s-Triazine 系 反應性 染料에 관한 研究 (제3보).[1,2] 2 個의 發色團을 포함한 Monofluorotriazine 反應性 染料의 合成

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(1982. 12. 20 접수)

Studies on the *s*-Triazinyl Reactive Dyes (III).[1,2] Synthesis of Dichromophoric Monofluorotriazinyl Reactive Dye

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(Received October 20, 1982)

요 약. 새로운 반응성염료 개발의 일환으로 trifluoro-*s*-triazine 을 반응성분으로 이용하여 한 분자에 2개의 서로 다른 chromophore 를 가지는 반응성염료를 합성한 다음, 이의 가수분해속도와 면섬유에 대한 염색성을 조사하였다. 이 염료의 유사 일차 가수분해속도상수, k_w 는 pH=10.0, 온도 60°C 에서 $k_w = 2.6 \times 10^{-2}$ min^{-1} 로서 monochlorotriazine 반응성염료보다 높은 값을 보였으며 염착률과 고착율 역시 monochlorotriazine 계 염료보다 우수하였다. 얻어진 반응성 염료는 황색계열로서 수율은 75 % 였다.

ABSTRACT. Triazinyl reactive dye containing two different chromophore was synthesized by using trifluro-*s*-triazine as reactive component. The yield of this dye was 72 % and its colour was yellowish red as a mixed shade. The hydrolysis rate and dyeing properties of this dye were studied and compared with monochlorotriazinyl reactive dye. It was found that monofluorotriazinyl reactive dye showed much higher hydrolysis rate than monochlorotriazinyl reactive dye.

1. INTRODUCTION

For a century after Perkin's discovery of Mauve in 1856 the synthetic dyes applicable to cotton were broadly of three types: (1) direct dyes attached to the cellulose macromolecule by hydrogen bonding, van der Waals or dispersion forces; (2) vat dyes precipitated in the fiber by various method such as reduction and oxidation reaction; (3) reactive dyes combined with the cellulose hydroxyl group forming covalent bonding.

The reactive dyes represent by far the most important development in synthetic dyes owing to their ease of application and the brilliance of colour. There are several types of reactive dyes containing different reactive groups. In principle, a reactive dye should contain a leaving group(X) which can undergo nucleophilic displacement by a hydroxyl group of cellulose(Dye-X+Cell−O$^{\ominus}$→Dye-O-Cell+X$^{\ominus}$), or an activated C=C bond which is able to add to a hydroxyl group of cellulose forming ether(Dye-CH=CH$_2$+Cell−OH→Dye-CH$_2$-CH$_2$-O-Cell). Trichloro-s-triazine, which has been known for almost hundred years, is a remark-

able substance with tremendous potentialities as an intermediate for synthesis of reactive dyes.

In 1956[3], ICI marketed triazinyl dye containing two chlorine atoms, Procion M dyes, applicable to cellulosic fiber. In 1957[4], Cibacron dyes(Ciba) and Procion H(ICI), monochlorotriazinyl dyes, were marketed. Moreover, lately, the first monofluorotriazinyl reactive dyes were developed, and they were applicable to cellulosic fiber. They contained the triazinyl group as a reactive component, it formed a strong covalent bond with the free hydroxyl or other suitable group in the fiber.

Reactive dyes have been used extensively because of having benefits of bright colour and good fastness by a simple dyeing method. It is known that good fastness of reactive dyes was due to strong covalent bonds with hydroxyl group or amino group of fiber.

In this work, we prepared monofluorotriazinyl reactive dyes containing two different chromophore. These dyes with two different chromophores in a molecule show a mixed shade[5]. That is a same result of color combination. The rate of hydrolysis and dyeing properties were examined and compared with monochlor-

otriazinyl reactive dye containing the same chromophore. For this purpose, the monofluoro triazinyl(III) and monochlorotriazinyl(IV) reactive dyes containing the same chromophore were synthesized.

