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## Vinylsulfone계 반응성염료의 안정성과 반응성

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### Stability and Reactivity of Vinylsulfonyl Reactive Dyes

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**초 록**—11종류의 cellulose에 고착된 vinylsulfone(VS)계 반응성 염료(F-type)의 알칼리 가수분해 거동과 염료와 섬유의 결합 안정성을 cellophane film을 이용한 film권층법에 의하여 조사하였다. F-type은 알칼리 속에서 분해되어 VS type을 생성하고 VS type은 가수분해에 의해 hydroxyethylsulfone(Hy)을 생성하거나 cellulose와 재결합하여 F-type을 생성하였다. F-type은 알칼리 처리에 의해 cellulose의 수산기의 위치에 기인하는 bimodal 가수분해 거동(fast and slow hydrolysis)을 나타내었다. Orange 7과 Yellow 17는 cellulose와의 반응성이 높고 F-type의 초기 분해속도가 빠르며 일반적으로 fast 가수분해속도가 slow 가수분해 속도보다 약 5배 정도 큼을 알 수 있었다. 또한 조사된 대부분의 염료의 경우 slow 가수분해 속도는 거의 유사함을 알 수 있었다.

#### 1. Introduction

The reversibility of reactive dye-cellulose bond has been suggested by Stamm in the reaction scheme of VS dyes<sup>1)</sup>. Senn and Zollinger<sup>2)</sup> estimated the hydrolysis of dye-cellulose bond for many kinds of reactive dyes in a wide range of pH. Bond stability for C.I. Reactive Blue 19 was only estimated in VS dyes. The present authors<sup>3)</sup> investigated the hydrolysis of VS dyes and estimated the rate constants of the reaction between VS types and  $\beta$ -hydroxyethylsulfonyl(Hy) ones. The rate cons-

tants of the forward and backward reaction of dimerization varied widely with VS dyes examined. In the present study, bond scission of eleven VS reactive dyes fixed on a sheet of cellophane(F-types) is examined by immersing the dyed film in an aqueous alkaline solution. The migration and the reaction of reactive dyes on cellulose immersed in the alkaline bath are also investigated by the cylindrical film roll method. It is confirmed that the VS types are formed from the reactive dyeings in the alkaline treatment and are further hydrolyzed to yield the hydroxyethylsulfonyl types or

to reproduce the F-types accompanied with partial migration.

## 2. Experimental

### 2.1 Dyes Used

VS dyes used were supplied by Mitsubishi Chemical Corp. and Sumitomo Chemical Co. Ltd. Their chemical structures are shown by C.I. Constitution Number as shown in Table 1. These dyes were used without further purification for dyeing. The molar extinction coefficients were determined by the same method as before. Chemicals used were of reagent grade.

### 2.2 Substrates

Cellophane sheets cut in 5.5 cm wide and 60 cm long were scoured in boiling water to remove impurities and dyed by the alkali shock method with sodium carbonate or by immersing the films in the dye bath containing sodium carbonate(20g/l)

and sodium hydrogencarbonate(20g/l)(pH 9.6) at 50°C. The dyed films were scoured thoroughly in boiling water after dyeing.

Several sheets of dyed cellophane(cut in 2 cm long) were allowed to be immersed in an aqueous sodium carbonate(0.10 mol/l) solution at 50°C without stirring, because stirring was confirmed to give no effect on the rate of desorption. The external solution was renewed sometimes to avoid the re-adsorption of desorbed species. The optical densities of each film before and after the immersion for different duration were measured at  $\lambda_{max}$  to obtain the degree of hydrolysis. After the immersion each film was thoroughly scoured in boiling water and was dried before the optical measurement. Two sheets of dyed and undyed cellophane were rolled on a glass tubing. On the rolled film layer, a sheet of undyed film was further rolled. The length of rolled film was so adjusted that from the surface of a glass tubing there were alternate dyed and undyed layers(total 12 layers) and six undyed ones. The F-types exist initially in the

Table 1. VS dyes used, initial concentration,  $C_0$ , relative concentrations,  $C_{F0}/C_0$  and  $C_{S0}/C_0$  for F-types undergoing fast and slow hydrolysis, and their rates of formation,  $k_F$  and  $k_S$ , and of bond scission,  $k_{-F}$  and  $k_{-S}$ , at pH 10.9 and 50°C.

