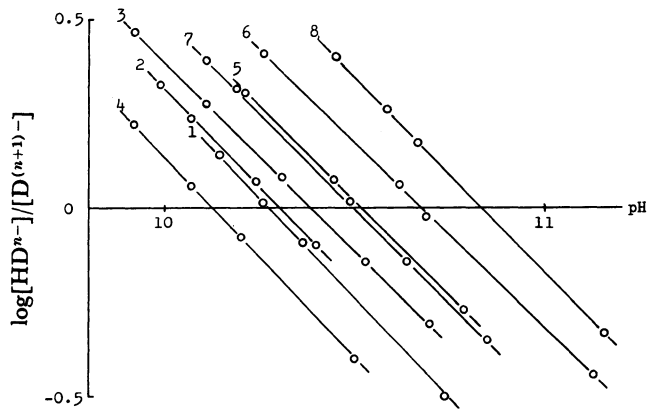


Fig. 1. Relations between log[HD^{n-}]/[D$^{(n+1)-}$] and pH for the determinations of the acid dissociation constants of the dyes at 21 °C (μ: 0.2(KNO$_3$)).
Number attached to each curve is the same as that given in Table 1.

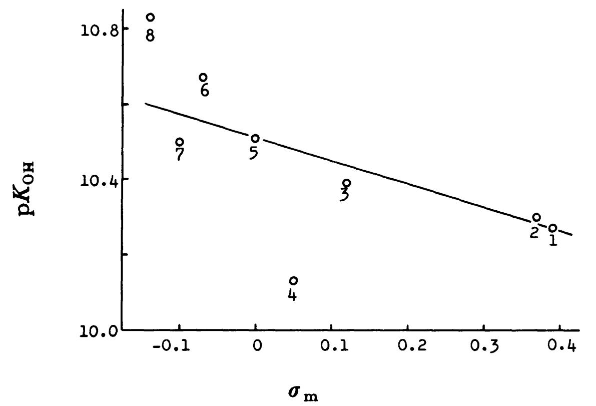


Fig. 2. Relation between the acid dissociation constants of the dyes and the Hammett's σ_m values of their substituents.
pK_{OH} = 10.51—0.62 σ_m(n: 6, γ: −0.901).
Number attached to each point is the same as that given in Table 1.

and pH for the ozone decolorations of the dyes is shown in Fig. 3. The log k_{obsd} values of these reactions increased linearly with increasing pH of the solutions in the pH ranges of about the half-neutralization points of the hydroxyl groups of the dyes to 6.0. The slopes of these regression lines were 0.039(NO. 6)—0.171(NO. 4), and the average value of them was 0.119. This average value of the slopes showed nearly the same as those: 0.13 and 0.116 of the results that had been shown in Refs. 3 and 4 respectively. These results suggested that the pH dependence of the decoloration rates was scarcely variable in all the ozone decoloration reactions of those monoazo dyes.

The Relationship between the Basicities of the Dyes and the Ozone Reactivities of Them. In order

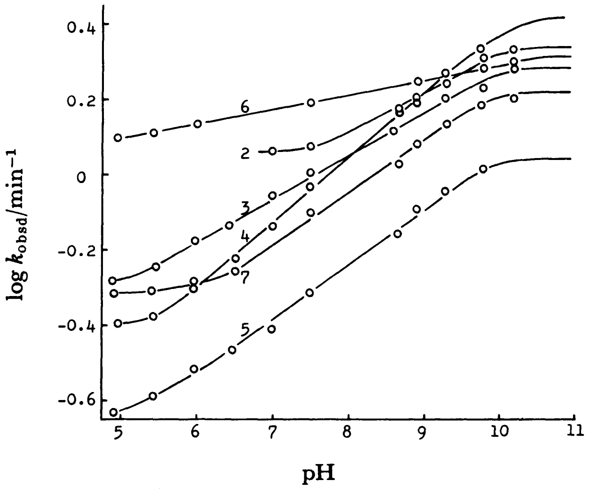


Fig. 3. Relations between the logarithms of pseudo-first-order rate constants and pH for the decoloration reactions of the dyes with ozone at 25 °C.
Number attached to each curve is the same as that given in Table 1.

