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〈Research Paper〉

# Hydrolytic Behavior of Vinylsulfonyl Reactive Dyes

## *- Easiness of Dimerization -*

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**Abstract:** The aim of the current study is to identify the dimerization and decomposition kinetics of the F-$D_M$ type. The regeneration of F-VS from $F_iF_j$-$D_M$ or the reversibility of the dimerizations were investigated. The order of real rate constants of the dimerization($'k_D^{ij}$) would seem to be similar to that of rate constants of a dimerization($k_D^{ij}$) for VS dyes at a given pH because of the constancy of the equilibrium constants($K_a^j$-value). The reverse reactions of the $D_M$ types are appeared to occur in two steps, the deprotonation of α-carbon of the $D_M$ types and disproportionation. The ratio of the decomposition of the $D_M$ type to F-Hy and F-VS appears to be related with the ratio of $K_i/K_j$. Similarities were also found among various other reactions, including homo- and mixed dimerization. VS dyes undergoing fast hydrolysis have difficulty in forming a dimer. The higher the reactivity with cellulose or hydroxide ion, the smaller the dimerization. The easiness of the dimerization was thus found to be inversely proportional to the rate of hydrolysis.

**Keywords:** *VS dye, hydrolysis, admixture, rate constant, dimerization*

## 1. Introduction

Vinylsulfonyl(VS) dyes have grown to become the largest dye class of reactive dyes. For technological and scientific reasons, the hydrolysis of reactive dyes is a very important process. Aqueous solutions of reactive dyes become unreactive towards fiber through hydrolysis. Hydrolysis is the same type of reaction as fixation to the functional groups of fibers, in particular to cellulose hydroxyl groups. The reactions of reactive dyes can be classified into two main mechanisms, i.e., substitution and addition. A large number of dyes that exhibit a substitution reaction carry reactive groups based on nitrogen-containing heteroaromatic groups. Heteroaromatic nitrogen atoms, because of their electronegativity, cause an electron deficiency in the adjacent carbon atoms, which then become susceptible to a nucleophilic substitution reaction. The reaction mechanism of VS dyes differs from other reactive dyes, such as chlorotriazinyl dyes. The reaction occurs via nucleophilic addition(Michael addition). This reaction mechanism of VS dyes was previously reviewed by Stamm1). The kinetics and mechanism of hydrolysis of mono-(MCT) and dichlorotriazinyl(DCT) reactive dyes have been intensively studied to understand the reaction mechanism of reactive dyeing2-4). Despite the widespread application of VS dyes for cellulose fiber, fundamental studies on the kinetics of hydrolysis are rather rare. Zhu et al.5) determined the reaction rate constants of the alkaline hydrolysis and alcoholysis of a VS reactive dye and found that the ratio of the reaction rate constants of this reactive dye with n-propanol, iso-propanol, and water is 1.00 : 0.19 : 0.52. He et al.6) studied the alkaline hydrolysis of some bifunctional reactive dyes using $^1$H-NMR and found that the rate constant of hydrolysis of VS group is three to four times larger than that of the MCT group.

The reaction mechanism of VS dyes in an admixture is given below(cf. Scheme 1). The VS(F-VS) type is able to undergo an addition reaction with water to yield the hydroxyethylsulfonyl(F-Hy) type, which is normally inactive to dyeing. Rys and Stamm investigated the hydrolytic reaction of Yellow 17 and Blue 19 and

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confirmed the formation of the Hy type by paper chromatography[7]. The VS type and Hy type react further to give the dimer(F-D and F-$D_M$) as a by-product in the hydrolysis of VS groups. Panchartek et al.[8] reported an unknown ether type product as a by-product of the alkaline hydrolysis of VS dyes for the first time. Rys and Stamm have shown this by-product to be bis(arylsulfonyl)ether[7]. Thus, they also confirmed the formation of a homo-dimer(F-D) by paper chromatography using the corresponding synthesized samples.

In addition the formation of a mixed-dimer(F-$D_M$) during the hydrolysis of two dyes was reported, although the reason why the probability of F-D or F-$D_M$ formation was so different when changing the kind of dye still remains unknown. From the view point of the reaction mechanism, the formation and decomposition of F-$D_M$ have been rarely studied, yet this is required to elucidate the detailed mechanism of Michael addition. Therefore, the aim of the current study is to identify the dimerization and decomposition kinetics of the F-$D_M$ type.

Accordingly, the hydrolytic behavior in an admixture of ten VS reactive dyes is examined in an aqueous alkaline solution. The rate constants of hydrolysis reactions for the ten VS dyes and those for the dimerization in admixture are estimated. The rate constants for various combinations are compared with those for hydrolysis and for the reaction with cellulose, plus the similarity between the various reactions of the VS dyes is discussed.

## 2. Experimental

### 2.1 Reactive dyes

The VS dyes examined are summarized in Table 1. The Hy types of these dyes were purified by the same method as described previously[9]. The molar extinction coefficients of the Hy type for each dye at various wavelengths in water are listed in Table 1. It was confirmed that the $\varepsilon_{max}$ for the VS dyes used showed no variation relative to the reaction of the VS groups. The components of the dye were analyzed by high pressure liquid chromatography(HPLC). The hydrolytic behavior was examined by the same experimental method as reported previously[10-12]. In order to determine the kinetic aspects of the elementary process of