C. I. Reactive	C. I. Constitution Number	$C_0 \times 10^2$ (mol/kg)	$C_{F0}/C_0$	$k_{-F} \times 10^4$ ( $\text{min}^{-1}$ )	$C_{S0}/C_0$	$k_{-S} \times 10^4$ ( $\text{min}^{-1}$ )	$k_C^2$ ( $\text{min}^{-1}$ )	$k_F$ ( $\text{min}^{-1}$ )	$k_S$ ( $\text{min}^{-1}$ )	$k_{-F}/k_F$ $\times 10^4$	$k_{-S}/k_S$ $\times 10^4$
Yellow 13	18,990	0.317	0.35	4.86	0.65	0.97	4.0	1.4	2.6	3.5	0.37
Yellow 14	19,036	0.158	0.35	3.96	0.65	0.69	5.0	1.75	3.25	2.3	0.21
Yellow 17	18,852	3.49	0.52	16.7	0.48	0.97	10.3	5.36	4.94	3.1	0.20
Orange 7	17,756	2.09	0.40	6.25	0.60	1.25	17.8	7.12	10.7	0.9	0.12
Orange 16	17,757	1.63	0.35	5.90	0.65	1.11	5.8	2.03	3.77	2.9	0.29
Red 22	14,824	2.43	0.20	6.25	0.80	0.83	9.0	1.8	7.2	3.5	0.12
Red 23	16,202	0.937	0.05	8.58	0.95	0.69	4.8	0.24	4.56	36.2	0.15
Violet 4	18,096	1.07	0	—	1.0	0.56	2.3	—	2.3	—	0.24
Violet 5	18,097	1.16	0.25	7.29	1.75	1.04	7.0	1.75	5.25	4.2	0.20
Blue 19	61,200	3.31	0.05	6.25	1.95	0.83	8.0	0.40	7.6	15.6	0.11
Blue	—	2.73	0.15	5.90	0.85	1.39	—	—	—	—	—

a) Values at pH 10.9 and 50°C estimated from the values obtained previously.

b) Sample of  $C_0 = 5.90 \times 10^{-3}$  mol/kg gave the same results.

c) not determined

(2n-1) th layers(n=1-6), while no species in the 2nth layers(n=1-6) and in the more than 12th layers. The optical densities of each layer after the alkaline treatment were measured before and after being thoroughly scoured in boiling water. Those measured before the scouring correspond to Ai or Bi, and those after the scouring to Fi or Gi, respectively.

### 3. Results and Discussion

#### 3.1 Bond Scission of Fixed Dyes on Cellophane

The hydrolytic behavior of eleven VS dyes fixed on cellophane in an aqueous alkaline solution is shown in Fig. 1. The initial concentration,  $C_0$ , of Yellow 17 and the dyeing method(pH 9.6 and 10.9)

