

〈研究論文(學術)〉

Vinylsulfone계 반응성 염료의 가수분해(III)

—혼합이량체의 형성—

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Hydrolysis of Vinylsulfonyl Reactive Dyes (III)

—Formation of Mixed Dimers—

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요약—알칼리 수용액 중에서의 Vinylsulfone(VS)계 반응성염료의 혼합상태의 가수분해 반응을 정량적으로 조사하였다. 혼합이량체의 생성 및 분해반응 속도상수를 각각의 염료의 가수분해반응에서 구한 속도상수를 이용하여 계산하였다. 단독이량체를 생성하는 염료들을 조합하였을 경우에는 혼합이량체가 생성되었다. C. I. Reactive Blue 19가 다른 VS계 염료들과 혼합되었을 경우에는 일반적으로 혼합이량체가 생성되었다. Blue 19와 Orange 16의 조합의 경우에는 낮은 염료농도에서만 혼합이량체가 생성되었으며, Red 22의 경우에는 단독 및 혼합이량체가 생성되지않았다. 단독이량체가 생성되지않는 Orange 7는 다른 VS계 염료들과의 조합에서 혼합이량체를 생성함을 확인하였다. Yellow 17의 혼합이량체의 분해속도 상수값이 가장 큼을 알 수 있었다.

1. INTRODUCTION

The hydrolysis of five vinylsulfonyl(VS) reactive dyes were investigated previously. The rate constants of dimerization for C. I. Reactive Yellow 17, Orange 16 and Blue 19 were estimated.¹⁾ It was found that the rate constants of dimerization and decomposition for these dyes varied widely with dyes. But no dimer for C. I. Reactive Orange 7 and Red 22 was detected under experimental conditions examined²⁾. Rys and Stamm³⁾ proved the formation of bis(arylsulfonylethyl) ether as the by-product in the hydrolysis of C. I. Reactive Yellow 17 and Blue

19, and showed the formation of mixed-dimer between two dyes. But the reason why some dyes form their dimer but the others does not has not been elucidated.

In the present paper, the hydrolytic behavior in admixture of five vinylsulfonyl reactive dyes are examined in an aqueous alkaline medium. Using the rate constants measured in the previous paper^{1, 2)}, those for the dimerization in admixture are estimated. The rate constants for various combination are compared with those for hydrolysis and reaction with cellulose, and the correlation between the logarithms of rate constants is discussed.

Table 1. VS dyes used

No.	C. I. Reactive	C. I. Constitution No.	Mol. Wt.	Commercial dyes used
1	Blue 19	61200	626.6	Sumifix Brilliant Blue R
2	Yellow 17	18852	693.0	Diamira Golden Yellow G
3	Orange 16	17757	617.5	Diamira Brilliant Orange 3R
4	Orange 7	17756	617.5	Diamira Brillinat Orange RR
5	Violet 5	18097	799.2	Diamira Red Violet 5R

Table 2. Chromatographic conditions

Apparatus	Shimadzu LC-6A type HPLC
Column	Wakogel LC ODS-10H 100mm(length) ϕ = 6.0mm I. D.
Mobile phase	10mM(NH ₄) ₂ HPO ₄ : Methanol(v/v) = 55 : 45(Yellow 17), 70 : 30 (Orange 7), 70 : 30(Orange 16), 82 : 18(Violet 4) and 50 : 50(Blue 19)
Flow rate	1.0ml/min
Temperature	30°C
Detector	Visible : 429nm(Yellow 17), 490 nm(Orange 7), 490nm(Orange 16), 559nm(Violet 5) and 600nm(Blue 19)
Integrator	Chromatopack CR-3A type

2. EXPERIMENTAL

2.1 Reactive Dyes

The VS dyes examined are shown in Table 1 and their chemical structures are shown by C. I. Constitution Number. Their commercial dyes were purified by the same method as before¹⁾. The components of dyes were analyzed by high pressure liquid chromatography. The chroma-