**Table 1.** VS Dyes used and $\varepsilon_{max}$(cm dm$^3$/mol) of Hy type for each dye at various wavelengths

| No. | C. I. Reactive | Wavelength(nm) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 419 | 429 | 490 | 510 | 520 | 546 | 559 | 594 | 600 |
| | $\lambda_{max}$ for | $F_6$ | $F_2$ | $F_3$, $F_4$ | $F_7$ | $F_8$ | $F_9$ | $F_5$ | $F_{10}$ | $F_1$ |
| 1 | Blue 19 | - | 1530 | 2700 | - | - | - | 10400 | - | 14100 |
| 2 | Yellow 17 | - | 25500 | 8490 | - | - | - | - | - | 0 |
| 3 | Orange 16 | - | 11100 | 24800 | - | - | - | - | - | 0 |
| 4 | Orange 7 | - | 10700 | 18500 | - | - | - | - | - | 0 |
| 5 | Violet 5 | - | - | - | - | - | - | 21400 | - | 4410 |
| 6 | Yellow 14 | 24600 | - | - | - | - | - | - | - | - |
| 7 | Red 22 | - | - | - | 23100 | - | - | - | - | - |
| 8 | Red 23 | - | - | - | - | 23800 | - | - | - | - |
| 9 | Violet 4 | - | - | - | - | - | 19500 | - | - | - |
| 10 | Blue | - | - | - | - | - | - | - | 15600 | - |

*Blue: no color index number

dimerization in an admixture, i.e., mixed-dimerization, $F_i$-VS and $F_j$-Hy(i≠j, vise-versa) were used as the starting materials. The mixed-dimerization was then carried out in these admixture solutions at constant pHs adjusted by NaOH. The chemicals and synthetic methods of F-Hy were also the same as before[10].

## 2.2 Reaction scheme of hydrolysis in mixture

The reaction of the VS dyes in an admixture is given in Scheme 1. $F_i$-VS was converted into $F_i$-Hy in an alkaline solution. $F_i$-VS and $F_i$-Hy were reacted to produce $F_{ii}$-D. In an admixture, $F_iF_j$-$D_M$ is also formed due to the reaction between the $F_i$-Hy of the i-th dye and the $F_j$-VS of the j-th dye and vice-versa. The hydrolysis reactions, including dimerization for the admixture of the $F_i$- and $F_j$-dyes(i≠j), are written as shown in Scheme 1. Here, although the conversion of $F_i$-VS to $F_i$-Hy has already been authorized, the validity of the elementary scheme leading to $F_iF_j$-$D_M$ will be discussed later. Four out of seven equations describing the changes in the concentrations of the eight species, $F_i$-VS, $F_i$-Hy, $F_{ii}$-D and $F_iF_j$-$D_M$ relative to time are:

$$d[F_i\text{-VS}]/dt = -{}'k_w^{i}[F_i\text{-VS}] - {}'k_D^{ii}[F_i\text{-VS}][F_i\text{-Hy}] + {}'k_{-D}^{ii}[F_{ii}\text{-D}] - {}'k_D^{ij}[F_i\text{-VS}][F_j\text{-Hy}] + {}'k_{-D}^{ij}[F_iF_j\text{-}D_M] \cdots\cdots\cdots\cdots (1)$$

$$d[F_i\text{-Hy}]/dt = {}'k_w^{i}[F_i\text{-VS}] - {}'k_D^{ii}[F_i\text{-VS}][F_i\text{-Hy}] + {}'k_{-D}^{ii}[F_{ii}\text{-D}] - {}'k_D^{ij}[F_i\text{-VS}][F_j\text{-Hy}] + {}'k_{-D}^{ij}[F_iF_j\text{-}D_M] \cdots\cdots\cdots (2)$$

$$d[F_{ii}\text{-D}]/dt = {}'k_D^{ii}[F_i\text{-VS}][F_i\text{-Hy}] - {}'k_{-D}^{ii}[F_{ii}\text{-D}] \cdots\cdots\cdots\cdots (3)$$

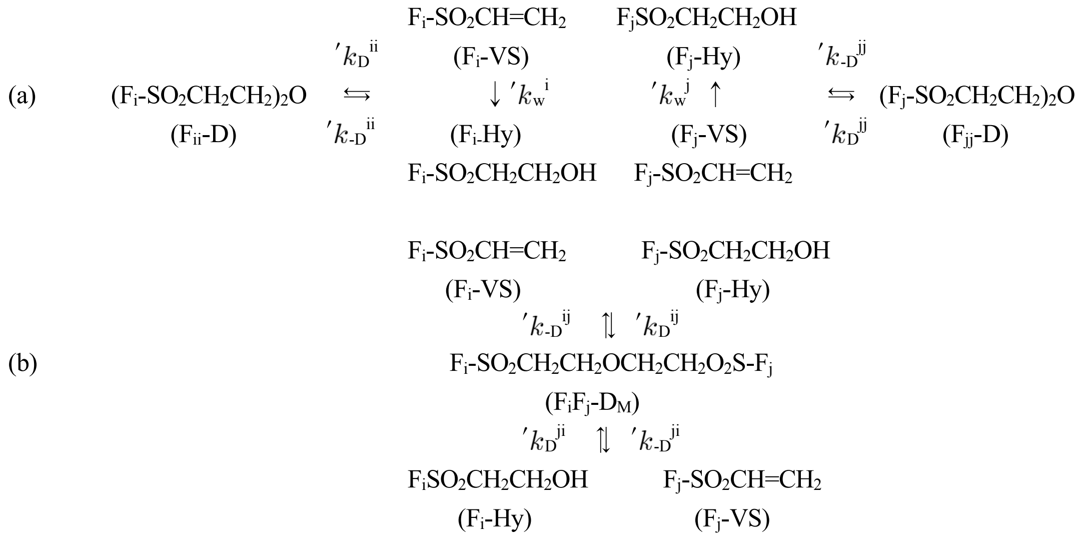
$$d[F_iF_j\text{-}D_M]/dt = {}'k_D^{ij}[F_i\text{-VS}][F_j\text{-Hy}] + {}'k_D^{ji}[F_j\text{-VS}][F_i\text{-Hy}] - {}'k_{-D}^{ij}[F_iF_j\text{-}D_M] - {}'k_{-D}^{ji}[F_iF_j\text{-}D_M] \cdots\cdots\cdots (4)$$

where [ ] denotes the concentration(mol/$dm^3$) of the corresponding component and various k's are defined in the Nomenclature. The remaining three equations for the $F_j$-VS, $F_j$-Hy, and $F_{jj}$-D species, besides $F_iF_j$-$D_M$ species, can be obtained by exchanging i and j with each other in each equation: Eqs. (1') - (3').

