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The Hydrolysis of the Reactive Groups, and Side Reaction, for a Mixed Bifunctional Reactive Dye (CI Reactive Red 194) and Related Compounds

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ABSTRACT

The hydrolysis of CI Reactive Red 194 and model compounds was investigated at 50°C by high pressure liquid chromatography (HPLC). In order to examine the effects of a m-*vinylsulfonyl substituent in the phenyl group bound with the triazine nucleus via an imino group on the reactivity of monochlorotriazinyl (MCT) groups, the hydrolysis of CI Reactive Red 3 was also examined at 50°C. A reaction scheme for the alkaline hydrolysis of both the dyes was determined. In addition to the normal hydrolysis of vinylsulfonyl (VS) and MCT groups, the imino bridge groups between the chromophore and the triazine nucleus are also hydrolysed. The pseudofirst-order rate constants for both the dyes in the reaction scheme were estimated at pH 9–12 and 50°C. The hydrolysis of either the VS or MCT groups for CI Reactive Red 194 has a large influence on the reactivity of the other VS, MCT or imino bridge group which remain unhydrolysed.*

1 INTRODUCTION

Review texts by Beech[1] and Siegel[2] on the reactive groups of reactive dyes refer to several early patents[3–5] on mixed bifunctional reactive dyes. According to Siegel, Cassella was the first firm to recognize the value of dyes which combine two different reactive groups in a molecule.[3] Early patents for reactive dyes containing a 4-(*m*- or *p*-sulfatoethylsulfonylanilino)-6-chloro-1,3,5-triazinyl group as the reactive system originated from Hoechst[4] and ICI.[5]

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Some of these dyes, e.g., CI Reactive Red 194 and CI Reactive Red 240 are noted in a patent applied for by Hoechst[4] in 1961. However, the first commercial dye range having such a reactive system, i.e. the Sumifix Supra dyes, was introduced by Sumitomo Chemical Co. Ltd[6–8] in 1980. Since then, other dye manufacturers have introduced similar dye ranges, e.g. Remazol SN (Hoechst Mitsubishi Kasei Co. Ltd), Cibacron C (Ciba-Geigy), and Basilene FM (BASF).

He *et al.*[9] studied the hydrolysis of bifunctional reactive dyes by means of [^{1}H] NMR and chloride ion-selective electrode. Abeta *et al.*[10] investigated the hydrolysis reaction of 18 isomeric dyes based on phenylazo-H acid, including CI Reactive Reds 194, 198 and 240, by high pressure liquid chromatography (HPLC) and reported the usual mechanism of hydrolysis for the vinylsulfonyl (VS) and monochlorotriazinyl (MCT) groups. The present authors[11] have determined the diffusion constants in cellulose, and the rate constants of reaction with cellulose, for two dyes by means of the method of cylindrical film roll.

In preliminary experiments on the analysis of the hydrolytic products of CI Reactive Red 194 by HPLC, an unidentified red component with a very short retention time on an octadecyl silica (ODS) column has been shown to be formed in considerable amount, in addition to the reaction products from the hydrolysis of MCT and VS groups. Gasparič concluded that the imino bridges between arylamines and a heterocyclic ring such as *s*-triazine and pyrimidine are hydrolysed under severe alkaline conditions (2·5 M NaOH at 200°C) to give arylamines.[12] Senn, Stamm and Zollinger[13] reported the splitting of metanilic acid bound with the triazine ring of a monochlorotriazinyl anthraquinone dye on cotton at the boil over a wide range of pH. The present authors suspected that either of the arylamines, which can be generated by the hydrolysis of the two kinds of imino bridge groups bound with *s*-triazine, might correspond to the unidentified component.

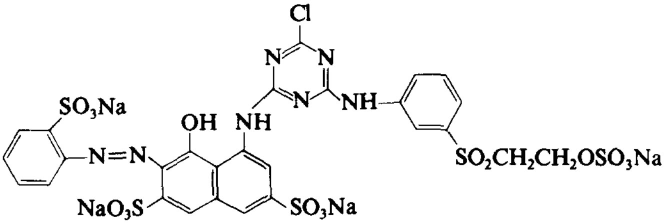
In the present paper, the reaction mechanism of a mixed bifunctional reactive dye, CI Reactive Red 194, containing a VS group and a MCT group in the dye molecule, is investigated using HPLC. Besides the ordinary hydrolysis of VS and MCT groups, hydrolysis of the imino bridge groups was confirmed to occur. Whether chlorotriazinyl dyes bound with H acid via an imino bridge group exhibit the same fission behaviour of the imino groups or not is also examined.

2 EXPERIMENTAL

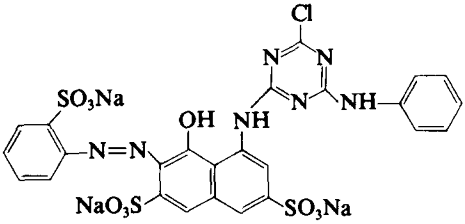
2.1 Materials

CI Reactive Red 194, which contains VS and reactive MCT groups (**I**), and derived dyes in which (a) only VS groups are hydrolysed to give *β*-hydroxyethylsulfonyl groups (**II**), (b) only MCT groups are hydrolysed (**III**), and (c) VS and MCT groups are both hydrolysed (**IV**) were used. They were supplied by Sumitomo Chemical Co. Ltd. CI Reactive Red 1 and CI Reactive Red 3 were supplied by Nippon Kayaku Co. Ltd. Their chemical structures, CI Generic Names and CI Constitution Number (if available), are shown below.

