Effects of Cyclodextrins on Fading of Azo Dyes with Sodium Sulfite

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Abstract : Effects of cyclodextrins (CyD) on fading of various azo dyes such as 1-arylazo-2-naphthols, 1-arylazo-4-naphthols, and 2-arylazo-1-naphthols with sodium sulfite at 30°C were investigated. Fading was found to occur as a result of adding of sulfite to a conjugate enone moiety (C-addition) or to a conjugate iminone moiety (N-addition) in the hydrazone tautomer. In the case of C-addition mainly conducted for 1-aryazonaphthols, the addition of β -CyD lessened the rate of fading through formation of an inclusion complex at the naphthol site of the dye. α -CyD had only limited effect on the fading rate since the cavity was too small to permit dye inclusion. Inclusion complexes were confirmed by vis-spectral change in the dyes subsequent to the addition of CyD. α -CyD caused remarkable retardation of fading for 2-arylazo-1-naphthols following N-addition. Inclusion of the dyes at the aryl site that would promote complexation was considered as explanation for this. β -CyD acted as an efficient retarding agent in the N-addition process. Retarding efficiency of fading due to CyD is discussed based on substituent effects, disposition of dyes in CyD cavities, reaction sites of the dyes, and the binding constant (K_a).

Key words : cyclodextrin, binding constant, fading, azo dye, sodium sulfite

1 Introduction

Cyclodextrins (CyD) are cyclic oligomers consisting of α -D-(+)-glucopyranose residues, and include various compounds specifically into their relatively hydrophobic cavity¹⁾. In particular, since Cramer's systematic publication relating to azo dye-CyD complex formation²⁾, the complexes have been characterized by many researchers by means of X-ray diffraction³⁾⁻⁵⁾, NMR spectroscopy^{6),7)}, temperature jump^{2),8),10)}, pressure jump¹¹⁾, UV, CD, and fluorescence spectrophotometries^{2),10)-13)}. However, the majority of published studies on the azo-CyD complexes have been largely concerned on stability of the complex, and there are few reports focussing on reactions of azo dyes in the presence of CyD. In this respect, Sanchez et. al. have recently reported the effect of β -CyD on thermal *Z-E* isomerization of some azo dyes¹⁴⁾.

In order to acquire more marked CyD-effects such as rate-enhancement, rate-retardation, and high regioselectivities, bimolecular reaction systems are doubtlessly better choice. In the previous papers^{15),16)}, we have reported that azo dyes clearly fade with sodium sulfite through an addition of sodium sulfite to a conjugate enone moiety (C=C-C=O) [C-addition] or a conjugate iminone moiety (N=C-C=O) [N-addition] in hydrozone tautomer of the dyes. Upon the addition of CyD to this reaction system, the fading of the dyes must be retarded, depending on tightness of the CyD complexes as well as on the attacking sites of sulfite. We describe herein our results as to the fading of a variety of azo dyes with sodium sulfite in the presence of α - and β -CyDs.

2 Experimentals

2.1 Instruments and Materials

The chemical structures of azo dyes used were shown in Fig.1. These dyes were prepared from

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Fig.1 Structures of Used Dyes.

the coupling reactions of naphthol derivatives with diazonium salts of aniline or 1-naphthylamine derivatives according to conventional procedures¹⁷⁾, and purified either by recrystallization from water or ethanol, or in the case of the more soluble dyes, by precipitation with sodium acetate. The purity of the dyes was confirmed by paper chromatography (developer ; butanol : pyridine : water = 6 : 3 : 4). α - and β -CyDs were purchased from Nacalai Tesque and used without further purifications. ¹H and ¹³C-NMR spectra were recorded on a Hitachi R-1900 spectrometer. UV-vis spectra were conducted on a Shimadzu UV-260 spectrophotometer.

2.2 Binding Constant

The binding constants (K_a) for azo dye-CyD complexes were determined spectrophotometrically at 20°C. The spectral changes of azo dyes ($1.25 \times 10^{-5} - 5.0 \times 10^{-5}$ M) in the absence and the presence of CyD ($0 - 1.0 \times 10^{-2}$ M) were measured at pH 7.0. The K_a values were calculated according to the following equation²⁾.

$$[D][\text{CyD}]/\Delta A = 1/(K_a \Delta \epsilon_c) + [\text{CyD}]/\Delta \epsilon_c$$

where $[D]$ is the total concentration of a dye, $[\text{CyD}]$ is the total concentration of CyD, $\Delta \epsilon_c$ is the difference between the molar absorption coefficients for free and complexed dyes and ΔA is the change of absorbance of the dye on the addition of CyD.