## 2.3 Calculation method of rate constants

The rate constants in the above equations, such as ${}'k_w^{i}$, ${}'k_w^{j}$, ${}'k_D^{ii}$, ${}'k_D^{jj}$, ${}'k_{-D}^{ii}$ and ${}'k_{-D}^{jj}$, were calculated using the same method as reported previously[10,11]. The fittest rate constant values for various reactions were obtained using a grid search method[13]. The Hamming method and a fourth-order Runge-Kutta method were used for the numerical calculation[14].

The rate constants(${}'k_w^{i}$ and ${}'k_w^{j}$) previously obtained and those of the homo-dimerization(${}'k_D^{ii}$, ${}'k_D^{jj}$, ${}'k_{-D}^{ii}$ and ${}'k_{-D}^{jj}$) for the starting VS dyes were used after converting them to values at corresponding pHs. The rate constants for the $D_M$ type were obtained from two kinds of experiments. The values of ${}'k_D^{ij}$ and ${}'k_{-D}^{ij}$ for the $D_M$ type were estimated based on a mixed dimerization between $F_i$-VS and $F_j$-Hy(Experiment 1),



(a)

$$\begin{array}{ccccccc} & & F_i\text{-}SO_2CH{=}CH_2 & & F_jSO_2CH_2CH_2OH & & \\ & {}'k_D^{ii} & (F_i\text{-VS}) & & (F_j\text{-Hy}) & {}'k_{-D}^{jj} & \\ (F_i\text{-}SO_2CH_2CH_2)_2O & \leftrightarrows & \downarrow {}'k_w^{i} & & {}'k_w^{j} \uparrow & \leftrightarrows & (F_j\text{-}SO_2CH_2CH_2)_2O \\ (F_{ii}\text{-D}) & {}'k_{-D}^{ii} & (F_i\text{-Hy}) & & (F_j\text{-VS}) & {}'k_D^{jj} & (F_{jj}\text{-D}) \\ & & F_i\text{-}SO_2CH_2CH_2OH & & F_j\text{-}SO_2CH{=}CH_2 & & \end{array}$$

(b)

$$\begin{array}{ccc} F_i\text{-}SO_2CH{=}CH_2 & & F_j\text{-}SO_2CH_2CH_2OH \\ (F_i\text{-VS}) & & (F_j\text{-Hy}) \\ & {}'k_{-D}^{ij} \; \upharpoonleft\!\downharpoonright \; {}'k_D^{ij} & \\ & F_i\text{-}SO_2CH_2CH_2OCH_2CH_2O_2S\text{-}F_j & \\ & (F_iF_j\text{-}D_M) & \\ & {}'k_D^{ji} \; \upharpoonleft\!\downharpoonright \; {}'k_{-D}^{ji} & \\ F_iSO_2CH_2CH_2OH & & F_j\text{-}SO_2CH{=}CH_2 \\ (F_i\text{-Hy}) & & (F_j\text{-VS}) \end{array}$$

**Scheme 1.** (a) Reaction mechanism of homo-dimerization, (b) Reaction mechanism of mixed-dimerization of the VS dyes while those of $'k_{D}^{ji}$ and $'k_{-D}^{ji}$ were estimated based on the reaction between $F_j$-VS and $F_i$-Hy(Experiment 2).

In order to produce the $D_M$ type and decompose it on both sides, as shown by Scheme 1, the following conditions are required:

$$'k_{W}^{i} \leq [F_j\text{-Hy}]\,'k_{D}^{ij} \cdots\cdots \quad (5)$$

$$'k_{D}^{ij}\ 'k_{-D}^{ij} \leq 1 \cdots\cdots \quad (6)$$

From the equality of equations (5) and (6), the initial values of $'k_{D}^{ij}(0)$ and $'k_{-D}^{ij}(0)$ were estimated. Using the second-order rate constants for each dye, the values of $k_{W}^{i'}$, $k_{W}^{j'}$, $k_{D}^{ii}$, $'k_{D}^{jj}$, $'k_{-D}^{ii}$ and $'k_{-D}^{jj}$ were calculated at a given experimental pH. The values of the kinetic parameters were calculated stepwise.

In the first step, assuming that $'k_{D}^{ji} = 'k_{-D}^{ji} = 0$, the values of $'k_{D}^{ij}(1)$ and $'k_{-D}^{ij}(1)$ for the $D_M$ type formed in Experiment 1 were determined using the least mean square method using the initial values mentioned above, and the values of $k_{W}^{i'}$, $k_{W}^{j'}$, $k_{D}^{ii}$, $'k_{D}^{jj}$, $'k_{-D}^{ii}$ and $'k_{-D}^{jj}$ were estimated for the individual dyes so as to minimize the variance between the theoretical profiles described by eqs. (1) - (4) and the experimental profiles of Experiment 1. Plus assuming that $'k_{D}^{ij} = 'k_{-D}^{ij} = 0$, those of $'k_{D}^{ji}(1)$ and $'k_{-D}^{ji}(1)$ for the $D_M$ type formed in Experiment 2 were similarly determined.