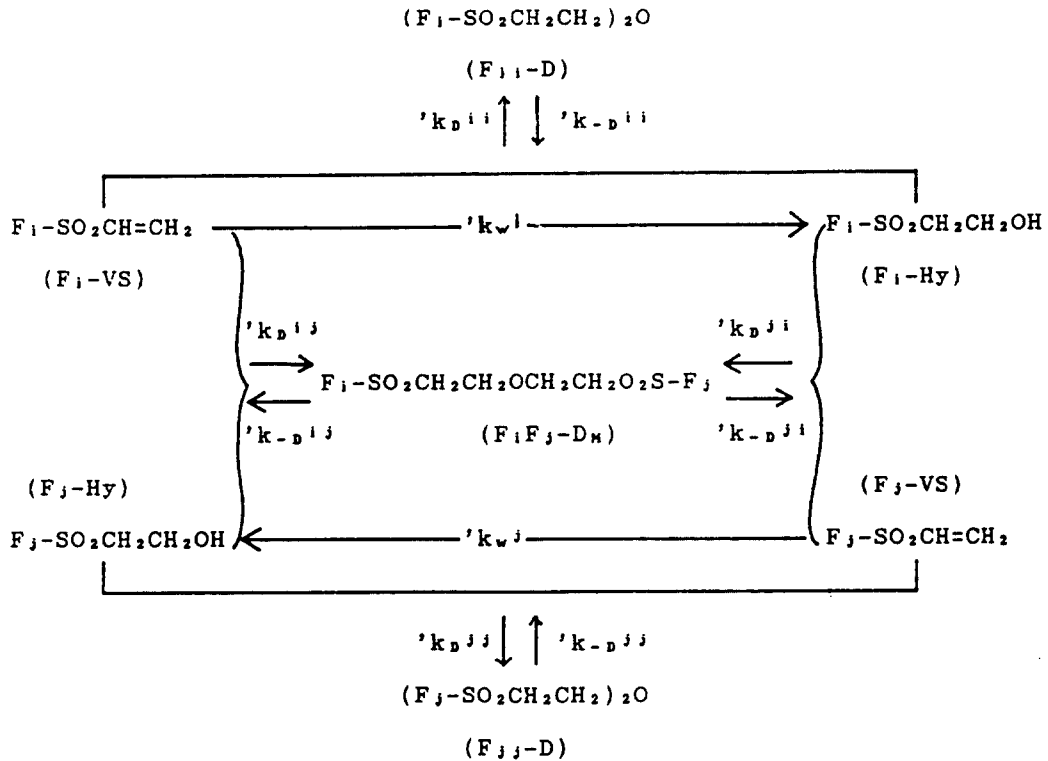
tographic conditions are shown in Table 2.

Because of proportionality of the retention time of the corresponding components for different dyes and their combinations, each component was detected at respective λ_{max} 's for two VS dyes mixed. The assignments of each component were the same as before except for mixed-dimer.^{1,2)} The experiment of mixed-dimerization was carried out by a mixing the Hy type of one dye and the VS type of the other dye. The experimental methods for hydrolysis were the same as before except for mixing of dyes. The chemicals and synthetic methods of the Hy type of each dye as model compounds were the same as before.^{1,2)}

2.2 Reaction Scheme of Dimerization in Mixture

The reaction scheme of VS dyes was given in the previous paper.^{1,2)} The VS type is converted into the Hy type in an alkaline solution. The VS and Hy types are reacted to give the homo-dimer(D) of ether type. In admixture, a mixed-dimer(D_M) of ether type is also formed by the reaction between the Hy type of a dye and the VS type of the other dye.

