

Reaction Mechanism of Sulfatoethylsulfon Dye with Silk

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In order to elucidate the reaction mechanism between sulfatoethyl-sulfon dye and silk, the reactions of sulfatoethylsulfon dye (Ester) and Vinylsulfon dye (Vinyl) of C. I. Reactive Blue 19 with silk and water were examined. At pH 5 Vinyl reacted with silk more strongly than Ester, and at pH 7 both dyes manifested the same reaction. At pH 9 the amount of Ester reacted with silk was approximately equal to that of Vinyl for the first two hours, and Ester reacted somewhat more strongly than Vinyl, thereafter. The rate of the reaction of Ester with water was almost the same as that of Vinyl. Also, Ester was converted completely to other components (that is, to Vinyl, Hydroxyl and Ether) during the short time in alkaline solution. From these results it was concluded that Ester was decomposed to Vinyl in the dyeing process, which was then reacted with silk by means of the nucleophilic addition.

The reactive dye was at first marketed thirty years ago. The studies on this dye was of a wide range. Recently, the reports concerning the synthesis of the new reactive dyes and the dyeabilities of these dyes (Kamel *et al.*, 1982; Stapleton and Waters, 1981, and others) and the decomposition behaviors (Kamel *et al.*, 1982, and others) are available. However, there are little outstanding advances in regard to the reaction mechanism. Thus far it has been presumed that a sulfatoethylsulfon dye is converted into the vinylsulfon dye, then the latter reacts with fiber during the dyeing process (Bohnert, 1959; Von der Eltz, 1959; Heynd, 1962; Rys and Stamm, 1966). On the other hand, Bhagwanth and his associates (1970) have proposed the theory that a sulfatoethylsulfon dye reacts directly with cellulose by nucleophilic substitution. But, there seems to be no paper dealing with these two theories and examining such reaction mechani-

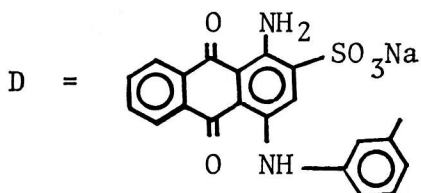
sms with the protein fibers. Thus, in order to elucidate the reaction mechanism of a sulfatoethylsulfon dye with silk, either nucleophilic addition or nucleophilic substitution, we measured the rate of reactions of sulfatoethylsulfon and vinylsulfon dyes of C. I. Reactive Blue 19 with silk and water.

Materials and Methods

The raw silk yarns were scoured in the solution containing both of sodium carbonate and sodium hydrogencarbonate (overall concentration was 0.01 mol dm⁻³) under boiling for 90 minutes (liquor ratio 100 : 1). Degummed silk yarns (termed silk) obtained were washed thoroughly in water and acetic acid solution of 0.01 mol dm⁻³, and finally water, then, bone-dried.

Two reactive dyes, the sulfatoethylsulfon dye (abbreviated Ester) and the vinylsulfon dye (Vinyl) of C. I. Reactive Blue 19, were used. The

Ester was purified from Remazol Brilliant Blue R by dimethylsulfoxide-acetone method (Shimizu, 1972), and the Vinyl was synthesized from the same marketed dye and then purified by recrystallization from water (Shimizu, 1975 a). The purity of the sample was confirmed by paper-chromatography. The chemical structures of these dyes are shown below.



Ester : $D-SO_2CH_2CH_2OSO_3Na$

Vinyl : $D-SO_2CH=CH_2$

Dyeing

The dyeings were conducted under the following condition : Silk Ig, concentration of dye 1.5×10^{-3} mol dm⁻³, pH 5, 7, 9, liquor ratio 50 : 1, temperature 80°C

After dyeing the silk was taken out and treated solution four times with the solution mixed with 50% urea and 1% Nonypol 80 (liquor ratio 50 : 1) under boiling for 3 min to extract the unreacted dye. The amount of reacted dye was determined by both the solubilization method (Shimizu, 1975 b) and the following equation :

$$(a) = (b) - ((c) + (d))$$

(a) : the amount of reacted dye, (b) : overall amount of the dye in the system, (c) : the amount of the dye remaining in the bath, (d) : the amount of dye extracted.