2.3 Fading Rate Constants

A solution of sodium sulfite was added to a dye solution adjusted at pH 7.0 with phosphate buffer in the absence and the presence of CyD. Concentrations of these solutions were $1.25 - 2.0 \times 10^{-5}$ M for a dye, $0 - 2.0 \times 10^{-3}$ M for CyD, and $1.5 \times 10^{-3} - 5.0 \times 10^{-2}$ M for sodium sulfite. The reaction mixture was transferred into a quartz cell, immersed in the thermostatted bath maintaining at $30 \pm 0.5^\circ\text{C}$, and the fading reaction was pursued spectrophotometrically at appropriate intervals. The second-order rate constants of fading (k_0) were obtained by application of pseudo-first-order kinetics to the observed spectral changes.

2.4 Fading Product

After completion of a fading reaction with sodium sulfite in a phosphate buffer solution, tetraphenylphosphonium bromide (TPPB) was added to the reaction solution and the fading product was extracted with dichloromethane as an ion-complex of TPPB. The extract was concentrated and dried under vacuum. The ¹H-NMR spectrum of the oily residue was measured in CDCl₃. The chemical shifts were given in δ values using TMS as an internal standard. ¹H-NMR spectra of the fading products were also obtained directly from the fading reaction in a NMR sample-tube using D₂O as a solvent.

The reaction solutions of Dye-11, 14, 15, and 17 were subjected to paper chromatography after decolorization. The spots of arylamines were identified by successive spray of solutions of hydrochloric acid, sodium nitrite, and NW-acid (1-naphthol-4-sulfonic acid).

3 Results and Discussion

3.1 Fading Product

As reported previously, fading of azo dyes with sodium sulfite occurred through nucleophilic addition of sodium sulfite to the hydrazone tautomer of the dyes and could be classified into two types of reactions, C-addition and N-addition, based on UV-vis spectral behavior and the reaction sites of the dyes, which depended strongly

Scheme 1 Fading Mechanism.

on the structures of dyes¹⁶⁾. As the mechanisms were shown in **Scheme 1**, the fading products in C-addition are Michael adducts of sodium sulfite to a conjugate enone moiety in the hydrazone tautomer. However, C-addition is inhibited in steric origin when a bulky substituent such as a sulfo group lies near the reaction site, or when the hydrazone tautomer of azo dyes cannot have a conjugate enone moiety. In these cases, sulfite initially adds to α -nitrogen of the hydrazone tautomer of the dye (N-addition), followed by reduction of azo group to form two different amines, although N-addition shows much lower reactivity than C-addition.

The fading rate constants (k_0) of azo dyes employed here with sodium sulfite at 30°C were obtained from spectrophotometric behavior and listed in **Table 1**. These rate constants are classified distinctly into two groups; a group of relatively high reactivities ($289 - 1030 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$) as seen for Dye-1-8 and a group of low reactivities ($2.76 - 40.3 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$) as seen for Dye-9-17. Although spectral changes observed for these dyes by sodium sulfite were not shown here, isosbestic points in the visible region (near 405–468 nm) were observed for the former group with a decrease in absorbance of dye at λ_{max} , and conversely, no isosbestic point in the visible region was observed for the latter group. These spectral

characteristics and the reactivities are in good agreements with those of C-addition and N-addition, respectively as reported previously^{15),16)}.

In order to confirm the structure of fading products of Dye-2-4 and 8 with sodium sulfite, ^1H and ^{13}C -NMR spectra in D_2O were measured. The NMR data are shown in **Table 2**. In the ^1H -NMR spectra two proton signals appeared at δ 3.0-4.9 with small coupling constant ($J = 0.5\text{-}0.8 \text{ Hz}$). Furthermore, the ^1H -NMR spectra of the products as TPPB ion-complexes in CDCl_3 showed three proton signals at δ 2.2-4.9 coupling with each other (ABX system) and one singlet at δ 9.9-14.7. The spectral difference in D_2O and CDCl_3 indicates that an amino proton and a *trans*-proton to a sulfo group were deuterated in D_2O . From comparison with previously reported data for Dye-1, and 5-7^{15),16)}, the fading products of Dye-2-4 and 8 were determined as C-adducts of sulfite (Michael adducts, 18 for 1-arylaazo-4-naphthols and 19 for 1-arylaazo-2-naphthols) as exemplified in **Scheme 1**. The ^{13}C -NMR spectra of the fading products of Dye-2, 3, and 8 in D_2O , in which signals due to a methine carbon and a carbonyl carbon appeared at δ 55.7-60.0 and 196-199 respectively, support these structures. Since the fading product of Dye-4 was hardly soluble in D_2O , the ^{13}C -NMR spectrum was measured in CDCl_3 as an ion-complex with TPPB.