2. EXPERIMENTAL

Proton NMR spectra were taken on Varian EM-360A spectrometer in D_2O relative to 3-(Trimethyl silyl)-1-propane-sulfonic acid sodium salt as internal standard. Infrared spectra were taken on Perkin-Elmer 735B Spectrometer. UV-VIS spectra were recorded on a Cary 14 Spectrophotometer. Analytical thin layer chromatography was performed on silical gel coated plastic plates(Baker-flex IB2-F)

Synthesis of trifluoro-s-triazine. In a dry polyethylene flask, finely devided cyanuric chloride (10.3 g, 0.06 mole) was placed, and cooled it to 0°C. Then hydrofluoric acid (8.5 ml) was added for 30 minutes at −10°C.

After completing the addition of hydrofluoric acid, the temperature was slowly raised to the room temp. After the solution was stirred for 5 hours, the desired product(6.3g, 82%) was obtained by fractional distillation at 72~74°C. The product was found to be identical with an authentic compound in all respects. bp 72~74°C (lit[6,7,8] 74°C);IR(Neat) 1550, 1380, 1170, 790 $cm^{-1}cm^{-1}$.

Synthesis of Chromophore I. Anisidine-2,5-disulfonic acid (14.5g, 0.05 mole) was dissolved in 150 ml of H_2O. The solution was cooled in a beaker surrounded by ice and stirred with electric motor. When the solution was cold (0°C~3°C), 22.8 ml of 2 N nitrite solution and 25ml of conc. HCl(35%) were added dropwise from a dropping funnel.

After completing the addition of nitrite, the mixture was stirred for 15 minutes and was then tested to make sure that it gives a strong blue

$\left(\equiv \text{(Dye1)} - NH_2 \right)$ I

$\left(\equiv \text{(Dye2)} - NH_2 \right)$ II

III

IV
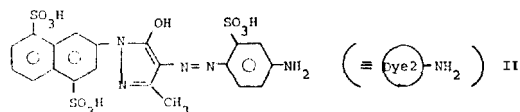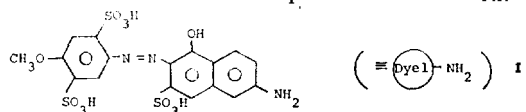
coloration with Congo red paper and a weak blue test with starchiodide paper. 2-Amino-5-hydroxy-naphthalene-7-sulfonic acid (J-acid, 12.0g, 0.05 mole) was stirred with 130 m*l* of water and 20 % sodium carbonate solution was added until the pH was to 7. Subsequently, the diazo solution was added into a J-acid solution for 40 minutes at 0~5°C. During the addition, the pH of solution was kept at 7 by adding a sodium carbonate solution. The mixture was stirred for 2 hours and the temperature was maintained 0~5°C. The end of reaction was tested by thin layer chromotography. After 2 hours, only one spot was developed. The chromophore I was precipitated with postassium chloride, filtered with suction, and dried in vacuum oven at 50°C. The desired product was obtained in 95 % yield (25.1 g) and was found to be identical with an authentic compound in reference[9]. Chromophore I; NMR δ 3.8(s, 3H), 6.6~8.2(m, 6 H); IR(KBr) 1570, 1440, 1180cm^{-1}; UV-VIS λ_{max} 496 nm in H$_2$O

Synthesis of chromophore II. To a solution of 4-nitro aniline 2-sulfonic acid(10.9 g, 0.05 mole) in H$_2$O 100 m*l* at room temperature was added 25 m*l* of conc. hydrochloricacid(35 %). The solution was cooled to 0~3°C. Then 22.8 m*l* of 2 N nitrite solution was added dropwise from a dropping funnel. After completing the addition of nitrite, the mixture was stirred for 10 minutes and was tested to make sure that it gives a strong blue coloration with Congo red paper and a weak blue test with starchiodide paper. C-acid pyrazolone (19.2 g, 0.05 mole) was stirred with 160 m*l* of water and 20 % sodium carbonnate solution was added until the pH was 5.3. Then the diazo solution was added into a C-acid pyrazolone solution for 40 minutes at 0~5°C. During the addition, the pH of solution was maintained at 5.0~5.5 by adding a sodium carbonate

solution. After coupling for 1 hour, sodium sulfide (Na$_2$S, 9 H$_2$O, 128 g) was added to reduce the nitro group and refluxed for 6 hours. The reaction mixture was allowed to cool slowly to the room temperature. The chromophore II was precipitated with postassium chloride, filtered with suction, and dried in vacuum oven at 50°C. The procedure is summarized on *Fig.* 1. The desired product was obtained in 93 % yield (30.2 g) and was found to be identical with an authentic compound in reference[10].