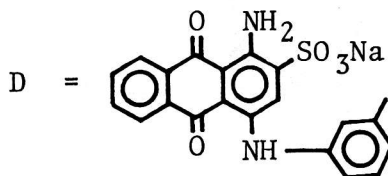
Rate of hydrolysis

The dye (Ester or Vinyl) of 10 μmol was dissolved in the buffer solution of 25 ml (the solution mixed with 0.05 mol dm⁻³ sodium carbonate and 0.01 mol dm⁻³ sodium hydrogencarbonate, pH 9) and kept at 80°C. After a certain time 1 ml of the treated solution was pipetted

out, to which a few drops of acetic acid were added, and used for paper chromatography.

n-Butanol/acetic acid/water (4/1/4, by volume, upper layer), was used as the developing agent. After the development for several hours, the bands of the unaltered Vinyl (or resulting one), hydrolyzed dye (Hydroxyl) and ether form (Ether) (Rys and Stamm, 1966 ; Shimizu, 1977) were cut off, extracted with 2.8% ammonia water. The amount of each compound was determined by colorimetry (the absorbance was measured at absorption maximum, 595 nm).

The chemical structures of Hydroxyl and Ether are shown below.



Hydroxyl : $D-SO_2CH_2CH_2OH$

Ether : $D-SO_2CH_2CH_2OCH_2CH_2SO_2-D$

Results and Discussion

The silks were dyed by Ester and Vinyl at 80°C in the solution of pH 5, 7 and 9, and the results are shown in Fig. 1. At pH 5 the rate of the reaction of Vinyl with silk was markedly larger than that of Ester. At pH 7 the rates of the reaction of Ester and Vinyl were nearly equal to each other, and at pH 9 both dyes had the same rates for the first two hours, but the reactivity of Ester was superior to Vinyl thereafter.

Thus, it seemed to be an evidence for the mechanism of nucleophilic addition that the rate of the reaction of Vinyl with silk was larger than that of Ester at pH 5. The lower reaction rate of Ester was considered to be due to the fact that Ester was converted to Vinyl slightly at pH 5. After Ester was boiled in the solution of pH 5 for four hours, the solution was analy-

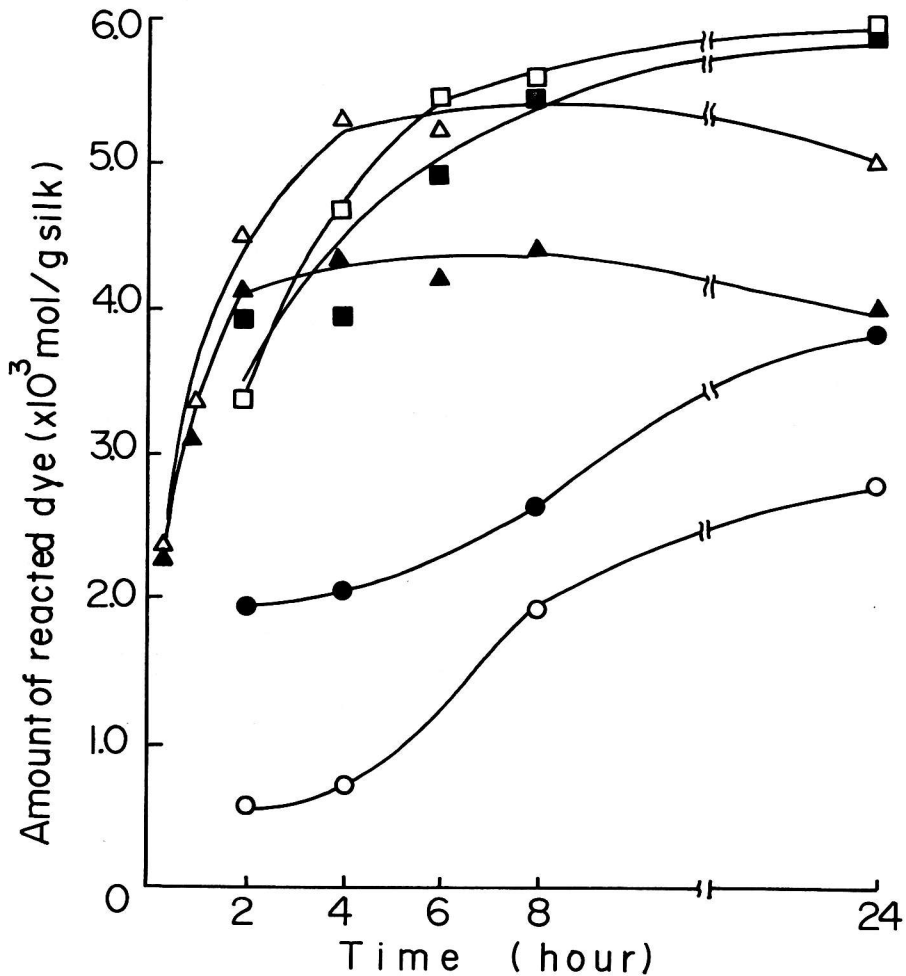


Fig. 1. The rate of the reaction of sulfatoethylsulfon and vinylsulfon dyes with silk at 80°C.