The reactions of dimerization in admixture are written as shown in Scheme 1. Thus, the changes in the concentrations of the VS, Hy, D and D_M types with time are given by :



Scheme 1

$$\begin{aligned}
 D(F_i - VS) / dt = & -'k_{w^i}(F_i - VS) - 'k_{D^{ii}}(F_i - VS) \\
 & (F_i - Hy) + 'k_{-D^{ii}}(F_{ii} - D) - 'k_{D^{ij}}(F_i - VS) (F_j - \\
 & Hy) + 'k_{-D^{ij}}(F_i F_j - DM) \quad (1)
 \end{aligned}$$

$$\begin{aligned}
 D(F_i - Hy) / dt = & 'k_{w^i}(F_i - VS) - 'k_{D^{ii}}(F_i - VS) (F_i - \\
 & Hy) + 'k_{-D^{ii}}(F_{ii} - D) - 'k_{D^{ij}}(F_i - VS) (F_i - VS) \\
 & (F_j - Hy) + 'k_{-D^{ij}}(F_i F_j - DM) \quad (2)
 \end{aligned}$$

$$\begin{aligned}
 D(F_{ii} - D) / dt = & 'k_{D^{ii}}(F_i - VS) (F_i - Hy) - 'k_{-D^{ii}}(F_{ii} - D) \\
 & \quad (3)
 \end{aligned}$$

$$\begin{aligned}
 D(F_i F_j - DM) / dt = & 'k_{D^{ij}}(F_i - VS) (F_j - Hy) + 'k_{D^{ji}} \\
 & (F_j - VS) (F_i - Hy) - 'k_{-D^{ij}}(F_i F_j - DM) - 'k_{-D^{ji}}(F_i F_j - DM) \quad (4)
 \end{aligned}$$

Where [] denotes the concentration(mol/dm³) of corresponding component.

2.3 Calculation Method of Rate Constants

The kinetic parameters can be obtained by the same method as before²⁾. The present authors estimated the rate constants for the hydrolysis reaction of the individual dye.^{1,2)}

Using the rate constants measured by the hydrolysis of each dye, those for the formation and decomposition of the mixed-dimer for VS dyes in mixture were determined. The fittest values of parameters can be obtained by a grid search method⁵⁾ by finding the minimum of the sum of the squared deviations between the experimental concentrations for each component and the theoretical ones described by the simultaneous equations (1)–(4). The Hamming method^{6a)} and a fourth-order Runge-Kutta method^{6b)} were used for numerical calculation.

3. RESULTS AND DISCUSSION

3.1 Assignment of Liquid Chromatograms

The formation of the mixed-dimer between

Yellow 17 and Blue 19 was confirmed by paper chromatography and the synthesis of corresponding mixed-dimer²¹. The liquid chromatograms of some samples for the mixture of C. I. Reactive Orange 16 and Blue 19 are shown in Fig. 1 as an example. The peaks of Hy type for both dyes were assigned by the corresponding synthesized samples of the Hy type. The peaks for the VS, D and D_M types were assigned by the same method as before by using paper chromatography.^{1,23}

In Fig. 1, the chromatogram(Fig. 1(a)) of the mixture of Orange 16 and Blue 19, which was analyzed at λ_{\max} of Blue 19 includes no components of Orange 16, and that(Fig. 1(b)) analyzed at λ_{\max} of Orange 16 also includes the

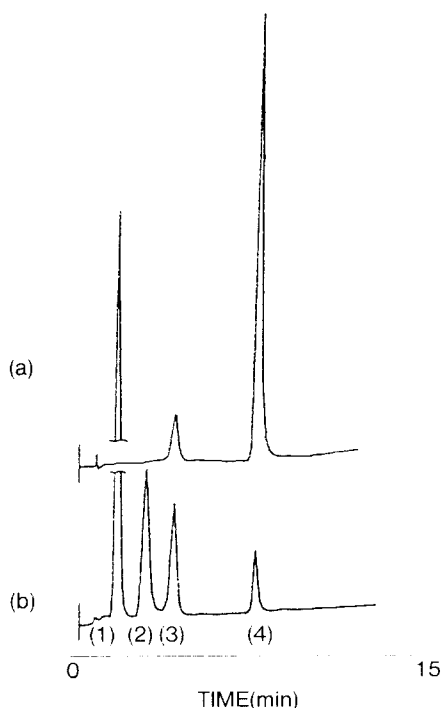


Fig. 1. Liquid chromatograms of (a) the mixture analyzed at λ_{\max} of Orange 16(D_M types was formed.) The Peaks (1), (2), (3), and (4) were assigned as the Hy, VS, D_M types of Orange 16, and the Hy type of Blue 19, respectively.

components of Blue 19 in the mixed-dimer. Then, the precise concentrations of Orange 16 are obtained by subtracting the corresponding concentration of Blue 19 from the total on of the mixed-dimer. From the ratio of molar extinction coefficients at λ_{\max} for each dye, the equimolar formation of mixed-dimer was confirmed. By use of the similar procedure, the concentrations of each component in various combinations were determined from the liquid chromatograms.