In contrast, the ^1H -NMR spectra of fading

Table 1 Fading Rate Constant (k_0) of Dyes with Sodium Sulfite at 30°C in the Absence of CyD, Binding Constant (Ka) of CyD with Dyes, and CyD-Effect on Fading Rates.

Dye	Rate constant(k_0) ^{a)} (10 ⁻⁴ M ⁻¹ s ⁻¹)	α -CyD				β -CyD			
		Ka (M ⁻¹)	20 ^{b)}	k_{CyD}/k_0 50 ^{b)}	100 ^{b)}	Ka (M ⁻¹)	20 ^{c)}	k_{CyD}/k_0 50 ^{c)}	100 ^{c)}
C-addition									
1	891	456±41	0.94	0.93	0.89	252±27	0.81	0.65	0.54
2	449	—	0.99	1.00	0.98	191±4	0.94	0.79	0.68
3	740	—	0.98	0.95	1.02	1180±70	0.46	0.28	0.20
4	1030	—	1.02	1.01	1.06	2890±340	0.70	0.51	0.39
5	416	—	1.00	1.01	1.05	1250±220	0.86	0.75	0.71
6	289	—	1.07	1.16	1.16	608±36	1.11	1.04	1.01
7	306	—	1.07	1.02	1.04	75±11	0.96	0.92	0.89
8	402	—	1.02	1.06	1.06	1370±110	0.96	0.81	0.65
N-addition									
9	4.68	2570±130	0.53	0.31	0.20	1920±120	0.65	0.46	0.31
10	40.3	3940±190	0.82	0.76	0.72	3240±190	0.65	0.61	0.58
11	2.76	4860±240	0.45	0.21	0.13	2000±100	0.52	0.34	0.24
12	9.67	1060±60	0.81	0.61	0.42	1650±80	0.90	0.70	0.52
13	6.30	909±91	0.69	0.51	0.35	1450±60	0.54	0.34	0.22
14	21.2	—	1.02	1.08	1.14	1150±60	0.56	0.34	0.20
15	16.3	—	1.09	1.11	1.03	2560±130	0.39	0.21	0.12
16	16.0	—	1.04	1.08	1.10	285±17	0.79	0.72	0.66
17	37.3	—	0.99	1.00	1.01	255±23	0.84	0.78	0.66

a) Average of duplicate runs. The error in these values is estimated to be 6%. b) Molar ratio of α -CyD and a dye. c) Molar ratio of β -CyD and a dye.

products of Dye-11, 14, 15, and 17 with sodium sulfite in D₂O did not show appreciable signals in the aliphatic regions except for methyl protons for Dye-11. Paper chromatogram of fading products of Dye-14, 15, and 17 gave same spot, the color of which changed from pale yellow to brilliant red by spraying a NW-acid solution ($R_f=0.46$). The spot was identified as naphthionic acid by comparison with the authentic sample. The main fading product for Dye-11 was *p*-toluidine from ¹H-NMR spectrum of the dichloromethane extract of the fading solution. Naphthionic acid for Dye-14, 15, and 17 and *p*-toluidine for Dye-11 were obtained in the yields of 85-98% and 99%, respectively (based on peak integration of ¹H-NMR spectra in D₂O). As reported previously for Dye-9, 10, 12, 13, and 16, the reduction of azo dyes to aromatic amines is characteristic for N-addition.

3·2 Effect of CyD

3·2·1 C-addition type

The effects of CyD on fading rates of Dye-1-8 with sodium sulfite are shown in **Table 1**, together with the binding constants (Ka) for the inclusion complex. The effects of CyD are expressed as the

rate-ratios of k_{CyD} (in the presence of CyD) and k_0 (in the absence of CyD). It should be noted that the fading of these dyes proceeds through C-addition of sulfite to the enone moiety at the naphthol side as mentioned above.