In the second step, using the values estimated in Step 1 as the initial values, the fittest values of $'k_{D}^{ji}(2)$ and $'k_{-D}^{ji}(2)$ were determined by the same method. These stepwise calculations were repeated by reducing the grid size until the fittest rate constant values of at least two significant figures did not vary with the step of the calculation, thereby confirming the condition: $v(i+1) \leq v(i)$. Although the values of the parameters for individual dyes inevitably contained some errors, they were still used without modification, because variations in the parameters of individual dyes within pH range of experimental errors did not affect the variance of the VS and Hy types.

## 3. Results and Discussion

### 3.1 Reaction behavior in an aqueous alkaline solution

In the case of an admixture of Yellow 17(VS) and Orange 16(Hy), $F_{22}$-D as well as $F_2F_3$-$D_M$ were identified upon mixing $F_2$-VS and $F_3$-Hy. In the initial stage of the reaction, $F_2$-VS reacted with $F_3$-Hy to form the $D_M$ type, while a part of $F_2$-VS was hydrolyzed to $F_2$-Hy. Although $F_2$-VS and $F_3$-Hy comprised the majority of the active species in the initial stage, it was rather surprising that the existence of a small amount of $F_2$-Hy yielded the D type at almost the same rate as the D type formation. Note that no $F_{33}$-D was formed in this system, and again the difference in the reactivity of F-Hy was clear.

To confirm the regeneration of F-VS from $F_iF_j$-$D_M$ or the reversibility of the dimerization, the following experiments were carried out:

1) A cellophane sheet was immersed into an aqueous solution of $F_i$-Hy adjusted to the usual coloring conditions for reactive dyeing, at pH 11, I=0.3 and 50℃ for 2 and 24 h. No coloration of the cellophane was confirmed.

2) A cellophane sheet was immersed for 2 and 24h into an aqueous admixture solution of $F_i$-Hy and $F_j$-VS($i \neq j$) adjusted to the coloring conditions by adding 0.1 mol dm$^{-3}$ $Na_2SO_4$ and 20 mmol dm$^{-3}$ NaOH.

Even after sufficient rinsing, the spectroscopic measurements confirmed coloration by $F_i$-dye besides $F_j$-dye. These results were the reverse when exchanging i with j. According to the results in Table 2, $F_iF_j$-$D_M$ was obviously formed. The phenomena described above were attributed to the regeneration of active $F_i$-VS through the formation of $F_iF_j$-$D_M$. Therefore, the following equilibrium can be deduced:

$$F_iF_j\text{-}D_M = [F_i\text{-Hy} + F_j\text{-VS}] \text{ or } [F_i\text{-VS} + F_j\text{-Hy}] \cdots\cdots \quad (7)$$

The results of similar coloring experiments are summarized in Table 2. As for $F_i$-Hy~$F_j$-VS couples with the same color name(such as Yellow 14 and 17,etc.), the regeneration reaction was unconfirmed due to difficulties in spectroscopically discriminating the component dye nuclei.

**Table 2.** Formation and reversibility of mixed-dimer for VS dyes

| $F_i$-VS <br> $F_j$-Hy | Blue 19 | Yellow 17 | Orange 16 | Orange 7 | Violet 5 | Yellow 14 | Red 22 | Red 23 | Violet 4 | Blue |
|---|---|---|---|---|---|---|---|---|---|---|
| Blue 19 | ○ | ○ | ○ | ○ | ○ | × | × | × | × | × |
| Yellow 17 | ○ | ○ | ○ | ○ | × | × | × | × | × | × |
| Orange 16 | ○ | ○ | ○ | - | × | × | × | - | - | - |
| Orange 7 | ○ | ○ | - | × | - | - | - | - | - | - |
| Violet 5 | ○ | × | × | - | × | - | - | - | - | - |
| Yellow 14 | × | - | × | - | - | × | - | - | - | - |
| Red 22 | × | × | × | × | - | - | × | - | - | - |
| Red 23 | × | × | - | - | - | - | - | - | - | - |
| Violet 4 | × | × | - | - | - | - | - | - | × | - |
| Blue | × | × | - | - | - | - | - | - | - | × |

O: formed, ×: not formed, -: not examined or impossible to be examined

## 3.2 Estimation of rate constants

### 3.2.1 Formation of mixed-dimer

The rate constants, $'k_{\mathrm{w}}^{\mathrm{i}}$, $'k_{\mathrm{D}}^{\mathrm{ii}}$ and $'k_{\mathrm{-D}}^{\mathrm{ii}}$ of the reactions for the ten VS dyes at pH 10.5 and 50℃, were calculated by the method reported previously[10,11]. It was confirmed for the Yellow 17, Blue 19 and Orange 16 dyes that a homo-dimer(D type) was formed under the conditions examined. However, no experiment exhibited the existence of D types for the other dyes. Therefore, contrary to the mechanism proposed so far, there were some VS dyes that formed no D types. The second-order reaction constants, $k_{\mathrm{w}}^{\mathrm{i}}$, $k_{\mathrm{D}}^{\mathrm{ii}}$ and $k_{\mathrm{-D}}^{\mathrm{ii}}$, for the ten VS dyes are listed in Table 3. The rate constants, $k_{\mathrm{w}}^{\mathrm{i}}$, for the ten VS dyes were within a range of 0.3 - 1.3 $dm^3$/mol min, as shown in Table 3.

The forward and backward rate constants of a mixed-dimerization, $'k_{\mathrm{D}}^{\mathrm{ij}}$ and $'k_{\mathrm{-D}}^{\mathrm{ij}}$ were calculated according to the method described above. Note, the theoretical concentration profiles estimated on the basis of the hydrolysis rate constants listed in Table 3 fit well with the experimental plots.