3.2 Estimation of Rate Constants

3.2.1 Mixed-dimerization

In order to minimize the number of components in the hydrolyses of a mixture, a solution of a dye after the complete hydrolysis was mixed with a solution of the sulfatoethylsulfonyl type for the other dye at a given pH. The variations in the concentrations of various components with time for three combinations of VS dyes are shown in Fig. 2-4. In case of Fig. 2, the Hy or VS type of Yellow 17 was mixed with VS or Hy type of Blue 19, respectively, at pH 11.43. Since the mixed-dimerization between Yellow 17 and Blue 19 occurred very fast, monotonous decreasing or increasing profiles for the mixed-dimer and both the Hy types were shown in the figures besides their initial increase or decrease, which is too fast to be drawn in this time scale.

The hydrolytic behavior of the mixture of Orange 16 and Blue 19 are shown in Fig. 3. Both the homo and mixed-dimers for Blue 19 were formed, but no homo-dimer for Orange 16 was detected due to the low dye concentration.²³ The hydrolytic behavior of the mixture between Orange 7 and Blue 19 are shown in Fig. 4, where Orange 7 producing no homo-dimer formed the mixed-dimer with Blue 19 in the hydrolysis.

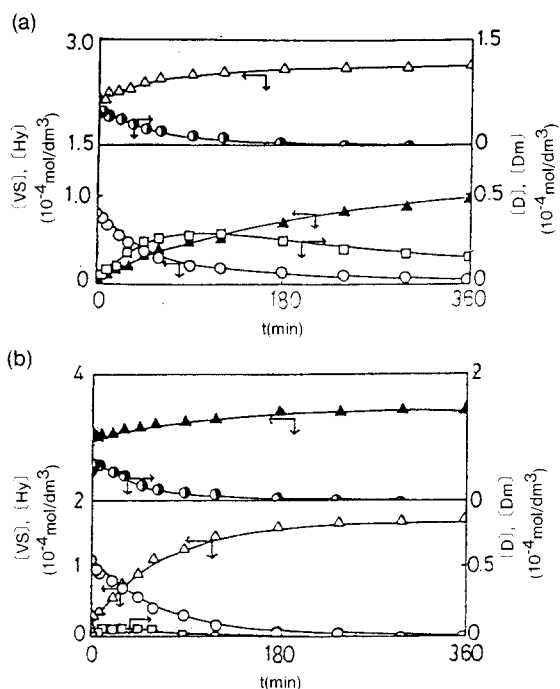


Fig. 2. Hydrolytic behavior of (a) the mixture of C. I. Reactive Yellow 17 (Hy) and Blue 19 (VS), and (b) the mixture of Blue 19 (VS) and Yellow 17 (Hy) at 50°C and pH 11.43. Solid lines describe the theoretical curves for the reaction of hydrolysis in mixture by use of the corresponding parameters of Table 3. Symbols (Blue 19) : ○ : VS type, ▲ : Hy type, □ : homo-dimer, Yellow 17 : ● : VS type, △ : Hy type, ■ : homo-dimer, ● : mixed-dimer) describe the experimental values of each component.