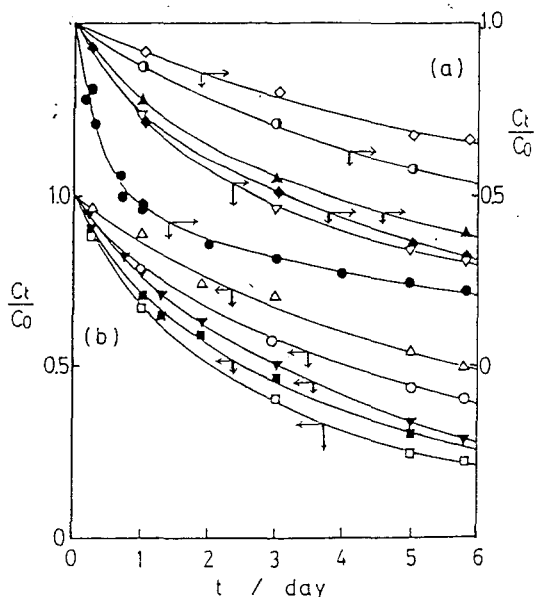


Fig. 1 Dye-cellulose bond scission of the F-types for VS dyes on cellophane immersed in an aqueous alkaline(0.10mol/dm<sup>3</sup> Na<sub>2</sub> CO<sub>3</sub>) solution at 50°C. (a) ▽, Yellow 13 ; ▲, Yellow 14 ; ●, Yellow 17 ; ⊙, Red 23 ; ◇, Violet 4 ; ◆, Violet 5 ; (b) □, Orange 7 ; ■, Orange 16 ; ○, Red 22 ; △, Blue 19 ; ▼, Blue.

were confirmed to give no effect on the rate of desorption. The present authors found also by a computer simulation that under the present conditions(a sheet of dyed cellophane, pH 10.9 and 50 °C), the rate of desorption was dependent only upon the rate constants of dye-fiber bond scission. The diffusion coefficient and affinity for the VS and Hy types and the rate of reaction with cellulose for the VS types give little effect on the rate of desorption. Thus, when plots of  $\ln C_t/C_0$  versus  $t$  are made, the pseudofirst-order rate constant of scission can be obtained, if they show a straight line. Only Violet 4 gave a straight line, and Red 23 and Blue 19 gave almost a straight line, supporting the pseudofirst-order mechanism, while the other dyes a bent line(Fig. 2(a)).

Then, it was assumed that VS dyes making a bent line show bimodal, fast and slow, hydrolytic behavior, whose rate constants are denoted by  $k_{-F}$  and  $k_{-S}$ , respectively. Since the fast hydrolysis proceeds preferentially, only the slow hydrolysis occurs after a sufficient time of alkaline treatment. By extrapolating the linear plots between  $\ln C_t/C_0$  and  $t$  after long treatment to time zero, the values of initial concentration  $C_{S0}$  and  $k_{-S}$  for the slow hydrolysis were estimated.

Yellow 17, Red 22, Violet 5, and Blue showed the typical behavior, supporting that this bimodal hydrolytic mechanism holds. The behavior for Yellow 17 and Violet 5 is drawn in Fig.2(a) as the example. Assuming that the fast and slow hydrolyses occur independently and by using the above-mentioned values of  $C_{S0}$ ,  $C_{F0}$ , and  $k_{-S}$  as the initial values, the fittest values of  $C_{S0}$ ,  $k_{-F}$ , and  $k_{-S}$  were determined by a least-mean square calculation so as to fit the sum of both the theoretical pseudofirst-order reaction profiles with the experimental hydrolytic profile after being smoothed. Fig. 2(b) shows that a superposition of two kinds of the pseudofirst-order hydrolyses agrees well with the experimental plots for two dyes. Although in the

