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HYDROLYSIS OF VINYLSULFONYL REACTIVE DYES

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ABSTRACT

The hydrolysis of two vinylsulfonyl reactive dyes, C. I. Reactive Orange 7 and Red 22 was investigated at 50°C. The rate constants of hydrolysis from the sulfatoethylsulfonyl (SES) type to the vinylsulfonyl (VS) type and those from the VS type to the hydroxyethylsulfonyl type were estimated. The former rate constants were about 5000 times larger than the latter ones. It was confirmed for both the dyes that no dimer of the bis (arylsulfonylethyl) ether type was formed under the conditions examined.

1. INTRODUCTION

The hydrolysis of reactive dyes is a very important process, since the reactive dyes are exclusively applied from the aqueous phase for the technological reasons. The kinetics and mechanism of hydrolysis of mono- and dichlorotriazinyl reactive dyes have been intensively studied to understand the reaction mechanism of reactive dyeing¹⁻³. In spite of the early marketing of vinylsulfonyl (VS) dyes, the fundamental studies on the kinetics of hydrolysis have been rather rare. According to Stamm⁴, the reaction mechanism of VS dyes consists of the 1, 2-trans-addition of an alcohol to a polarized double bond. This type of reaction is classified within the general scope of the Michael addition. Activation of the double bond results from the presence of electron-withdrawing substituents. The addition is initiated by a nucleophilic attack at the positive end of the polarized double bond. Stamm noted the reversible character of the dye-fiber bond for this type of dyes⁴. Rys and Stamm⁵ investigated the hydrolysis of C. I. Reactive Yellow 17 and Blue 19 and elucidated the reaction scheme of hydrolysis qualitatively. They have also shown that the bis (arylsulfonylethyl) ether was formed as a by-product. Bhagwanth et al⁶ proposed another mechanism of the reaction between VS dye and cellulose.

The VS groups are not normally present in commercial dye and the β -sulfatoethylsulfonyl (SES) groups are used as a useful less reactive precursor. The kinetics of the formation of VS type from the SES one for three dyes was studied by Bohnert⁷. The formation is very rapid under the alkaline conditions for the practical dyeing. Bohnert and Weingarten measured the rate of hydrolysis of the VS type for 9 Remazol dyes⁸, though they neglected the dimer formation.

On the other hand, the diffusion with simultaneous reaction in cellulose for VS reactive dyes was investigated in the temperature range between 40 and 60°C by the method of cylindrical film roll⁹. The *pseudofirst-order* rate constants of reaction with cellulose and the diffusion coefficients for VS dyes were estimated.

In the present study, the rate of formation of the VS type from the SES one and that of the hydroxyethylsulfonyl (Hy) type from the VS one for C. I. Reactive Orange 7 and Red 22 are estimated. Since the former reaction will be very faster than the latter, the experimental conditions to determine their rate constants separately are tried to find. Whether the dimer of ether type is formed or not is examined under various conditions. The reaction products at respective reaction time are analyzed by high pressure liquid chromatography (HPLC)¹⁰.

Table 1. Vinylsulfonyl dyes used

C. I. Reactive	C. I. Constitution No.	Mol. wt.	Commercial dyes used
Orange 7	17756	617.5	Diamira Brilliant Orange RR
Red 22	14824	590.5	Sumifix Red B

2. EXPERIMENTAL

2.1 Reactive Dyes

The VS reactive dyes examined are shown in Table 1 and their chemical structures are given by C. I. Constitution Number. Their commercial dye samples were purified by the use of organic solvents¹¹. A dye sample was dissolved in dimethylformamide (DMF) at room temperature and the solution was filtered to remove the insoluble ingredients. Acetone was added to the filtrate to precipitate the dye, which was filtered, washed with petroleum ether by using a Soxhlet's extractor. An incomplete washing left some DMF which spoiled the hydrolytic reactions.

Though the purification brought about the partial hydrolysis of SES type of highly reactive dyes, it was modified by the initial conditions of the reactions when the kinetic parameters were calculated. The other chemicals used were of reagent grade.

The molar concentration of each dyes was determined spectroscopically by using the Hy type purified by the salting-out method using sodium acetate.

2.2 Hydrolytic Reaction

The hydrolytic experiments were carried out at different pH's to check the constancy of the second-order rate constant of various reactions at 50°C. Kolthoff's buffer solution (pH 6.8 ~ 8.0, potassium phosphate + sodium tetraborate) was used in the reaction from the SES type to the VS one, while only sodium hydroxide was used as the alkaline agent in the hydrolysis of the VS type. The values of pH were measured by a Hitachi-Horiba pH meter at 50°C.