The mean values of $'k_{\mathrm{D}}^{\mathrm{ij}}/[OH^-]$ for the different dye combinations are listed in Table 4, since $'k_{\mathrm{D}}^{\mathrm{ij}}$ has a small pH dependence. The values of $'k_{\mathrm{D}}^{\mathrm{ij}}/[OH^-]$ and $'k_{\mathrm{-D}}^{\mathrm{ij}}/[OH^-]$ varied with the dye combinations. The value of $'k_{\mathrm{D}}^{11}/[OH^-]$ for Blue 19 was 1000 times larger than that of $'k_{\mathrm{D}}^{33}/[OH^-]$ for Orange 16, while that of $'k_{\mathrm{D}}^{21}/[OH^-]$ for the mixed-dimer of Yellow 17 and Blue 19 was forty times larger than that of $'k_{\mathrm{D}}^{24}/[OH^-]$ between Yellow 17 and Orange 7. In general, the differences in the rate constants for the $D_M$ type between the dye combinations were smaller than those for the D type. Because of the limitation of non-reactivity, only the mixed dimerization with Yellow 17 and Blue 19 was used to analyze the variation of the reaction relative to the dyes. Thus, the values of $'k_{\mathrm{D}}^{\mathrm{ij}}$, $'k_{\mathrm{D}}^{\mathrm{i1}}$, $'k_{\mathrm{D}}^{\mathrm{2j}}$ and $'k_{\mathrm{D}}^{\mathrm{i2}}$ would appear to vary reguarly according to the dye. The real second-order rate constant, $k_{\mathrm{D}}^{\mathrm{ij}}$ for the dimerization between $F_i$-VS and $F_j$-Hy can be defined by:

$$d[F_iF_j\text{-}D_M]/dt = k_{\mathrm{D}}^{\mathrm{ij}}[F_i\text{-VS}][F_j\text{-}SO_2CH_2CH_2O] \cdots\cdots (8)$$

$$= 'k_{\mathrm{D}}^{\mathrm{ij}}[F_i\text{-VS}][F_j\text{-Hy}] \cdots\cdots (9)$$

$$= k_{\mathrm{D}}^{\mathrm{ij}}[F_i\text{-VS}][F_j\text{-Hy}]/([H^+]/K_a^j+1) \cdots\cdots (10)$$

where $K_a^j$(mol $min^{-1}$) is the acid dissociation constant for the Hy type of the $F_j$-dye. From eqs. (8) - (10), the following relation exists between the apparent and real rate constants of the dimerization:

$$'k_{\mathrm{D}}^{\mathrm{ij}} = k_{\mathrm{D}}^{\mathrm{ij}}/([H^+]/K_a^j+1) \quad (I=1\text{-}4,\ j=1 \text{ and } 2) \cdots\cdots (11)$$

Then, the order of $'k_D^{ij}$ would seem to be similar to that of $k_D^{ij}$ for VS dyes at a given pH because of the constancy of the $K_a^j$-value. Except for the combinations of Yellow 17(Hy) and Violet 5(VS), and Blue 19(Hy) and Orange 16(VS), the order of the $'k_D^{ij}$ values was as follows:

Blue 19 > Yellow 17 > Orange 16 > Orange 7 > Violet 5 ·· (12)

This was the reverse of the reactivity of the VS dyes, thereby implying that the higher the reactivity with cellulose or hydroxide ion, the smaller the mixed dimerization. However, in the case of Orange 16(Hy), the order of the $'k_D^{ij}$ values was the reverse of that in (12), the ordinary order of reactivity for VS dyes. Since only two dyes reacted with $F_3$-Hy, the different behavior of Orange 16 was difficult to elucidate.

**Table 3.** Kinetic parameters for VS dyes at 50℃

| C. I. Reactive | $k_w^i$ (dm$^3$/mol min) | $'k_D^{ii}/[OH^-]$ (dm$^6$/ mol$^2$ min) | $k_{-D}^{ii}$ (dm$^3$/mol min) |
|---|---|---|---|
| Blue 19 | 0.689 | $1.04 \times 10^4$ | 0.572 |
| Yellow 17 | 1.03 | $1.03 \times 10^3$ | 20.8 |
| Orange 16 | 0.643 | 9.22 | $6.12 \times 10^{-3}$ |
| Orange 7 | 1.32 | × | × |
| Violet 5 | 0.743 | × | × |
| Yellow 14 | 0.553 | × | × |
| Red 22 | 0.744 | × | × |
| Red 23 | 0.651 | × | × |
| Violet 4 | 0.306 | × | × |
| Blue | 0.785 | × | × |

**Table 4.** Formation($''k_D^{ij}$) and decomposition($k_{-D}^{ij}$) rate constants for mixed-dimer of VS dyes at 50℃

| $F_i$-VS<br>$F_j$-Hy | Blue 19 (1) | Yellow 17 (2) | Orange 16 (3) | Orange 7 (4) | Violet 5 (5) |
|---|---|---|---|---|---|
| Blue 19 (1) | -<br>- | $''k_D^{21}=5.0\text{x}10^3$<br>$k_{-D}^{21}=2.2$ | $''k_D^{31}=2.8\text{x}10^3$<br>$k_{-D}^{31}=0.86$ | $''k_D^{41}=8.1\text{x}10^2$<br>$k_{-D}^{41}=0.151$ | $''k_D^{51}=4.0\text{x}10^3$<br>$k_{-D}^{51}=0.75$ |
| Yellow 17 (2) | $''k_D^{12}=3.1\text{x}10^3$<br>$k_{-D}^{12}=1.2$ | -<br>- | $''k_D^{32}=3.7\text{x}10^3$<br>$k_{-D}^{32}=2.7$ | $''k_D^{42}=3.9\text{x}10^2$<br>$k_{-D}^{42}=0.98$ | ×<br>× |
| Orange 16 (3) | $''k_D^{13}=1.5\text{x}10^3$<br>$k_{-D}^{13}=0.86$ | $''k_D^{23}=2.9\text{x}10^3$<br>$k_{-D}^{23}=1.5$ | -<br>- | ×<br>× | ×<br>× |
| Orange 7 (4) | $''k_D^{14}=5.1\text{x}10^2$<br>$k_{-D}^{14}=0.074$ | $''k_D^{24}=1.3\text{x}10^2$<br>$k_{-D}^{24}=0.35$ | ×<br>× | -<br>- | ×<br>× |
| Violet 5 (5) | $''k_D^{15}=2.4\text{x}10^3$<br>$k_{-D}^{15}=0.42$ | ×<br>× | ×<br>× | ×<br>× | -<br>- |