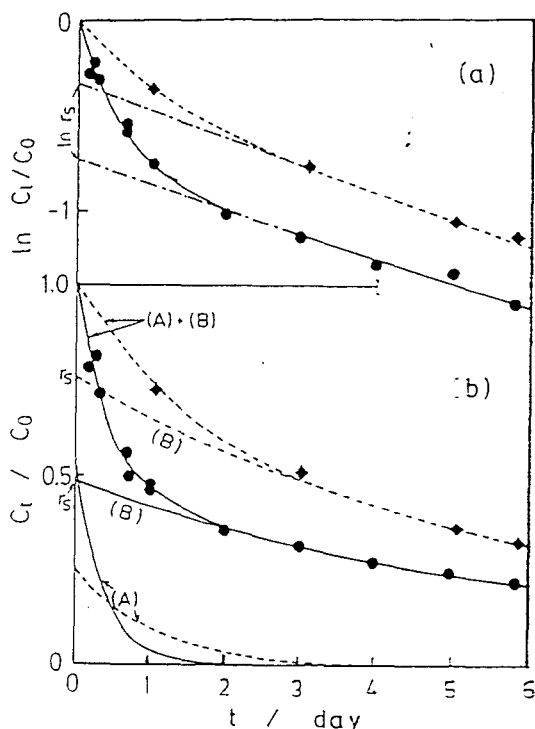


Fig. 2 (a) Relationship between  $\ln C_t/C_0$  and time, and (b) the theoretical summed-up profile  $\{C_t/C_0 = (C_{F0}/C_0)\exp(-k_{-F}t) + (C_{S0}/C_0)\exp(-k_{-S}t)\}$  of both the fast (A) and slow (B) pseudofirst-order hydrolyses described by the parameters shown in Table 1 for Violet 5 ( $\blacklozenge$ ) and Yellow 17 ( $\circ$ ) in an aqueous sodium carbonate ( $0.10 \text{ mol/dm}^3$ ) solution at  $50^\circ\text{C}$  and pH 10.9 Theoretical curve : solid line for Yellow 17 and broken line for Violet 5.

cases of Yellow 13, Yellow 14, Orange 7, and Orange 16 the convergence domain for the fittest values was wide due to the smaller values of  $k_{-F}/k_{-S}$  and the larger values of  $C_{F0}/C_{S0}$  than those for the other dyes, their values were also estimated by the same method. The relative concentration of F-types undergoing fast and slow hydrolyses and the values of their rates of scission are shown in Table 1.

The relative initial concentrations,  $C_{S0}/C_0$ , for the F-types undergoing slow hydrolysis were in general dominant, but those for Orange 7 and Yellow 17 which underwent the fastest initial hydrolysis were comparable to those for the F-type undergoing fast hydrolysis.

Bimodal hydrolytic behavior is supposed to correlate with the position of hydroxyl groups, 2- and 6-OH, in cellulose with which VS dyes react. Stamm<sup>4)</sup> reported that Blue 19 reacted mainly with 2-OH, but Bhagwanth<sup>5)</sup> reported a model VS compound reacted mainly with 6-OH. Since whether with which hydroxyl group of cellulose VS dyes react varies with dyes as being implied by the present study, their results may not be contradictory to each other. The F-types undergoing slow hydrolysis is supposed to correlate with the fixed species of 2-OH, if Stamm's result is taken into consideration.

From the values of the pseudofirst-order rate constant,  $k_c$ , with cellulose and the values of  $k_{-F}$ ,  $k_{-S}$ ,  $C_{F0}$ , and  $C_{S0}$  determined in the present paper, the values of various kinetic parameters for VS dyes were estimated as shown in Table 1. When the pseudofirst-order rate constants of reaction to yield the F-types undergoing fast and slow hydrolyses are denoted by  $k_F$  and  $k_S$ ,  $C_{F0}/C_0$  and  $C_{S0}/C_0$  may be equal to  $k_F/(k_F+k_S)$  and  $k_S/(k_F+k_S)$ , respectively. The values of  $k_c$  for VS dyes may be equal to those of  $k_F+k_S$ . It is worth noting that  $k_F$  and  $k_S$  are the product of the second-order rate constants of reaction and the concentration of the corresponding cellulose ion. Orange 7 and Yellow 17 with high reactivity with cellulose and high initial rate of scission may have similar values of  $k_F$  and  $k_S$ , while the other VS dyes larger value of  $k_S$  than that of  $k_F$ . In general, the F-types undergoing slow hydrolysis have very small value of  $k_{-S}/k_S$ , a high bond stability, while those undergoing fast hydrolysis have larger value of  $k_{-S}/k_S$ , a high reversibility as being mentioned below, than

that of  $k_{-s}/k_s$ . Although the formation of F-type undergoing the fast hydrolysis is slow, the F-types for Red 23 and Blue 19 have similar rates of bond scission to those for the other VS dyes.

On the whole, VS dyes with low affinity to cellulose gave smaller values of  $C_{F0}/C_0$ , although high values of  $C_{F0}/C_0$  were not given by all the dyes with high affinity.

The problem of reaction site of cellulose, however, remains to be solved.