An aqueous dye solution for hydrolysis was allowed to react under a sufficient stirring at 50.0°C after mixing the dye solution with a given alkaline solution at the same temperature. This was set as the starting point of reaction ($t = 0$). No effect of stirring on the rate of reactions was experimentally confirmed.

An aliquot of the reaction solution was pipetted out, neutralized at respective reaction time and then analyzed by HPLC. The time of half-neutralization was regarded to be the reaction time (t). The reverse phase mode of HPLC was used throughout the present study¹⁰. Chromatographic conditions used are shown in Table 2.

2.3 Synthesis of Model Compounds

Intermediates for the synthesis containing β -hydroxyethylsulfonyl group were supplied by Mitsubishi Kasei Corporation. The Hy type of C. I. Reactive Orange 7 was synthesized as follows¹²: Acetic anhydride was added to the γ -acid solution dissolved in 0.015M-NaOH at 50°C and was stirred vigorously for 15 min. Sodium carbonate was added to the solution and was stirred for 1 h at 90 ~ 95°C. 4-(β -Hydroxyethylsulfonyl) aniline was dissolved in 0.02M-hydrochloric acid and was diazotized below 5°C. Acetyl- γ -acid dissolved in 0.05M-sodium hydrogen carbonate was added to the diazonium salt solution at 5°C and stirred vigorously for 1 h below 5°C. After neutralizing the solution by hydrochloric acid, saturated sodium acetate solution was added to precipitate the dye. The precipitate was washed by ethanol by a Soxhlet's extractor. Repeating the salting out and washing, the purified sample of the Hy type was obtained.

The Hy type of C. I. Reactive Red 22 was synthesized by the use of 2-methoxy-4-(β -hydroxyethylsulfonyl)aniline and 1-naphthol-5-sulfonic acid and was purified by the same method as described above.

3. REACTION SCHEME OF VINYLSULFONYL DYE

The formation of the VS type from the SES one occurs almost instantly by the addition of alkali to the aqueous solution of the SES type^{7,8}. The activated double bond of VS group polarized strongly by the sulfonyl group is able to undergo an addition reaction with water by a base catalyst to yield the corresponding Hy type⁴. The Hy type may further react with the VS type to form a

Table 2. Chromatographic conditions

Apparatus	Shimadzu 6A-type HPLC
Column	Wakogel LC ODS-10H 100mm length, $\phi = 6.0$ mm I. D.
Mobile phase	10mM $(\text{NH}_4)_2\text{HPO}_4$: Methanol (v/v) = 70 : 30 (Orange 7) or 60 : 40 (Red 22)
Flow rate	1.0ml/min
Temperature	30°C
Detector	UV (254 nm) Visible : 490 nm (Orange 7) or 510 nm (Red 22)
Integrator	Chromatopack CR-3A type

dimer of ether type.

These reactions of VS dye are written as follows^{4,5,7,8}.

Thus, the change in the concentration of the SES, VS, Hy and D types are given by :

$$\frac{d[\text{SES}]}{dt} = -k_0[\text{SES}][\text{OH}^-] \quad (4)$$

$$\frac{d[\text{VS}]}{dt} = k_0[\text{SES}][\text{OH}^-] - k_1[\text{VS}][\text{OH}^-] - k_2[\text{VS}][\text{Hy}] + k_{-2}[\text{D}] \quad (5)$$

$$\frac{d[\text{Hy}]}{dt} = k_1[\text{VS}][\text{OH}^-] - k_2[\text{VS}][\text{Hy}] + k_{-2}[\text{D}] \quad (6)$$

$$\frac{d[\text{D}]}{dt} = k_2[\text{VS}][\text{Hy}] - k_{-2}[\text{D}] \quad (7)$$

where $[\dots]$ denotes the concentration (mol/dm^3) of corresponding component, $k_0(\text{dm}^3/\text{mol min})$ is the second-order rate constant of hydrolysis for the SES type, $k_1(\text{dm}^3/\text{mol min})$ is that of the hydrolysis for the VS type, $k_2(\text{dm}^3/\text{mol min})$ is that of the dimerization, and $k_{-2}(\text{min}^{-1})$ is the first-order rate constant of the reverse reaction of dimerization. Since the total concentration, $C(\text{mol/dm}^3)$ of the reaction system was kept constant, the condition (8) holds:

$$[\text{SES}] + [\text{VS}] + [\text{Hy}] + 2[\text{D}] = C \quad (8)$$

Fig. 1. Liquid chromatograms of (a) the commercial or purified samples, (b) the synthesized Hy type, (c) the hydrolysate of the SES type at pH 8.01, $t = 180$ min (The SES type was completely converted into the VS one (cf. Fig. 2).), and (d) the hydrolysate of the VS type at pH 11.20, $t = 120$ min for C. I. Reactive Orange 7 (About a half of the VS type was converted into the Hy one). The peaks (1), (2) and (3) were assigned as the SES, Hy and VS types, respectively (see text).