The gradual addition of β -CyD caused retardation of the fading significantly except for Dye-6. In contrast, α -CyD had slight effects on the rates of the fading except for Dye-1. These contrasting results can be primarily explained from inclusion of the dye at the naphthol side in CyD cavity. As well-known, β -CyD can form inclusion complexes with the naphthol-based dyes, but α -CyD cannot include the naphthol side of the dyes because of smaller diameter of its cavity^{2),9),11),12)}. The facts quite meet with our observed results as to spectral changes of the dyes in the visible regions by the addition of CyD (**Table 3**). Namely, upon the addition of β -CyD, shifts of λ_{max} of the dye and/or a decrease in the absorption at λ_{max} were observed to allow the determination of the Ka values, but α -CyD did not cause appreciable spectral changes except for Dye-1. The spectral changes of Dye-1 by α -CyD are fully anticipated from inclusion not

Table 2 Selective ^1H and ^{13}C -NMR Data of Fading Products.

Dye	NMR data of fading products (δ)
2	^1H (D_2O) ; 3.28 (d, 1 H, $J=0.5$ Hz, Ht), 4.81 (d, 1 H, $J=0.5$ Hz, Ha) ; ^1H (CDCl_3) ^{a)} ; 2.24 (dd, 1 H, $J=17.1$ and 6.8 Hz, Hc), 3.10 (dd, 1 H, $J=17.1$ and 1.0 Hz, Ht), 4.43 (dd, 1 H, $J=6.8$ and 1.0 Hz, Ha), 11.20 (s, 1 H, NH) ; ^{13}C (D_2O) ; 55.7 (d, C-2), 144.7 (s, C-1), 198.2 (s, C-4)
3	^1H (D_2O) ; 2.21 (s, 3 H, Me), 3.13 (d, 1 H, $J=0.8$ Hz, Ht), 4.77 (d, 1 H, $J=0.8$ Hz, Ha) ; ^1H (CDCl_3) ^{a)} ; 1.99 (s, 3 H, Me), 2.77 (dd, 1 H, $J=17.1$ and 7.7 Hz, Hc), 3.44 (dd, 1 H, $J=17.1$ and 1.0 Hz, Ht), 4.57 (dd, 1 H, $J=7.7$ and 1.0 Hz, Ha), 9.99 (s, 1 H, NH) ; ^{13}C (D_2O) ; 16.3 (q, Me), 58.4 (d, C-2), 144.5 (s, C-1), 198.4 (s, C-4)
4	^1H (D_2O) ; 3.16 (d, 1 H, $J=0.5$ Hz, Ht), 4.89 (d, 1 H, $J=0.5$ Hz, Ha) ; ^1H (CDCl_3) ^{a)} ; 2.98 (dd, 1 H, $J=16.7$ and 7.4 Hz, Hc), 3.63 (dd, 1 H, $J=16.7$ and 0.9 Hz, Ht), 4.88 (dd, 1 H, $J=7.4$ and 0.9 Hz, Ha), 11.08 (s, 1 H, NH) ; ^{13}C (CDCl_3) ^{a)} ; 39.2 (t, C-3), 58.1 (d, C-2), 142.1 (s, C-1), 195.1 (s, C-4)
8	^1H (D_2O) ; 3.01 (d, 1 H, $J=0.5$ Hz, Ht), 4.19 (d, 1 H, $J=0.5$ Hz, Ha) ; ^1H (CDCl_3) ^{a)} ; 2.94 (dd, 1 H, $J=17.1$ and 5.0 Hz, Hc), 3.59 (dd, 1 H, $J=17.1$ and 0.7 Hz, Ht), 4.31 (dd, 1 H, $J=5.0$ and 0.7 Hz, Ha), 14.65 (s, 1 H, NH) ; ^{13}C (D_2O) ; 60.0 (d, C-4), 144.0 (s, C-1), 196.5 (s, C-2)

a) Ion complex with TPPB.

at the naphthol side but at the hydrophobic benzene side.

When the inclusion with β -CyD at the naphthol side occurs, the reaction site (C-3) of 1-naphthol-based dyes (Dye-1-4) for sulfite is on the wall side of β -CyD in the complex, but the reaction site (C-4) of 2-naphthol-based dyes (Dye-5-8) is on the open side of β -CyD as illustrated in Fig.2. Therefore, β -CyD will protect 1-naphthol-based dyes more effectively from attack of sulfite than 2-naphthol-based dyes. These are typical cases ; remarkable retardation for Dye-3 and 4, and less effective retardation for Dye-5 and 8 than expected from their large Ka values. Furthermore,

Table 3 Spectral Characteristics in the Absence and the Presence of CyD.