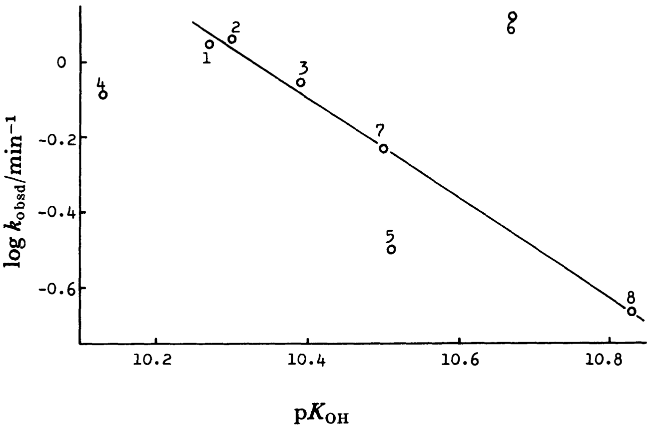


Fig. 4. Relation between log k_{obsd} and pK_{OH} for the decoloration reactions of the dyes with ozone at pH 7.0 and 25 °C.
log k_{obsd} = 13.77—1.333 pK_{OH}(n: 5, γ: −0.997).
Number attached to each point is the same as that given in Table 1.

to reveal the mechanism of these ozone decoloration reactions, the investigation on the pK_{OH} dependence of the decoloration rates was also made in this work. The relationship between log k_{obsd} and pK_{OH} of PANSA is shown in Fig. 4. It showed a good linearity with the exception of 4, 5, and 6(log k_{obsd}=13.77−1.333 pK_{OH}(n=5, γ=−0.997)). The negative slope of this regression line suggested the global process to be nucleophilic. In this case, the variation of log k_{obsd} with pK_{OH} was larger than that shown in the ozone decolorations of the monoazo dyes bearing only sulfo substituents(pH 7.0, log k_{obsd}= 1.955−0.207 pK_{OH})[3] and larger than that shown in the ozone decolorations of PANDSA(pH 7.0, log

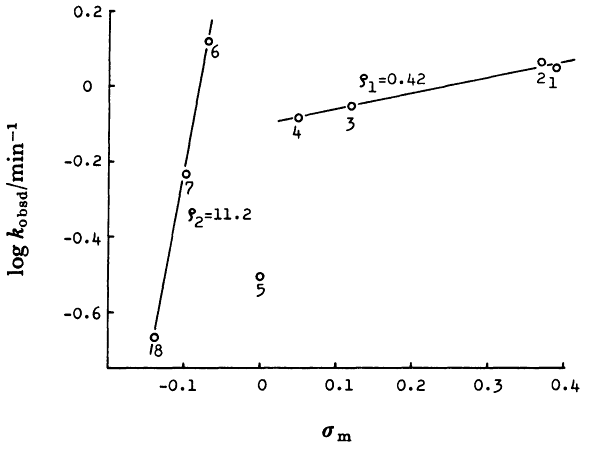


Fig. 5. Hammett plot for the decoloration reactions of the dyes with ozone at pH 7.0 and 25 °C.
Number attached to each point is the same as that given in Table 1.

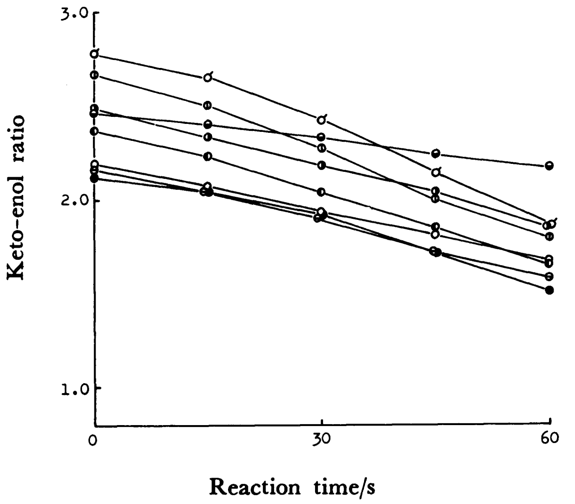


Fig. 6. Changes of the keto-enol ratios with reaction time for the decoloration reactions of the dyes with ozone at pH 7.0 and 25 °C.
●: 1, ⊖: 2, ◐: 3, ○: 4, ◒: 5, ⦶: 6, ◑: 7, ơ: 8.
Number attached to each curve is the same as that given in Table 1.