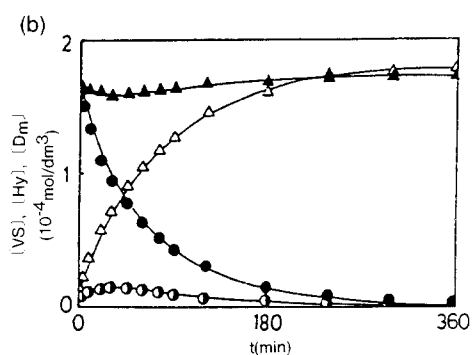
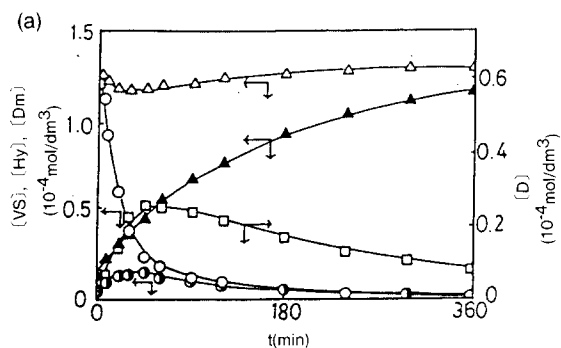


Fig. 3. Hydrolytic behavior of (a) the mixture of C. I. Reactive Orange 16 (Hy) and Blue 19(VS), and (b) the mixture of Orange 16(VS) and Blue 19(Hy) at 50°C and pH 11.65. Solid lines describe the theoretical curves for the reaction of hydrolysis in mixture by use of the corresponding parameters of Table 3. Symbols (Blue 19 : ○ : VS type, ▲ : Hy type, □ : homo-dimer, Orange 16 : ● : VS type, △ : Hy type, ● : mixed-dimer) describe the experimental values of each component.

The rate constants for the formation and decomposition of the mixed-dimer for the different dye combinations were determined by using the kinetic parameters obtained by the hydrolysis of individual dye. The values of k_{D^j} for forward reaction and those of k_{-D^j} for backward reaction of the mixed-dimerization are listed in Table 3. Their values divided by $[OH^-]$ for the different dye combinations are listed in Table 4.

As shown in Table 4, the values of rate constants, k_{D^j} , for formation of the mixed-dimer varied with dye combinations. But the differences in the rate constants for the mixed-dimer between dye combinations were smaller than those of the homo-dimer. The value of rate constant, k_{D^j} , for formation of the homo-dimer for Blue 19 was 1000 times larger than that

for Orange 16. But the value of rate constant, k_{D}^{ij} , for formation of the mixed-dimer for a mixture of the VS type of Yellow 17 and the Hy type of Blue 19 was ten times larger than that for a mixture of the VS type of Yellow

17 and the Hy type of Orange 7.

The reaction mechanism for the dimerization was discussed in the previous paper and the values of k_{D}^{ij} for homo-dimer varied with dyes and those included a term of the dissociation

Table 3. Rate constants for the mixed-dimerization of VS dyes at 50°C

C. I. Reactive		pH	k_{D}^{ij} (dm ³ /mol min)	k_{-D}^{ij} (min ⁻¹)	k_{D}^{ij} (dm ³ /mol min)	k_{-D}^{ij} (min ⁻¹)
VS(10 ⁻⁴ mol/dm ³)	Hy(10 ⁻⁴ mol/dm ³)					
Blue 19 (1.34) ^a	Yellow 17 (2.53)	11.43	46	0.018	74	0.033
Yellow 17 (1.71)	Blue 19 (3.32)					
Blue 19 (1.32)	Orange 16 (1.28)	11.65	36	0.022	72	0.021
Orange 16 (1.79)	Blue 19 (1.72)					
Blue 19 (1.32)	Orange 16 (2.55)	11.65	36	0.019	66	0.021
Orange 16 (1.79)	Blue 19 (3.43)					
Blue 19 (1.32)	Orange 16 (3.84)	11.65	38	0.023	72	0.021
Orange 16 (1.79)	Blue 19 (5.16)					
Yellow 17 (1.64)	Orange 16 (1.58)	11.42	42	0.022	54	0.039
Orange 16 (1.76)	Yellow 17 (1.62)					
Blue 19 (1.94)	Orange 7 (3.06)	11.43	12	0.0011	6.0	0.015
Orange 7 (1.66)	Yellow 17 (2.54)					
Yellow 17 (1.76)	Orange 7 (2.48)	11.44	2.0	0.0054	6.0	0.015
Orange 7 (1.66)	Yellow 17 (2.54)					
Blue 19 (1.84)	Violet 5 (3.26)	11.43	36	0.0061	58	0.011
Violet 5 (1.66)	Blue 19 (3.12)					

Dye combinations of the upper side in each row correspond to Experiment 1, and those of lower side to Experiment 2.