4. RESULTS AND DISCUSSION

4.1 Assignment of Liquid Chromatograms

Fig. 1 shows the liquid chromatograms of commercial and purified samples, the Hy type of synthesized samples and the reactant solutions for C. I. Reactive Orange 7. The liquid chromatograms for Red 22 were similar to those for Orange 7. The peak of the Hy type for both the dyes was assigned by the corresponding synthesized sample. The peaks of the SES and VS types were assigned by the main component of commercial sample (cf. (a) in Fig. 1) and the hydrolysis product of the SES type under the neutral conditions (cf. (c) in Fig. 1), respectively. According to the method which Rys and Stamm⁵ used to confirm qualitatively the formation of the VS and Hy types, the R_F -values were obtained by using the eluent: *n*-butanol: ethanol: water = 4: 3: 3. The order of the R_F -values for their components of both the dyes was same as their results, though their values were different with dyes. The order of the retention time for these dyes was confirmed to coincide with that of R_F -values. Since the second peak of liquid chromatogram and the second R_F -value were assigned to the Hy type, the first

and the third ones were assigned to the SES and VS ones, respectively. Fig. 1 shows also that the commercial sample contained a small amount of the Hy and VS types.

4.2 Estimation of Rate Constants

4.2.1 Hydrolysis of the SES Type

Fig. 2 shows the hydrolytic behaviors of the SES type for C. I. Reactive Orange 7. The SES type was gradually converted into the VS one with time, but no hydrolysis of the VS type occurred as shown by no increase in the peak area of Hy type, a separation of the SES hydrolysis from the VS one.

Since the VS type was not hydrolyzed in the neutral region as shown in Fig. 2, the rate constant of the conversion of the SES type into the VS one can be calculated by eq. (4).

Since the pH of the reactant solution was kept constant by a buffer solution, the reaction became of *pseudofirst-order* whose rate constant is k_0' (min^{-1}) and was integrated as follows:

$$\log ([\text{SES}]/C_0) = -k_0' t' \quad (9)$$

where $t' = t - t_0$, $t(\text{min})$ is the reaction time observed, and $C_0(\text{mol}/\text{dm}^3)$ is $[\text{SES}]$ at $t' = 0$.

By omitting the data at the initial stage of reaction where the variation of concentration is very large and

Fig. 2. Hydrolytic behaviors of the SES type to give the VS one for C. I. Reactive Orange 7 at 50°C and at pH 6.81 (○), pH 7.32 (△) and pH 8.01 (□), respectively, and the variation in the concentration (■) of the Hy type during the hydrolysis at pH 8.01. The concentration of the Hy type was constant throughout the reaction. The dotted lines show an initial stage of reaction before t_0 (see text).

Fig. 3. Hydrolytic behaviors of the VS type to give the Hy one for C. I. Reactive Red 22 at 50°C and pH 10.74 (○), pH 11.12 (△), and pH 11.41 (□), respectively. The dotted lines show an initial stage of reaction before t_0 (see text). The VS type was completely converted into the Hy type after sufficiently long time.

the values of reaction time can not so accurately be measured, the fitting of each data was improved in the calculation of k_0' . An appropriate reaction time to minimize the scattering of data was determined to be t_0 (cf. Fig. 2).

The values of k_0' was proportional to the pH values of the reactant solution as expected. The k_0 -values at 50°C are also listed in Table 3. The k_0 -value for Orange 7 is higher than that for Red 22. Bohnert⁷ measured the k_0 -values for Red 22 at 20 ~ 40°C. The value at 50°C was estimated by an extrapolation to be 9.73×10^2 dm³/mol min, a smaller value than that of the present study.

4.2.2 Hydrolysis of the VS Type

Fig. 3 shows the hydrolytic behavior of the VS type for C. I. Reactive Red 22. In these experiments, the wavelength of detector (254, 490 or 510 nm) was checked to give no influence on the chromatogram. No variation in the absorption spectra of the reactant solution as

well as the constancy of the total peak area of chromatogram were also confirmed within a limited reaction time, indicating no change in the molecular skeleton and the satisfaction of boundary condition (8). But when the hydrolytic reaction was allowed to continue for more than 10 h at pH ≥ 10.8 , some measurable decrease in the absorption spectra and the total peak area of chromatogram were detected.

The SES type was immediately converted into the VS one by the addition of alkali as shown by the fact that no peak of the SES type was observed, and the VS type produced was gradually converted into the Hy one. Thus, if the pH higher than 11 is used, only the hydrolysis of the VS type can be analyzed. It was confirmed that after the SES type was hydrolyzed the pH of reactant solution was kept constant.

