Kinetic of mixed-dimerization and correlation between rate constants of vinylsulfonyl reactive dyes

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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. 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. 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 molar extinction coefficients of the Hy type for each dye at various wavelengths in water are listed in Table 1. The components of the dye were analyzed by high pressure liquid chromatography(HPLC).
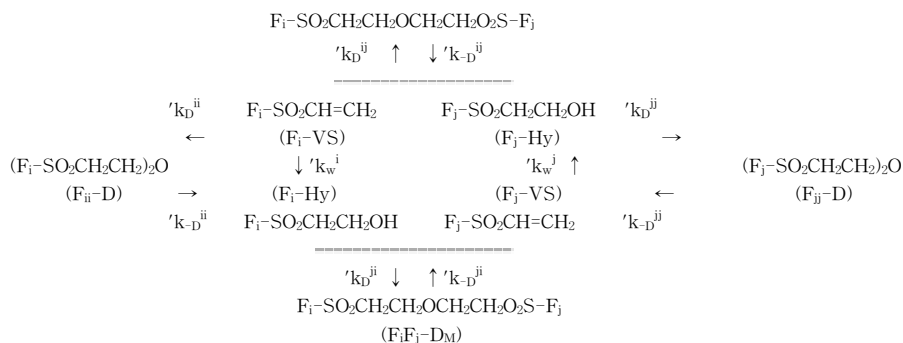The mixed-dimerization was then carried out in these admixture solutions at constant pHs adjusted by NaOH.

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.

Table 1. VS Dyes Used and ε_{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
	λ_{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	–

$$F_i\text{-}SO_2CH_2CH_2OCH_2CH_2O_2S\text{-}F_j$$
$$'k_D^{ij} \ \uparrow \quad \downarrow \ 'k_{-D}^{ij}$$

$$'k_D^{ii} \quad F_i\text{-}SO_2CH=CH_2 \qquad F_j\text{-}SO_2CH_2CH_2OH \quad 'k_D^{jj}$$
$$\leftarrow \qquad (F_i\text{-}VS) \qquad\qquad (F_j\text{-}Hy) \qquad\qquad \rightarrow$$
$$(F_i\text{-}SO_2CH_2CH_2)_2O \qquad\qquad \downarrow \ 'k_w^i \qquad\qquad 'k_w^j \ \uparrow \qquad\qquad (F_j\text{-}SO_2CH_2CH_2)_2O$$
$$(F_{ii}\text{-}D) \qquad \rightarrow \qquad (F_i\text{-}Hy) \qquad\qquad (F_j\text{-}VS) \qquad \leftarrow \qquad (F_{jj}\text{-}D)$$
$$'k_{-D}^{ii} \quad F_i\text{-}SO_2CH_2CH_2OH \qquad F_j\text{-}SO_2CH=CH_2 \quad 'k_{-D}^{jj}$$

$$'k_D^{ji} \downarrow \quad \uparrow \ 'k_{-D}^{ji}$$
$$F_i\text{-}SO_2CH_2CH_2OCH_2CH_2O_2S\text{-}F_j$$
$$(F_iF_j\text{-}D_M)$$

Scheme 1

3. Results and discussion

3.1 Formation of mixed-dimer

The forward and backward rate constants of a mixed-dimerization, $'k_D^{ij}$ and $'k_{-D}^{ij}$, were calculated according to the method described above. The mean values of $'k_D^{ij}/[OH^-]$ for the different dye combinations are listed in Table 2, since $'k_D^{ij}$ has a small pH dependence. The values of $'k_D^{ij}/[OH^-]$ and $'k_{-D}^{ij}/[OH^-]$ varied with the dye combinations. The value of $'k_D^{11}/[OH^-]$ for Blue 19 was 1000 times larger than that of $'k_D^{33}/[OH^-]$ for Orange 16, while that of $'k_D^{21}/[OH^-]$ for the mixed-dimer of Yellow 17 and Blue 19 was forty times larger than that of $'k_D^{24}/[OH^-]$ 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.

Table 2. Formation($''k_D^{ij}$) and Decomposition(k_{-D}^{ij}) Rate Constants for Mixed-dimer of VS Dyes at 50℃.

Fi-VS / Fj-Hy	Blue 19 (1)	Yellow 17 (2)	Orange 16 (3)	Orange 7 (4)	Violet 5 (5)
Blue 19 (1)	– / –	$''k_D^{21}=5.0\times10^3$ / $k_{-D}^{21}=2.2$	$''k_D^{31}=2.8\times10^3$ / $k_{-D}^{31}=0.86$	$''k_D^{41}=8.1\times10^2$ / $k_{-D}^{41}=0.151$	$''k_D^{51}=4.0\times10^3$ / $k_{-D}^{51}=0.75$
Yellow 17 (2)	$''k_D^{12}=3.1\times10^3$ / $k_{-D}^{12}=1.2$	– / –	$''k_D^{32}=3.7\times10^3$ / $k_{-D}^{32}=2.7$	$''k_D^{42}=3.9\times10^2$ / $k_{-D}^{42}=0.98$	x / x
Orange 16 (3)	$''k_D^{13}=1.5\times10^3$ / $k_{-D}^{13}=0.86$	$''k_D^{23}=2.9\times10^3$ / $k_{-D}^{23}=1.5$	– / –	– / –	x / x
Orange 7 (4)	$''k_D^{14}=5.1\times10^2$ / $k_{-D}^{14}=0.074$	$''k_D^{24}=1.3\times10^2$ / $k_{-D}^{24}=0.35$	– / –	x / x	x / x
Violet 5 (5)	$''k_D^{15}=2.4\times10^3$ / $k_{-D}^{15}=0.42$	x / x	x / x	– / –	x / x