Chromophore II; NMR δ 2.5(s, 3H), 7.3~9.2(m, 8H); IR(KBr) 1570, 1400, 1150, 1050 cm^{-1}; UV-VIS λ_{max} 448nm in H$_2$O

Synthesis of monofluorotriazinyl reactive dye. As the previous reports[1,2] to this study, triazinyl reactive dyes containing one or two similar chromophore were synthesized by using trifluoro-*s*-triazine as reactive component. Trifluoro-*s*-triazine has been known to react readily with nucleophilic reagents.[1,2] The difluorotriazinyl group can be readily introduced into the amino substituted intermediates by reaction with trifluoro-*s*-triazine, but the secondary fluorine atom is less readily replaced than the first. If the second fluorine atom is removed by reaction with an amino
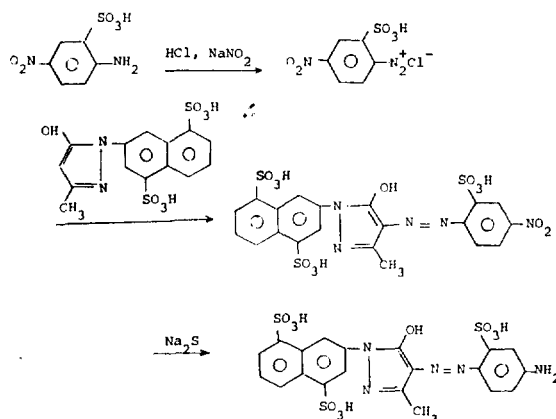

Fig. 1. Synthesis of Chromophore II.

compound, a monofluoro triazinyl reactive dye can be obtained. Chromophore I(5.3g, 0.01 mole) was dissolved in H_2O 120 ml and adjusted to pH 5.5. Cyanuric fluoride (1.4 g. 0.01 mole) in acetone 20 ml was slowly added to the chromophore I solution at $0 \sim 3°C$. During the addition, the pH of the solution was maintained 5.5 by the 10 % sodium carbonate solution. After completing the addition of cyanuric fluroide, the mixture was stirred for 30 minutes. Then chromophore II (6.5 g, 0.01 mole) in H_2O 120 ml was added to the difluorotriazinyl dye solution at $0 \sim 5°C$, pH 6.5. After adding the chromophore II, temperature was slowly raised to the 25°C. At this temperature, the mixture was stirred for 4 hours. The end of reaction was tested by developing the thin layer chromatography. The final monofluoro reactive dye was obtained by salting out with KCl, filtering, vacuum drying and grinding to a fine powder. The synthesized dyes were purified by the usual way using organic solvents.[11,12] These dyes were washed with acetone several times to remove the moisture completely. Then, it was dissolved in DMF to remove the salt. The DMF-dye solution was then poured slowly into ethylether, the precipitate was obtained, and filtered, dried in vacuum. By the same purifying method, the dye was purified three times and the purity of the dye was identified by UV-visible spectrophotometer (Carry 14). And any other spots of impurities were not separated when developed by thin layer chromatography. The desired product was obtained in 72 % yield (9.2g).

Monofluorotriazinyl reactive dye; IR(KBr) 1560, 1450, 1240, 1020, 1020 cm^{-1}; UV-VIS λ_{max} 415nm, 535 nm in H_2O.