Dye	$\lambda_{\text{max}}(\text{nm})^{\text{a)}$	α -CyD		β -CyD	
		$\lambda_{\text{max}}(\text{nm})^{\text{b)}$	$A_{\text{CyD}}/A_0^{\text{b),c)}$	$\lambda_{\text{max}}(\text{nm})^{\text{b)}$	$A_{\text{CyD}}/A_0^{\text{b),c)}$
1	473	476	0.95	477	0.77
2	468	468	1.02	472	0.97
3	471	471	0.99	469	0.74
4	482	482	1.01	481	0.82
5	482	482	0.99	484	0.86
6	479	479	1.00	482	0.90
7	476	476	0.99	477	0.98
8	503	503	1.02	507	1.00
9	489	497	0.88	491	0.88
10	496	501	0.94	498	0.93
11	496	505	0.93	498	0.86
12	489	493	0.87	491	0.88
13	501	504	0.89	500	0.84
14	513	513	1.01	516	0.93
15	523	523	1.00	523	0.89
16	486	486	1.01	489	0.95
17	519	519	1.01	520	0.96

a) In the absence of CyD. b) At $[\text{CyD}] / [\text{Dye}] = 100$.c) Ratio of absorbance at λ_{max} in the presence (A_{CyD}) and the absence of CyD (A_0). **Fig.2.** Inclusion Complexes of 1-arylaazo-4-naphthol(a) and 1-arylaazo-2-naphthol(b).

substituents on the dyes dramatically change efficiency of retardation by CyD. Though Dye-6 was included in relatively large Ka value, no retardation by β -CyD was observed possibly because inclusion at the naphthol site was rather difficult because of steric inhibition of C-6 sulfo group.

Thus, the rate-retardation efficiency of β -CyD was Dye-3 > Dye-4 > Dye-1 > Dye-2 for 1-naphthol-based dyes, and Dye-8 > Dye-5 > Dye-7 > Dye-6 for 2-naphthol-based dyes. The order shows influence of substituents on naphthol site and other site. Hydrophobic 2'-Me makes retardation more effective, and the Ka value larger as anticipated from deep inclusion. Conversely, a hydrophilic and bulky sulfo group at 2'- or 8-position inhibits the inclusion to make retardation

less effective. From these results, the rate-retardation is safely concluded to be caused by disposition of guest in CyD cavity, stability of complex as well as reaction sites.

3·2·2 N-addition type

This reaction starts from the addition of sulfite to α -nitrogen of hydrazone tautomer. Therefore, the situation is quite different from the C-addition type. Effects of CyD on the fading of Dye-9-17 are also shown in **Table 1** together with the Ka values. In particular, the addition of α -CyD strongly inhibited the fading for Dye-9-13 bearing a phenyl group at other side, in contrast with fading behavior of the corresponding Dye-1-3, and Dye 5-7. These striking differences are probably responsible for the shapes of the dye molecules because the molecular structure of 1-aryazonaphthols is L-letter shape, but that of 2-aryazonaphthols is relatively straight line-shape favorable for CyD-complexation. In fact, the CPK modeling of α -CyD complexation with the dyes reveals that the aryl site of 1-aryazonaphthols is obliged to be included shallowly in α -CyD cavity by steric inhibition due to C-8 and *peri*-H at the naphthol site, even if included, but that of 2-aryazonaphthols can be disposed deeply in α -CyD cavity. As a result, the azo group (reaction site) of 2-aryazonaphthols attains to the rim of α -CyD. Remarkable spectral changes for Dye-9-13 by the addition of α -CyD as well as large Ka values of these dyes with α -CyD reflect the difference in the binding situation for both regioisomers distinctly. Specific fitness of the 2-aryazo-isomers to α -CyD cavity must play a definitive role in the striking retardation of the fading reactions starting with the addition of sulfite to α -nitrogen of the hydrazone form. On the other hand, α -CyD for fading of Dye-14, 15, and 17 bearing two naphthyl residues was always ineffective because of too small diameter of the cavity to include the residue.

In parallel with behavior of α -CyD for inclusion of 1-aryl and 2-aryazonaphthols, β -CyD also distinguishes between inclusion of both regioisomers, although less distinctive than α -CyD. Dye-14 and 15, 2-aryazonaphthols, are incorporated into β -CyD cavity in large Ka values to undergo remarkable retardation of the fading. But Dye-16 and 17, 1-aryazonaphthols are incorporated into CyD cavity in small Ka values, and consequently the reaction site of the dyes is open to attack of

sulfite because of shallow inclusion probably in steric origin.