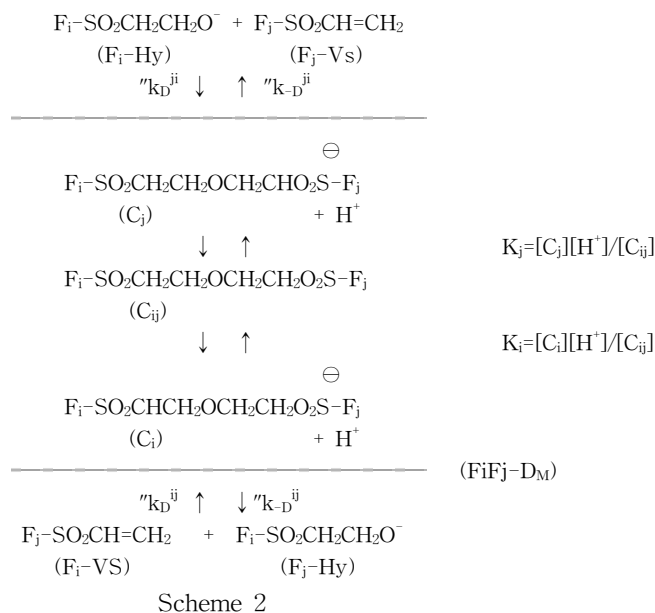$''k_D^{ij} = 'k_D^{ij}/[OH^-]$, $k_{-D}^{ij} = 'k_{-D}^{ij}/[OH^-]$

3.2 Decomposition of mixed-dimer

The decomposition of $F_iF_j-D_M(i\neq j)$ 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. 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. 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 mxed-dimerization and hydrolysis

As mentioned above, certain similarities among the values of k_w^i, k_D^{ij} and k_{-D}^{ij} were found. 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. Fig. 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. 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

$$F_i-SO_2CH_2CH_2O^- + F_j-SO_2CH=CH_2$$
$$(F_i-Hy) \qquad (F_j-Vs)$$
$$''k_D^{ji} \downarrow \quad \uparrow \ ''k_{-D}^{ji}$$

$$\overset{\ominus}{F_i-SO_2CH_2CH_2OCH_2CHO_2S-F_j}$$
$$(C_j) \qquad\qquad + H^+ \qquad\qquad K_j=[C_j][H^+]/[C_{ij}]$$
$$\downarrow \quad \uparrow$$
$$F_i-SO_2CH_2CH_2OCH_2CH_2O_2S-F_j$$
$$(C_{ij}) \qquad\qquad\qquad\qquad K_i=[C_i][H^+]/[C_{ij}]$$
$$\downarrow \quad \uparrow$$
$$\overset{\ominus}{F_i-SO_2CHCH_2OCH_2CH_2O_2S-F_j}$$
$$(C_i) \qquad\qquad + H^+$$

$$(FiFj-D_M)$$

$$''k_D^{ij} \uparrow \quad \downarrow ''k_{-D}^{ij}$$
$$F_j-SO_2CH=CH_2 \ + \ F_i-SO_2CH_2CH_2O^-$$
$$(F_i-VS) \qquad\qquad (F_j-Hy)$$

Scheme 2

of disproportionationand 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.

3.3 Correlation between mxed-dimerization and hydrolysis

As mentioned above, certain similarities among the values of k_w^i, k_D^{ij} and k_{-D}^{ij} were found. As the reference reaction or a measure of the substituent constants, the logarithms
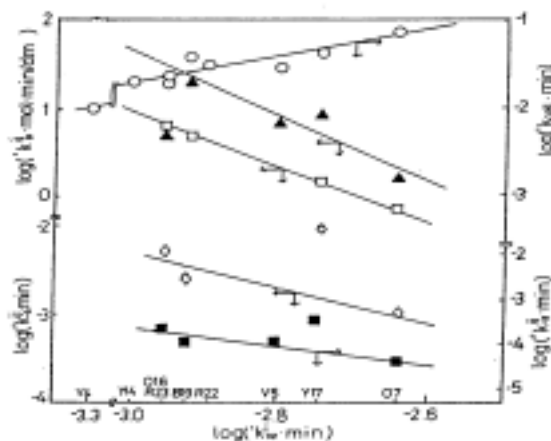

Fig. 1. Correlations of logarithms of rate constants in formation of mixed-dimer($'k_D^{i1}$ and $'k_D^{i2}$), decomposition of mixed-dimer($'k_{-D}^{i1}$ and $'k_{-D}^{i2}$),reaction with cellulose($'k_{cell}$), and those for hydrolysis($'k_w^i$) of VS dyes at pH 10.5.(○:$'k_{cell}$, ▲:$'k_D^{i1}$,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

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. Fig. 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. 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.

4. Conclusion

Hydrolytic reactions in an aqueous alkaline solution containing individual and different VS reactive dye combinations were kinetically investigated. 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 decomposition of the D_M type depended on the easiness of the ionization of the D_M type. The easiness of the dimerization depended on the rate of hydrolysis. Similarities were also found among various other reactions, including homo- and mixed dimerization.