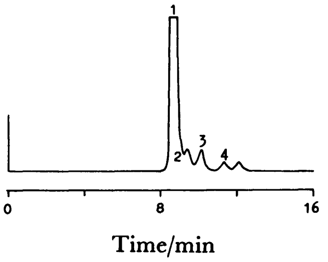


Fig. 7. Typical HPLC chromatogram of the ozone oxidation products of the dye.
Dye: 5, Flow rate: 1 cm^3 min^{-1}, Detector: UV 210 nm.
1: Nitrate, 2: Oxalic acid, 3: Maleic acid, 4: Glyoxylic acid.

k_{obsd}=0.937−0.0911 pK_{OH})[4] as expected.

The relationship between the Hammett's σ_m values and log k_{obsd} for the ozone decolorations of the dyes is shown in Fig. 5. The obtained ρ values were: 0.42(ρ_1) for the dyes bearing the electron-withdrawing groups and 11.2(ρ_2) for those bearing the electron-releasing groups. The positive ρ values indicated that the global process of these reactions was nucleophilic in nature, but $\rho_1 < \rho_2$ and the discontinuity in the relationship showed that the electrophilic process played an important role in these ozone decoloration reactions. In the ozone decoloration reactions of these dyes, the variation of the decoloration rates was larger than, but the characteristic of the Hammett plot was similar to, those shown in the ozone decoloration reactions of PANDSA. From these results, the ozone decoloration reactions of these dyes appeared to proceed by nearly the same mechanism as those of PANDSA.

The Changes of the Keto-Enol Ratios of the Dyes with Their Ozone Decoloration Reactions. These dyes exist as the hydroxy azo-keto hydrazo tautomeric equilibria in aqueous solutions. In this work, the effect of the tautomeric equilibria of the dyes on their ozone decoloration rates was investigated. Burawoy and Thompson[6] examined the tautomeric equilibria of arylazonaphthols using electronic spectra, and indicated that the absorption maxima near 480 and 420 nm were due to the keto hydrazo form and the hydroxy azo form respectively. As an index of the tautomeric equilibria, the ratio(A_{CO}/A_{OH}, keto-enol ratio) of the absorbance at the absorption maximum appeared near 480 nm (A_{CO}) to that at the shoulder near 420 nm (A_{OH}) was taken up. The changes of the keto-enol ratios with the ozone decolorations of these dyes are shown in Fig. 6. In the case of the ozone decolorations of PANDSA,[4] the percent residual values of the keto-enol raios after the ozone treatments of PANDSA for 60 s were 50.7—63.4% (average value: 56.3%). The values obtained in this work were 66.9—87.9% (average value: 73.3%). The two couples of dyes; 2, 4 and 5, 7, the initial values of the keto-enol ratios for two dyes of each couple were nearly the same, suggested that the ozone decoloration rates of the dyes increased with increasing the reduction rates of their keto-enol ratios. Therefore, the unexpected behavior of 5 in the Hammett plot (Fig. 5) seemed to be mainly based on the low reduction rate of its keto-enol ratio compared with the reduction rates of those of the others in these ozone decoloration reactions. From these results, initial attack of ozone on the dye molecule was anticipated to take place at the

NC double bond of its keto hydrazo form in a similar manner as described in the ozonolysis of PANDSA.[4)]

Oxidation Products of the Dyes. Initial ozone oxidation products of phenylazonaphthol dyes had already been reported in the previous paper.[3)] In the present work, fatty acids from the ozonations of these dyes were analyzed by the high-performance liquid chromatograph using a Shodex Ionpak C-811 column (50 cm 8 cm i.d, Showadenko Co., Ltd.) and 0.1% H_3PO_4 as eluent. The typical chromatogram is presented in Fig. 7. In all these reactions, the formations of maleic acid, glyoxylic acid, and oxalic acid were confirmed. Maleic acid seems to be the precursor for glyoxylic acid and oxalic acid, and glyoxylic acid seems to be that for oxalic acid. Consequently, it seems likely that the main organic product that was finally produced in these ozone oxidizing reactions is oxalic acid. Nitrate ion was also detected in the resulting reaction mixtures. This indicates that a part of the azo group of the dye appeared to oxidized to nitrate.

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