Table 4. Kinetic parameters for the dimerization of VS dyes at 50°C

F _i -VS	Blue 19(1)	Yellow 17(2)	Orange 16(3)	Orange 7(4)	Violet 5(5)
F _j -Hy	(k _w ¹ =0.689)	(k _w ² =1.03)	(k _w ³ =0.643)	(k _w ⁴ =1.32)	(k _w ⁵ =0.743)
Blue 19 (1)	$k_{D}^{11}=1.04 \times 10^4$ $k_{-D}^{11}=0.572$	$k_{D}^{12}=5.0 \times 10^3$ $k_{-D}^{21}=2.2$	$k_{D}^{31}=2.8 \times 10^3$ $k_{-D}^{31}=0.86$	$k_{D}^{41}=8.1 \times 10^2$ $k_{-D}^{41}=0.151$	$k_{D}^{51}=4.4 \times 10^3$ $k_{-D}^{51}=0.75$
Yellow 17 (2)	$k_{D}^{12}=3.1 \times 10^3$ $k_{-D}^{12}=1.2$	$k_{D}^{22}=1.03 \times 10^3$ $k_{-D}^{22}=20.8$	$k_{D}^{32}=3.7 \times 10^3$ $k_{-D}^{32}=2.7$	$k_{D}^{42}=3.9 \times 10^2$ $k_{-D}^{42}=0.98$	×
Orange 16 (3)	$k_{D}^{13}=1.5 \times 10^3$ $k_{-D}^{13}=0.86$	$k_{D}^{23}=2.9 \times 10^3$ $k_{-D}^{23}=1.5$	$k_{D}^{33}=9.22$ $k_{-D}^{33}=6.12 \times 10^{-3}$	—	×
Orange 7 (4)	$k_{D}^{14}=5.1 \times 10^2$ $k_{-D}^{14}=0.42$	$k_{D}^{24}=1.3 \times 10^2$ ×	—	×	—
Orange 5 (5)	$k_{D}^{15}=2.4 \times 10^3$ $k_{-D}^{15}=0.42$	×	—	×	—

$k_{D}^{ij}(\text{dm}^6/\text{mol}^2 \text{ min})=k_{D}^{ij}/[\text{OH}^-]$, $k_{-D}^{ij}(\text{dm}^3/\text{mol min})=k_{-D}^{ij}/[\text{OH}^-]$
 $k_w^6=0.553$, $k_w^7=0.744$, $k_w^8=0.651$, $k_w^9=0.306$, $k_w^{10}=0.785$