$''k_D^{ij} = {'k_D^{ij}}/[OH^-]$, $k_{-D}^{ij} = {'k_{-D}^{ij}}/[OH^-]$

### 3.2.2 Decomposition of mixed-dimer

The decomposition of $F_iF_j$-$D_M$(i≠j) yielded $F_i$-Hy and $F_j$-VS from the VS dyes, other than Blue 19, in their highest concentrations. In general, VS dyes have a higher tendency to form D and $D_M$ types and exhibit a property where the $D_M$ types are decomposed to give F-Hy in a higher concentration than F-VS. In the case of disproportionation of the $D_M$ type, the order of the values of $k_{-D}^{1i}$ or $k_{-D}^{2i}$ appeared to have no monotonous tendency as the order in (12). Yet the ratios of $k_{-D}^{2i}/k_{-D}^{i2}$(i= 1-5) for Yellow 17 showed the same order as in (12). This behavior can be interpreted as follows: The $D_M$ types were decomposed on both sides, as shown in reaction scheme 2. The reverse reactions of the $D_M$ types are appeared to occur in two steps, the deprotonation of α-carbon of the $D_M$ types and disproportionation. However, in the present study, it was assumed that the $D_M$ types with either α-carbon deprotonates or non-ionized species existed in an equilibrium(cf. Scheme 2). Thus, assuming that an equilibrium exists among two kinds of ionized species($C_i$ and $C_j$) and a non-ionized species($C_{ij}$) for the $D_M$ types at a given pH, the total concentrations and equilibrium constants($K_i$ and $K_j$) can be given by:

$$[C_i] + [C_j] + [C_{ij}] = [F_iF_j\text{-}D_M] \cdots\cdots\cdots\cdots\cdots\cdots\cdots (13)$$

$$K_i = [C_i][H^+]/[C_{ij}] \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (14)$$

Substituting eq. (14) into eq. (13), produces the following relations are obtained:

$$[C_i]/[F_iF_j\text{-}D_M] = K_i/(K_i + K_j + [H^+]) \cdots\cdots\cdots\cdots (15)$$

The apparent rate constants($'k_{-D}^{ij}$ and $'k_{-D}^{ji}$) for the reverse reaction of the $D_M$ type are related with the real rate constants($''k_{-D}^{ij}$ and $''k_{-D}^{ji}$) as follows:

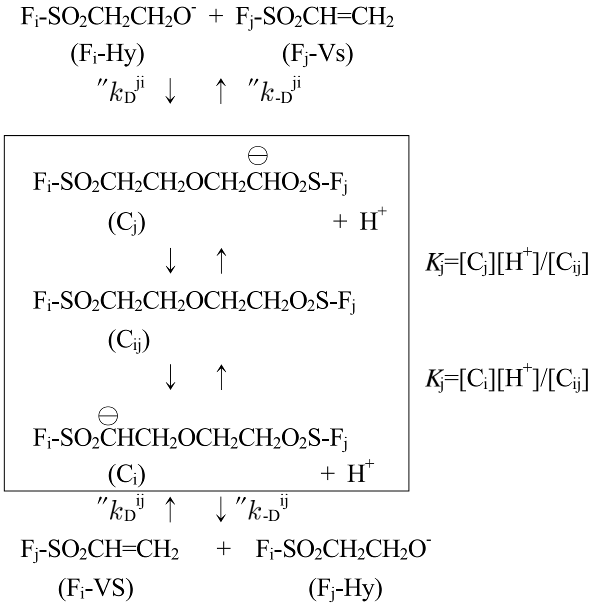
$$'k_{-D}^{ij}[F_iF_j\text{-}D_M] = ''k_{-D}^{ij}[C_i] \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (16)$$

$$'k_{-D}^{ji}[F_iF_j\text{-}D_M] = ''k_{-D}^{ji}[C_j] \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (17)$$

From eqs. (15) - (17), the relative rate of deproportionation can be given by:

$$'k_{-D}^{ji}/'k_{-D}^{ij} = k_{-D}^{ji}/k_{-D}^{ij} = (''k_{-D}^{ji}/''k_{-D}^{ij})(K_i/K_j) \cdots\cdots (18)$$

Thus, the ratio of the decomposition of the $D_M$ type to F-Hy and F-VS appears to be related with the ratio of $K_i/K_j$. Since the position of deprotonation seems to have little effect on the bond stability, the ratio of $''k_{-D}^{ji}/''k_{-D}^{ij}$ is nearly equal to unity. As such, the ratio of $k_{-D}^{ji}/k_{-D}^{ij}$ can describe the ratio of $K_i/K_j$ or which position deprotonates. It is thus proposed that the reverse reaction of the $D_M$ type occurred according to the mechanism of Scheme 2. Also the deprotonation processes in the reverse reaction may determine the reformation ratios of



**Scheme 2.** Deprotonation processes in the reverse reaction of mixed-dimer

F-VS and F-Hy for the component dyes. According to Scheme 2, the end products of the VS dyes would seem to exist as a mixture of protonated and deprotonated compounds under alkaline conditions.