Anal. Calcd for $C_{40}H_{24}N_{11}O_{21}S_6K_6F \cdot 5H_2O$: C. 31.39; 2.22; N, 10.07 Found: C, 31.29; H, 2.36; N, 10.18
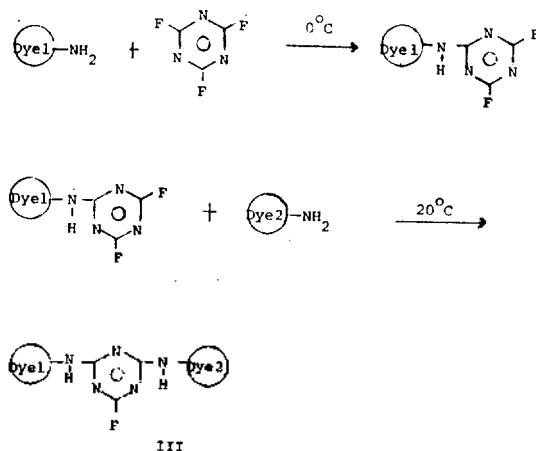
The procedure is summarized on *Fig.* 2.

Fig. 2. Synthesis of dichromophoric monofluorotriazinyl reactive dye. The UV-visible spectra of chromophore I, chromophore II and dichromophoric monofluorotriazinyl reactive dye III were shown in *Fig.* 3. The dye III showed a absorption spectrum at λ_{max} 535 nm and 415 nm.
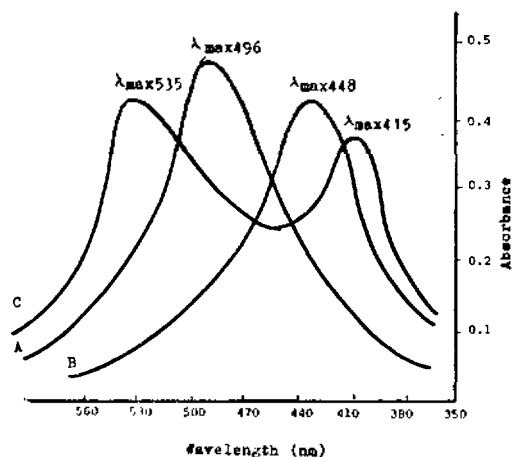

Fig. 3. Spectra of chromophores and dye in the visible range in H_2O; A. chromophore I λ_{max} 496 nm in H_2O; B. chromophore II λ_{max} 448 nm in H_2O; C. monofluorotriazinyl reactive dye λ_{max} 535, 415 nm in H_2O

Rate of Hydrolysis[13,14] The hydrolysis rate of dye was determined by measuring the concentration of remaining active dye in solution at time t. 2×10^{-2} mole/l of dye solution was maintained 60°C and stirred constantly. A al-

kaline buffer solution (pH-10.0) was made up from mixture of $0.05M$ sodium bicarbonate and $0.1M$ sodium hydroxide. [15] After suitable intervals the dye solution was taken and applied to paper chromatorgraphy. The $10\,\mu l$ of a solution containing about 30 g per litre was a convenient quantity. The paper chromatograms were developed ina conventional partition chromatography apparatus by ascending method using a mixture of diethylamine, pyridine, amyl alcohol and ammonia as eluenting agent. After development for 5 hours, the active dye and hydrolyzed dye were separated, then the active part was extracted in the 20 ml DMF at 130°C for 10 min. The relative percentage of the active dye was estimated by the value of absorbance at λ_{max} in visible spectra. The R_f value of active and hydrolyzed dye were as follows.

Active dye (R_f) ; 0.62

Hydrolyzed dye (R_f) ; 0.21

Dyeing properties Some dyeing properties of dye III on cellulose were examined. The dyes were exhausted on cellulose for 30 min at 40°C, under the following conditions;

L.R., 30 : 1; dye 1%; Na_2SO_4 30g/l. After exhausting for 30 minutes, Na_2CO_3 3g/l was added to dye bath for fixing.

After dyeing for 60 min., unfixed dye remaining on the cellulose was removed by extracting with DMF at 130°C.

A DMF solution was analyzed for the absorbance at λ_{max} in the visible spectra to obtain a fixing yield.

The calculation of amount of exhausted and fixed dye was determined by the previously prepared calculation curve using spectrophotometer.