### 3.2 Reversibility of Dye-Cellulose Bond

In the beginning, the VS and Hy types adsorbed on cellophane for six dyes shown in Table 2 were confirmed to be completely removed by boiling the adsorbed film in water for 20 min. The fixed species could not be practically removed by immersing the dyed film in boiling water at neutral.

The dye distribution in dyed cellophane and the dye-fiber bond stability in an alkaline treatment were examined by the cylindrical film roll method using dyed and undyed cellophane. The distribution of various species for Yellow 17 after an alkaline treatment at 50°C for 24 h are shown in Fig. 3 as an example.

Although the degree of migration  $G_i/C_0$  varied with dyes, the F-types for all the VS dyes migrated into the undyed layers to reproduce the F-types in the alkaline treatment as shown by the presence of F-types  $G_i$  in the initially undyed layers (Fig. 3 and Table 2). This fact shows that under the alkaline conditions the F-types of all the VS reactive dyeings revert to the VS types, which during migrating react with water to lose the reactivity or again with cellulose to reproduce the F-types, a slow migration of the F-type accompanied with partial hydrolysis. In some cases, the dimer between the VS and Hy types may be formed in the processes.

### 3.3 Dye Distribution after Alkaline Treatment

When the relationship between  $(A_i-F_i)$  or  $(B_i-G_i)$

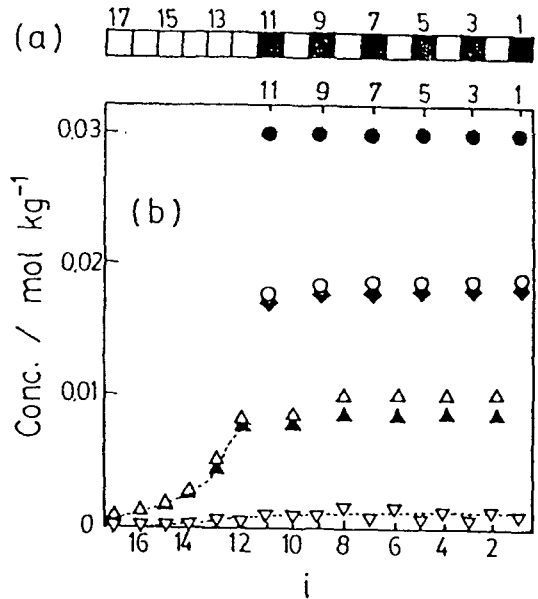


Fig. 3 (a) Initial state (■, F-type; □, undyed) of film layers and (b) distribution of various species (●,  $C_0$ ; ○,  $A_1$ ; ◆,  $F_1$ ; △,  $B_1$ ; ▲,  $G_1$ ; ▽,  $D_1$ ) of Yellow 17 in initially dyed and undyed cellophane layers after dipping in an aqueous alkaline (0.05 mol/dm<sup>3</sup> Na<sub>2</sub>CO<sub>3</sub>) solution at 50°C and pH 10.7 for 24h.

and  $i(1 \leq i \leq 17)$  is plotted, the unfixed (Hy+VS (+ their dimer)) species  $D_i$  are evenly distributed as shown in Fig. 3. Within the tenth layer, the VS species reverted from the initially dyed layers seemed to migrate to the next layers, indicating no reduction of total dyes. The fact that  $C_0 - A_i$  equals to  $B_{i+1}$  shows that the reverted VS species diffuse evenly into the adjacent initially undyed layers.

The mean concentrations of various species within the tenth layer for six VS dyes after an alkaline treatment are summarized in Table 2 ( $1 \leq i \leq 6$ ). The apparent alkaline stability for six VS dyes estimated by the mean value of  $F_i/C_0$  ( $1 \leq i \leq 7$ ) was in the following order as shown in Table 2 :

$$\text{Blue 19} \rangle \text{Blue} \rangle \text{Red 22} \rangle \text{Orange 16} \\ = \text{Orange 7} \rangle \text{Yellow 17} \quad (1)$$

**Table 2. Mean Distribution of Various Species for VS Dyes after an Alkaline Treatment(0.05 mol/dm<sup>3</sup> Na<sub>2</sub>CO<sub>3</sub>) at 50°C and pH 10.7 for 24 h(1 ≤ i ≤ 9) and analyses of Reversibility of Dye-Cellulose Bond.**