### 3.3 Correlation between mixed-dimerization and hydrolysis

As mentioned above, certain similarities among the values of $k_w^i$, $k_D^{ij}$ and $k_{-D}^{ij}$ were found. The general form of the similarity was a linear relationship between the logarithms of the rate constants for a reaction and those for the other reaction[15,16]. Although these phenomena have been analyzed based on the substitution effect on the reaction rates or the equilibria and various formulations such as Hammett equations have been proposed, no equation can be accurately applied to the reactions of VS dyes due to the lack of substituent constants.

As the reference reaction or a measure of the substituent constants, the logarithms of the $'k_w^i$-values were plotted on the abscissa axis and those of the other rate constants for various reactions on the ordinate axis. Figure 1 shows that linear regressions between $\log'k_w^i$ and $\log'k_D^{ij}$ were obtained with the correlation coefficients R=0.99 for j=2 and R=0.94 for j=1. The units of the rate constants had no effect on the R-values. Other linear regressions between $\log'k_w^i$ and the logarithms of $'k_{cell}$(R=0.95), $'k_{-D}^{i1}$(0.91) and $'k_{-D}^{i2}$(R=0.80) are also shown. The existence of similarities between the rates of disproportionation and hydrolysis implies that Scheme 2 holds as mentioned above.

From the existence of the linear relationships between the rate constants of various reactions and $'k_D^{ij}$ or $'k_{-D}^{ij}$, it was confirmed that the mixed dimerization had a close relation with the usual reactivity of the VS dyes. In general, the higher $'k_w^i$ values VS dyes have, the smaller them $'k_D^{ij}$ values, as shown in Figure 1. Thus, VS dyes undergoing fast hydrolysis have difficulty in forming a dimer. The easiness of the dimerization was thus found to be inversely proportional to the rate of hydrolysis. At the same time, some clear deviations were also observed, see Figure 1.

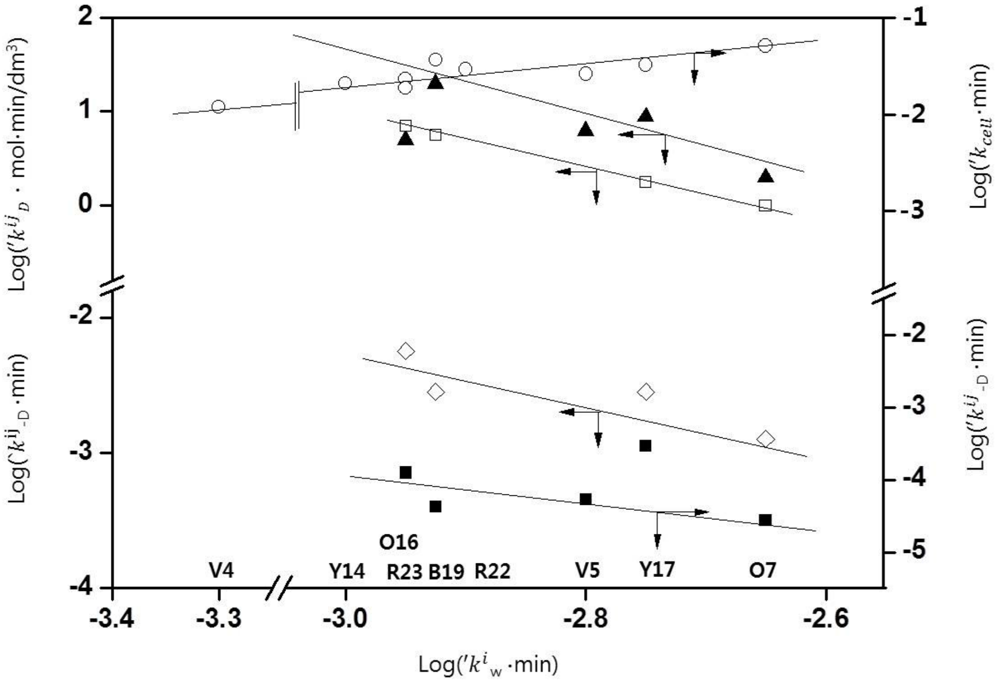


**Figure 1.** Correlations of logarithms of rate constants in formation of mixed-dimer($'k_D^{i1}$ and $'k_D^{i2}$), decomposition of mixed-dimer($'k_{-D}^{i1}$ and $'k_{-D}^{i2}$), reaction with cellulose($'k_{cell}$), and those for hydrolysis ($'k_w^i$) of VS dyes at pH 10.5(○:$'k_{cell}$ , ▲:$'k_D^{i1}$ , □:$'k_D^{i2}$ , ■:$'k_{-D}^{i1}$, ◇:$'k_{-D}^{i2}$).

## 4. Conclusion

Hydrolytic reactions in an aqueous alkaline solution containing individual and different VS reactive dye combinations were kinetically investigated. The rate constants of hydrolysis and those of the homo dimerization for ten VS dyes were estimated. The rate constants for the formation and decomposition of a mixed-dimer were determined using the rate constants estimated in the hydrolysis of each dye. The reversibility of the $D_M$ type between VS dyes was confirmed by dyeing cellophane with the F-Hy of one dye and adding the F-VS of an other dye. The decomposition of the $D_M$ type depended on the easiness of the ionization of the $D_M$ type. In general, those VS dyes with a higher tendency to form D and $D_M$ types also exhibited a property whereby the $D_M$ types were decomposed to produce F-Hy in a higher concentration than F-VS. The easiness of the dimerization depended on the rate of hydrolysis. Similarities were also found among various other reactions, including homo- and mixed dimerization.