Since the concentration of VS was undetectable at infi-

Table 3. Rate constants of reactions for the SES type at 50°C

C. I. Reactive	Total conc. of dye (mol/dm ³)	t_0 (min)	Conc. of SES at t_0 (mol/dm ³)	pH	$k_0' \times 10^2$ (min ⁻¹)	$k_0 \times 10^{-3}$ (dm ³ /mol min)
Orange 7	7.64×10^{-4}	5	6.82×10^{-4}	6.81	0.265	7.28 ± 0.17
	8.04×10^{-4}	10	6.60×10^{-4}	7.32	0.848	
	7.58×10^{-4}	15	3.76×10^{-4}	8.01	3.95	
Red 22	8.31×10^{-4}	5	8.10×10^{-4}	6.81	0.106	2.89 ± 0.13
	8.58×10^{-4}	10	8.06×10^{-4}	7.32	0.342	
	8.21×10^{-4}	20	5.86×10^{-4}	8.01	1.52	

Table 4. Rate constants of reactions for the VS type at 50°C

C. I. Reactive	Total conc. of dye (mol/dm ³)	t_0 (min)	Conc. of VS at t_0 (mol/dm ³)	pH	$k_1' \times 10^2$ (min ⁻¹)	$k_1 \times 10^{-3}$ (dm ³ /mol min)
Orange 7	7.63×10^{-4}	10	7.21×10^{-4}	10.82	5.15	1.32 ± 0.09
	7.63×10^{-4}	10	6.68×10^{-4}	11.20	10.3	
	5.21×10^{-3}	20	3.48×10^{-3}	11.43	20.3	
	7.64×10^{-4}	20	4.49×10^{-4}	11.52	23.7	
Red 22	8.16×10^{-4}	10	7.22×10^{-4}	10.74	2.24	0.741 ± 0.002
	8.16×10^{-4}	10	7.18×10^{-4}	11.12	5.35	
	5.75×10^{-3}	10	4.54×10^{-3}	11.41	10.4	

nite reaction time though this Michael reaction may have a reversible character, the second-order rate constant for the reverse reaction of the hydrolysis of VS type was estimated to be zero (cf. Fig. 3). On the other hand, the dimerization of these dyes was not observed at all, i. e. k_2 and $k_{-2} = 0$ (see below). In common with case of the SES hydrolysis, the VS type showed a large variation of the concentration at the initial stage of reaction. The term t_0 was also introduced in this case as well as to remove the effect of existence of SES accompanied with the variation of pH.

Then, eq. (5) becomes of *pseudofirst-order* and the integration gives an equation of the same type except for the component, where k_1' (min^{-1}) is the *pseudofirst-order* rate constant of for the reaction of VS type to the Hy type.

The k_1' -values for Orange 7 and Red 22 are listed in Table 4. The values of k_1' for two dyes were proportional to the pH of the reactant solution. Then, the k_1' -values for Orange 7 and Red 22 can be calculated as shown in Table 4. The value for Orange 7 was larger than that for Red 22. The k_1' -values which Bohnert and Weingarten⁸ estimated in a sodium carbonate solution by a reactive dyeing were larger than those of the present study.

Rys and Stamm⁵ proved the formation of dimer of bis-(arylsulfonylethyl)ether type for C. I. Reactive Yellow 17 and Blue 19 as well as their mixed dimer. With both the dyes, whether the dimer was formed or not was examined by increasing the reactant concentration or by the addition of the Hy type of the same concentration. However, no experiment showed the existence of dimer for both the dyes. Both the dyes seem to have smaller dissociation constant of the hydroxyl group than the other VS reactive dyes which form dimer. Since the high-

est dye concentration examined is in the order of 10 mM, they imply absence of any dimer for both the dyes in the dye bath. Contrary to the mechanism proposed so far, there are some VS dyes which form no dimer.

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ビニルスルホン系反応染料の加水分解

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二つのビニルスルホン系反応染料, C. I. Reactive Orange 7 及び Red 22 の加水分解挙動を50℃で調べた。スルファトエチルスルホン (SES) 体がビニルスルホン (VS) 体になる加水分解反応は, VS 体がヒドロキシエチルスルホン (Hy) 体になる加水分解しない低い pH 条件下で, また, VS 体から Hy 体への加水分解反応は SES 体

が速やかに VS 体になる高い pH 条件下で行い, SES 体と VS 体の2次の加水分解速度定数を求めた。前者の速度定数は, 後者のそれより約5000倍大きい。この二つの染料の場合, いままで提案された反応機構と異なり, エーテル型の二量体は調べた条件下では生成しないことを確かめた。