C. I. Reactive	Yellow 17	Orange 7	Orange 16	Red 22	Blue 19	Blue
C <sub>0</sub> × 10 <sup>2</sup> (mol/kg)	2.94	4.73	3.82	4.19	1.22	5.65
A <sub>2n-1</sub> × 10 <sup>2</sup> (mol/kg)	1.89	4.03	3.12	3.12	3.77	4.92
F <sub>2n-1</sub> × 10 <sup>2</sup> (mol/kg)	1.81	3.82	3.10	3.49	2.17	4.79
B <sub>2n</sub> × 10 <sup>2</sup> (mol/kg)	1.02	0.668	0.687	0.379	0.144	0.692
G <sub>2n</sub> × 10 <sup>2</sup> (mol/kg)	0.877	0.657	0.682	0.355	0.109	0.633
F <sub>1</sub> /C <sub>0</sub>	0.616	0.808	0.810	0.833	0.931	0.848
(F <sub>1</sub> - G <sub>1-1</sub> )/ C <sub>0</sub>	0.317	0.669	0.638	0.748	0.885	0.734
G <sub>1</sub> /B <sub>1</sub>	0.860	0.984	0.993	0.937	0.757	0.915

The apparent stability shown by the order(1) is nearly similar to the stability examined above(cf. 3.1).

The apparent degree of scission estimated by  $1 - (F_i - G_{i+1})/C_0$  (1 ≤ i ≤ 7) was in the following order :

$$\text{Yellow 17} > \text{Orange 16} > \text{Orange 7} > \text{Blue} > \text{Red 22} \\ > \text{Blue 19} \quad (2)$$

This order is almost similar to the initial rate of scission examined above(cf. 4.1).

The fixation ratios G<sub>i</sub>/B<sub>i</sub> in the initially undyed layers for Yellow 17 and Blue 19 were a little smaller than those for the other dyes, implying an effect of dimerization of Yellow 17 and Blue 19 which have large values of k<sub>2</sub> compared with the other VS dyes. The VS types may react with the Hy type existing evenly in each layer to form the dimer which suppresses to reproduce the F-type. Since the value of k<sub>2</sub> for Orange 16 is very smaller

than those for these two dyes although it forms the dimer, no effect may be observed in the case of Orange 16.

On immersing in an aqueous alkaline solution, VS dyes fixed on cellulose show not only the reversibility but also the effect of dimerization if they have large values of k<sub>2</sub>.

#### 4. Summary

The VS dyes fixed on cellulose show the bimodal, slow and fast, hydrolytic behavior in an alkaline treatment. The bimodal character may correlate with the position of the hydroxyl groups in cellulose. The rate of faster scission for the F-types of a half of VS dyes examined is five times larger than that undergoing slow hydrolysis. The rate of scission for F-types of the other VS dyes undergoing fast hydrolysis is more than six to twenty times larger than that undergoing slow hydrolysis. The rates of slower hydrolysis are nearly the same for all VS dyes examined. The relative ratio of production for two kinds of F-types varies with dyes. In general, VS dyes with low affinity to cellulose showed low values of C<sub>F0</sub>/C<sub>0</sub>.

Under alkaline conditions, the F-types are hydrolyzed to yield the VS type which migrates in the substrate and reacts with cellulose to reproduce the F-type or with water to yield the Hy type which diffuse in cellulose and is desorbed into the external solution.

#### References

1. Stamm, O.A., *J. Soc. Dyers Colour.*, **80**, 416(1964).
2. Senn, R.C. and Zollinger, H., *Helv. Chim. Acta*, **46**, 781(1963).
3. Kim, I.H., *Sen'i Gakkaishi*, **45**, 167(1989).
4. Stamm, O.A., *Helv. Chim. Acta*, **46**, 3008(1963).
5. Bhagwanth, M.R.R., Rama Rao, A.U. and Venkataraman, K., *Ind. J. Chem.*, **6**, 397(1968).