## Nomenclature

| | |
|---|---|
| $F_i$ | i-th dye |
| $F_{ii}$-D | homo-dimer made of $F_i$-dye |
| $F_iF_j$-$D_M$ | mixed-dimer composed of $F_i$- and $F_j$-dye nuclei |
| $F_i$-Hy | Hy type of $F_i$-dye |
| $F_i$-VS | VS type of $F_i$-dye |
| i, j | dye number |
| $K_a^j$ | acid dissociation constant for Hy type of $F_j$-dye |
| $'k_{cell}$ | pseudofirst order rate constant of reaction with cellulose for VS dye |
| $k_D^{ii}$ | = $'k_D^{ii}/[OH^-](dm^6\ mol^{-2} min^{-1})$ |
| $'k_D^{ii}$ | apparent second-order rate constant of dimerization of $F_i$-dye($dm^3\ mol^{-1}\ min^{-1}$) |
| $k_{-D}^{ii}$ | = $'k_{-D}^{ii}/[OH^-](dm^3\ mol^{-1}\ min^{-1})$ |
| $'k_{-D}^{ii}$ | pseudofirst-order rate constant of decomposition of $F_{ii}$-D to form $F_i$-VS and $F_i$-Hy($min^{-1}$) |
| $k_D^{ij}$ | = $'k_D^{ij}/[OH^-](dm^6\ mol^{-2}\ min^{-1})$ |
| $'k_D^{ij}$ | apparent second-order rate constant of dimerization of $F_i$-VS and $F_j$-Hy($dm^3\ mol^{-1}\ min^{-1}$) |
| $'k_D^{ij}(n)$ | fittest value of $'k_D^{ij}$ obtained in n-th step |
| $k_{-D}^{ij}$ | = $'k_{-D}^{ij}/[OH^-](dm^3\ mol^{-1}\ min^{-1})$ |
| $'k_{-D}^{ij}$ | pseudofirst-order rate constant of disproportionation of mixed-dimer to form $F_i$-VS and $F_j$-Hy($min^{-1}$) |
| $'k_{-D}^{ij}(n)$ | fittest value of $'k_{-D}^{ij}$ obtained in nth step |
| $k_w^i$ | = $'k_w^i/[OH^-](dm^3\ mol^{-1}\ min^{-1})$ |
| $'k_w^i$ | peudofirst-order rate constant of hydrolysis for VS type of $F_i$-dye($min^{-1}$) |
| $t$ | reaction time(min) |
| v(n) | variance in nth step |
| $\lambda_{max}$ | wavelength of maximum absorption(nm) |

## References

1. O. A. Stamm, Mechanisms of Reaction of Reactive Dyes with Cellulosic and Other Fibres, *J. Soc. Dyers Colour.*, **80**, 416(1964).
2. M. R. D. Giogi and A. Cerniani, Dyeing Kinetics of Monochlorotriazinyl Dyes for Nylon, *Text. Res. J.*, **57**, 563(1987).
3. W. Ingamel, H. H. Sumner, and G. Williams, The Mechanism of Dyeing with Procion Dyes II, *J. Soc. Dyers Colour.,* **78**, 274(1962).
4. S. Fisichella, S. Occhipinti, G. Alberghina, and M. E. Amato, Kinetics of Hydrolysis of Dichlorotriazinyl Dichlorotriazinyl Reactive Azo Dyes, *Text. Res. J.,* **51**, 683(1981).
5. L. He, Z. H. Zhu, and K. C. Chen, The Kinetics of the Hydrolysis and Alcoholysis of Some Model Monofluorotriazinyl Reactive Dyes, *Dyes and Pigment,* **11**, 123(1989).
6. Z. H. Zhu, K. C. Chen, J. X. Li, S. L. Chen, and S. L. Wang, $^1$H-NMR Study of the Hydrolysis of Some Model Pyrimidyl Reactive Dyes, *Dyes and Pigment,* **11**, 243(1989).
7. P. Rys and O. A. Stamm, Zur Reaktion Von Reaktivfarbstoffen Mit Cellulose Von Untersuchung Von Nebenprodukten Bei Der Applikation Von Reaktivfarbstoffen, *Helv. Chim. Acta*, **49**, 2287(1966).
8. J. Panchartek and Z. J. Allan, Aromatische Diazo-

und Azoverbindungen XLVII, Konstitutionsanalyse Von Sulfoester-reaktivfarbstoffen, *J. Collect. Czech. Chem. Commun.*, **27**, 268(1962).

9. H. U. Mehta, M. R. Radhakrishnan, and A. G. Chitale, A Study of the Abnormal Viscosity of Procion-dyed Cellulose in Cuprammonium Hydroxide, Hydroxide, *J. Soc. Dyers Colour.*, **78**, 552(1962).
10. I. H. Kim, H. Motomura, and Z. Morita, Hydrolysis of Vinylsulfonyl Reactive Dyes, *Sen'i Gakkaishi*, **45**, **45**, 167(1989).
11. H. Motomura, I. H. Kim, and Z. Morita, Kinetics of Dimerization of Vinylsulfonyl Reactive Dyes 1, *Sen'i Gakkaishi,* **47**, 598(1991).
12. Z. Morita, I. H. Kim, and H. Motomura, Stability and Reversibility of Dye-Cellulose Bond for Vinylsulfonyl Reactive Dyeings, *Dyes and Pigment*, **18**, 11(1992).
13. J. G. Becsey, L. Berke, and J. R. Callan, Nonlinear Least Squares Methods: A Direct Grid Search Approach, *J. Chem. Educ.,* **45**, 728(1968).
14. M. L. James, G. M. Smith, and J. C. Wolford, “Applied Numerical Methods for Digital Computation with FORTRAN”, International Textbook Company, Pennsylvania, 1985.
15. L. P. Hammet, “Physical Organic Chemistry”, McGraw-Hill, New York, 1970.
16. J. E. Leffler and E. Grunwald, “Rates and Equilibria of Organic Reactions”, Wiley, New York, 1963.