Substituents on the dyes again influence strongly the retardation of the fading as well as Ka values. However, efficiencies of retardation are not proportional to the Ka values. This is understandable since the more effective retardation must be caused by the more effective protection of the reaction site due to CyD inclusions. In other words, when the reaction site is extruded from CyD cavity, the retardation never occurs even when the Ka value is large. The typical example is Dye-10 bearing a nitro group. Judging from theoretical and experimental backgrounds^{18)~20)} that the nitrobenzene residue fits to CyD cavity, the reaction site, instead, seems extruded from CyD cavity. This specificity may be responsible for less efficient retardation despite of the large Ka value.

4 Conclusion

Fading of azo dyes with sodium sulfite retarded by addition of α -CyD and β -CyD through formation of inclusion complexes. α -CyD showed higher substrate-selectivity to cause more specific retardation than β -CyD. The retardation of the fading strongly depended on the reaction site of the dyes in addition to binding constants and disposition of dyes in CyD cavity. Substituents on the dyes controlled the efficiency of retardation. In a sense, fading behavior of the dyes may provide valuable information for disposition of the dyes in CyD cavity at dynamic state, otherwise not easy.

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[報文] 塩化鉄(Ⅲ)－塩化水素錯体を用いた N-クロロアセトアニリド類の Orton 転位

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N-クロロアセトアニリド (1) を塩化鉄(Ⅲ)－塩化水素錯体 ($\text{FeCl}_3\text{-HCl}$) のエーテル溶液に溶かして室温で放置すると、反応は 30 分で完結し、o-クロロアセトアニリド (10) と p-クロロアセトアニリド (11) が生成した。オルト-パラ比 (10/11) は $\text{FeCl}_3\text{-HCl}$ の濃度に依存し、最高 0.64 に達した。N-クロロ-2-メチルアセトアニリドからは 2 種類の、N-クロロ-3-メチルアセトアニリドからは 3 種類の転位生成物がそれぞれ見いだされた。

N-クロロ-2-メチルプロピオンアニリドと N-クロロ-2-メチルブチルアニリドからも、N-クロロ-2-メチルアセトアニリドの場合と同様に、相当する o-および p-クロロアニリドが得られ、アシル基が長くなると反応がわずかに速くなった。

1 の 3 種類の塩素誘導体はいずれも Orton 転位が起こることなく、相当するアニリドのみが得られた。メチル基と塩素をもつ N-クロロアセトアニリドと $\text{FeCl}_3\text{-HCl}$ との反応でも、Orton 転位は進行せず脱塩素反応のみが進み、それぞれに相当するアセトアニリドが得られた。1 と臭化鉄(Ⅲ)－臭化水素錯体 ($\text{FeBr}_3\text{-HBr}$) との反応からは、好収率で p-プロモアセトアニリドが生成した。

$\text{FeCl}_3\text{-HCl}$ を用いた 1 の Orton 転位では、パラ位は分子間転位で進行し、オルト位では分子間と分子内との転位が併発して反応が進行すると思われる。

(連絡者：山本二郎) Vol. 48, No. 5, 463 (1999)

[報文] 亜硫酸ナトリウムによるアゾ染料の退色に 及ぼすシクロデキストリンの効果

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亜硫酸ナトリウムによるアゾ染料 (1-アリルアゾ-2-ナフトール, 1-アリルアゾ-4-ナフトール, 2-アリルアゾ-1-ナフトール) の退色に及ぼすシクロデキストリン (CyD) の効果を 30℃ で検討した。染料の退色機構は染料のヒドラゾン互変異性体の共役エノンに対する亜硫酸の付加 (C-付加), 及び共役イミノンに対する亜硫酸の付加 (N-付加) といった染料の反応部位に応じて 2 種に大別できる。主に 1-アリルアゾナフトールでおきる C-付加においては、 β -CyD の添加により、染料のナフトール側で包接がおき、退色が抑制されるのに対し、空洞の径が小さい α -CyD の添加では、退色の抑制は見られなかった。一方、2-アリルアゾ-1-ナフトールに対しては、 α -CyD は顕著な退色の抑制効果が見られた。この場合の抑制効果は染料のアリル側で包接がおきることから理解した。また、 β -CyD は N-付加においても有効な抑制剤として作用した。このような CyD による退色の抑制効果について、置換基効果, CyD 空洞への染料取り込みの深淺, 染料の反応部位, 結合定数 (K_a) から考察した。

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