Starting dye	pH		
	5	7	9
Ester	○	□	△
Vinyl	●	■	▲

zed by paperchromatography. The amount of each component was estimated by the naked eyes, and it was apparent that the about half the amount of Ester was converted to Vinyl.

As mentioned above, the amount of Ester reacted increased beyond Vinyl at pH 9 after two-hour reaction period. In order to clarify this re-

ason, the reactions of Ester and Vinyl with water in the solution of pH 9 at 80°C were examined. The results obtained are shown in Fig. 2. This represents the relationship between time and the contents (%) of the components existing in the solution.

As the conversions of Ester or Vinyl to the

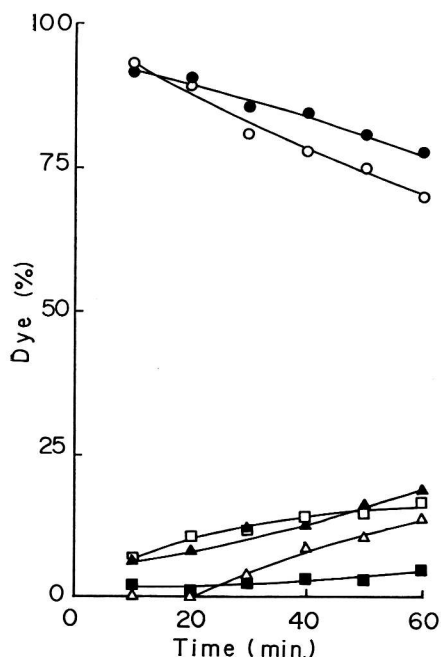


Fig. 2. The conversions of sulfatoethylsulfon and vinylsulfon dyes to other components in the buffer solution of pH 9 at 80°C.

Starting dye	Component		
	Vinyl	Hydroxyl	Ether
Ester	○	△	□
Vinyl	●	▲	■

Hydroxyl and the Ether are the hydrolysis processes, the rate of hydrolysis of Ester is almost equal to that of Vinyl. Therefore, the difference mentioned above cannot be explained by the rate of hydrolysis. Furthermore, as shown in Fig. 2, Ether adsorbed by silk was larger in quantity in the dyeing by the former than by the latter. The Ether adsorbed decomposes gradually with the lapse of time and forms Vinyl and Hydroxyl, then the Vinyl can react with silk (Shimizu, 1977). The difference of the amounts of Ester and Vinyl reacted with silk during 4 to 24 hours at pH 9 is due to the difference of the amounts of Ether existing in the bulk solution (con-

sequently in the silk) during the dyeing with both dyes.

It can also be seen from Fig. 2 that Ester is converted completely to Vinyl, Hydroxyl and Ether for the short time (even ten minutes). As Ester does not exist in the solution, the direct reaction of Ester with silk by the nucleophilic substitution is impossible. The unreacted dyes were extracted by dimethylsulfoxide from the dyed silk with Ester at 80°C for 20 min and the extracted solution was analyzed by paperchromatography. Thus, it became obvious that Ester did not exist also in the unreacted dyes adsorbed on silk.

From these results it was concluded that Ester was decomposed to Vinyl in the dyeing process, and the resulting Vinyl reacted with silk by the nucleophilic addition.

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道明美保子・清水慶昭・木村光雄：スルファトエチルスルホン型反応染料と絹の反応機構

スルファトエチルスルホン型反応染料と絹との反応機構を解明するため、C. I. Reactive Blue 19 のスルファトエチルスルホン型（エステル）とビニルスルホン型（ビニル）を用いて絹および水との反応を調べた。pH 5 ではビニルがエステルより反応し易く、pH 7 では同じ位であった。pH 9 では約2時間まではほぼ等しく、それ以後はエステルの方がビニルより若干固着度が大きかった。水との反応速度は両者大体同じであり、エステルはアルカリ性溶液中では短時間のうちに全て他の成分（すなわち、ビニル、ヒドロキシおよびエーテル）に変化してしまうことが明らかになった。従って、エステルは染色行程中にビニルに変化し、生じたビニルが求核付加により絹と反応すると結論する。