3. RESULTS AND DISCUSSIONS

Hydrolysis Properties of Dye. The rate of hydrolysis under defined pH and temperature

conditions is accepted as a measure of the reactivity, [16] the hydrolysis constant k_w (w stands for water), which has been determined at a constant temperature and a constant pH, is used as a measure for this purpose for this reaction of pseudo unimolecular order. The decrease with time $(-d(R))$ of the reactive dyestuff concentration (R) of a dyestuff solution is proportional to the dyestuff concentration and the base concentration $[OH^\ominus]$:

$$-\left(\frac{d(R)}{dt}\right)_T = k_{wbi}(R)[OH^\ominus] \qquad (1)$$

If the reaction takes place at a constant pH, $[OH^-]$ can be included in the constant k_{wbi}, so that a general expression is obtained for the determination of the quantity R

$$-\left(\frac{d(R)}{dt}\right)_{T,pH} = k_w(R) \qquad (2)$$

The value of k_w is obtained for (2) by integration, or expressed in logarithmic terms where x represents the dyestuff which has reacted during the time t;

$$-\int\frac{d(R)}{(R)} = k_w\ dt \qquad (3)$$

$$(R) = (R)_0\ \exp k_w t \qquad (4)$$

$$k_w = \frac{2.3}{t}\log\frac{(R)_0}{(R)_{0-x}} \qquad (5)$$

In the equations, $(R)_0$ is the quantity of reactive dyestuff at time $t=0$.

According to (5), k_w is easy to calculate if $(R)_0$ and x can be determined by analysis.

When the log $(R)_0/(R)_{0-x}$ is plotted against t, the data give very good straight line as shown in *Fig.* 4 and k_w can be calculated from the slope of the straight line.

$$k_w = slope \times 2.303(min^{-1}) \qquad (6)$$

The course of hydrolysis reaction of dye III has been followed by means of paper chromatography.

The results are illustrated in *Fig.* 4 where

the pseudo first order rate constant was
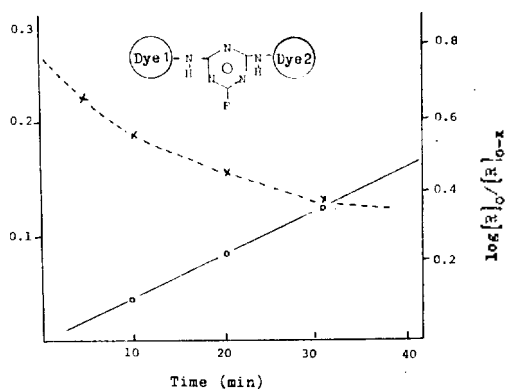
$$k_w = 2.6 \times 10^{-2} (min^{-1})$$

Fig. 4. Variation of optical density, *x*, and log $[R]_0$ $/[R]_{0-x}$, 0, with time (at 60°C, pH; 10.0)

Under the same alkaline conditions the pseudo unimolecular rate constants for monochlorotriazinyl reactive dye IV is

$$k_w = 3.2 \times 10^{-4} min^{-1}$$

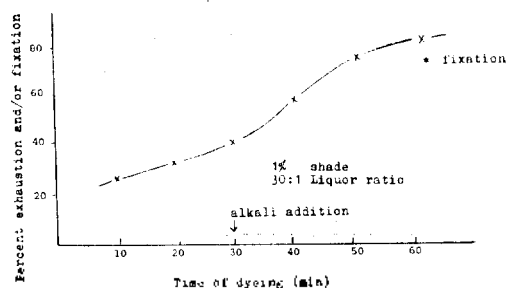**Dyeing properties.** The exhaustion curve and fixation of dye III were shown in *Fig.* 5.

Fig. 5. Rate of dyeing and fixation (40°C, Na₂SO g/*l*) of monofluorotriazinyl reactive dye

After a total dyeing time of 60 minutes, dye III showed a fixation yield 64 % and a exhaustion yield 72 %.

4. CONCLUSIONS

1. A reactive dye containing two different ch-

romophore was synthesized by using a trifluoro-s-triazine as reactive component.

2. The pseudo first order rate constant of monofluoro triazinyl reactive dye is much higher than monochloro triazinyl reactive dye.

3. Colour yields was 75 % and its color was yellowish red. Fastness properties are all within commercially acceptable limits.

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