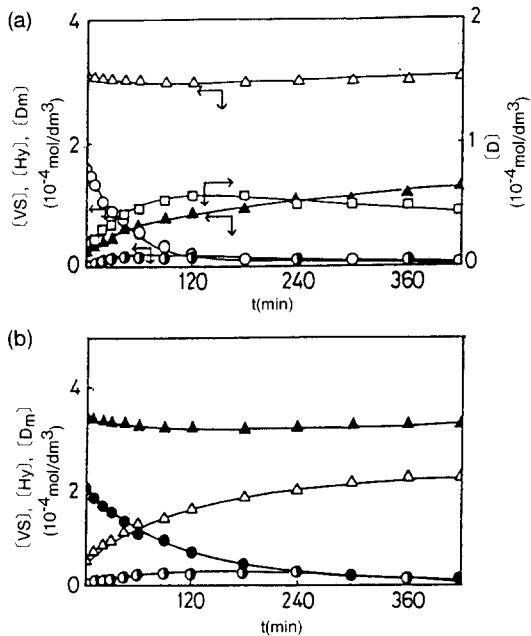


Fig. 4. Hydrolytic behavior of (a) the mixture of C. I. Reactive Orange 7(Hy) and Blue 19(VS), and (b) the mixture of Orange 7(VS) and Blue 19 (Hy) at 50°C and pH 11.43. Solid lines describe the theoretical curves for the reaction of hydrolysis in mixture by use of the corresponding parameters of Table 3. Symbols (Blue 19 : ○ : VS type, ▲ : Hy type, □ : homo-dimer, Orange 7 : ● : VS type, △ : Hy type, ● : mixed-dimer) describe the experimental values of each component.

constants, k_a^i , of β -hydroxyl group of the Hy type.²¹ And also the values of ${}^m k_D^{ij}$ for mixed-dimer included a term of K_a^i of the Hy type of each dye.

$${}^m k_D^{ij} = {}^m k_D^{ij} K_a^i \quad (5)$$

where ${}^m k_D^{ij}$ is the forward second-order rate constant of mixed-dimer and K_a^i is the acid dissociation constant of β -hydroxyl group for

the Hy type of each dye.

A combination of dyes producing the homo-dimer easily formed the mixed-dimer. For Red 22 which no homo-dimer was formed, it was confirmed that mixed-dimer was not formed under the conditions examined. In case of Orange 7 which no homo-dimer was also formed, the mixed-dimer was formed by hydrolysis in admixture with different dyes, but the values of ${}^m k_D^{ij}$ were small(cf. Table 4).

For the hydrolysis in admixture, the easiness of mixed-dimerization was ordered as following :

Blue 19 > Yellow 17 > Orange 16 > Orange 7

This order is almost similar to that of homo-dimer, From this result, the easiness of mixed-dimerization is also depends upon the degree of ionization of the Hy type of each dye and the kinetic parameters for mixed-dimerization.²¹

3.2.2 Decomposition of mixed-dimer

The mixed-dimer is decomposed to both sides, as shown in reaction scheme 1. The reverse reaction of mixed-dimer may occur in two steps, ionization of mixed-dimer and disproportionation with rate constants.

The composition of mixed-dimer from Blue 19 and VS dyes yielded the Hy type of Blue 19 in higher concentration than the VS type. For the mixed-dimer produced by a combination with Orange 7, on the other hand, the VS type of Orange 7 was produced in higher concentration than the Hy type In general, the VS dyes having higher tendency to form the homo and mixed-dimers show a property that the mixed-dimer are decomposed to give the Hy type in higher concentration than VS type.

In case of the mixed-dimer with Yellow 17, the values of k_D^{21} and k_D^{12} are larger than

those of k_{-D}^{ij} ($i, j \neq 2$) for other dye combinations. Thus, the reverse reactions of homo and mixed-dimerization for Yellow 17 were faster than the other reverse reactions, although the values of k_{-D}^{22} were larger than those of k_{-D}^{21} and k_{-D}^{12} .

Comparisons between dye combinations has shown that the rate constants of reverse reaction of the mixed-dimer vary with dye combinations. But the differences in the values of k_{-D}^{ij} between dye combinations were smaller than those of the homo-dimer.

4. SUMMARY

The hydrolytic reactions in an aqueous alkaline solution containing different vinylsulfonyl reactive dye combinations were kinetically investigated. The rate constants of the formation and decomposition for the mixed-dimer were determined by using the rate constants estimated in the hydrolysis of each dye. A combination of dyes yielding the homo-dimer formed the mixed-dimer. When Blue 19 was mixed with the other VS dyes, the mixed-dimer was usually formed. In a combination of Blue 19 and Orange 16, the mixed-dimer was formed even at the low dye concentrations. Red 22

formed neither mixed-dimer nor homo-dimer. In the Orange 7 yielding no homo-dimer formed the mixed-dimer in the hydrolysis in admixture with the different VS dyes. The values of the rate constants of decomposition for the mixed-dimer of Yellow 17 were the largest. The easiness of dimerization was depends upon the rate of hydrolysis.

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