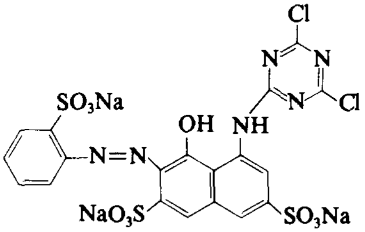
(1) CI Reactive Red 194[10]



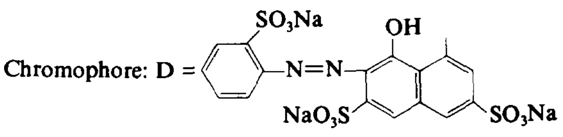
(2) CI Reactive Red 3, CI 18159 (**VIII**)



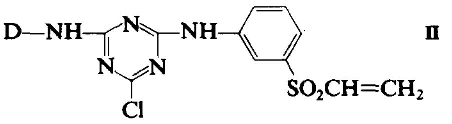
(3) CI Reactive Red 1, CI 18158



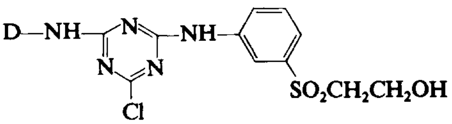
(4) Model compounds derived from CI Reactive Red 1, CI Reactive Red 3, and CI Reactive Red 194.



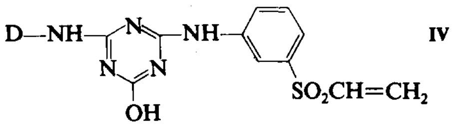
I



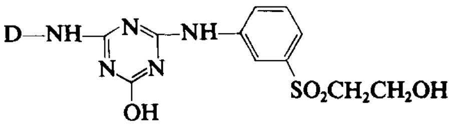
II



III

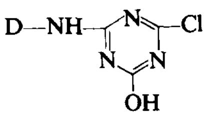


IV

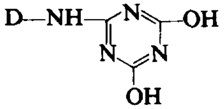


V $D{-}NH_2$

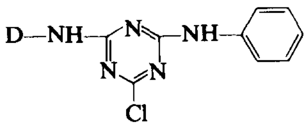
VI



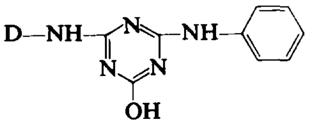
VII



VIII



IX



All dyes were used without further purification unless otherwise specified.

2.1.1 Synthesis of model compound, V

An arylamine (model compound **V**) was synthesized in order to examine whether the HPLC peak of the unidentified compound coincided with that of **V** or not. Orthanilic acid was diazotized and coupled with H acid at pH 9–10. After neutralizing with HCl, **V** was obtained by evaporation and filtration. After drying, it was dissolved in dimethylformamide (DMF) to remove inorganic salts and **V** was precipitated by adding acetone to the DMF solution. From the purified sample, the molar extinction coefficient for **V** was determined (cf. Table 1). Little variation in λ_{max} and ε was apparent over the concentration range of acetonitrile and methanol used in the HPLC studies.

2.1.2 Hydrolytic products from CI Reactive Red 1

In order to analyze the hydrolysis of CI Reactive Red 1 and CI Reactive Red 3 as well as the hydrolysis of the imino bridge group other than that between the chromophore and triazine nucleus, analogues having 2-chloro-4-hydroxy- and 2,4-dihydroxytriazine systems (model compounds **VI** and **VII**) were used.

VI: Hydrolysis of CI Reactive Red 1 was performed in 0·02 M NaOH at 25°C for 3 h. After neutralizing the solution, sodium acetate was added to precipitate the product. This treatment with sodium acetate was repeated several times. The conjoint precipitates were filtered and the sodium acetate in the final precipitate was Soxhlet extracted with absolute alcohol.

VII: **VI** was further hydrolysed in 0·2 M NaOH at 80°C for 2 h. The precipitate was purified by the same method as above.

2.2 Procedure

2.2.1 Hydrolysis of dyes

Hydrolysis of dyes was performed in buffer solutions and aqueous sodium hydroxide at 50°C (cf. Tables 2 and 4). After mixing the dye solution and the alkaline solution, an aliquot (1·00 ml) of the reaction solution was pipetted out at appropriate reaction time and added immediately to phosphoric acid solution to neutralize. The pH of the dye solutions was measured with a Horiba F-16 pH meter. The absorption spectra of dye samples were measured by an Ubest V-550 spectrophotometer (JASCO Corp.).

2.2.2 HPLC

Solutions from the hydrolysis reaction were analyzed by HPLC after the neutralization and the analytical conditions are shown in Table 1. The other gradient method was used to identify **V** or to distinguish **V** from other known components (cf. Fig. 2).

TABLE 1
Chromatographic Conditions for HPLC Analysis

Apparatus	Shimadzu LC-6A
Column	Asahipack ODP-50, 250 mm length, ϕ = 6·0 mm
Mobile Phase:	(5 mM $(NH_4)_2HPO_4$ + 5 mM $(NH_4)H_2PO_4$)/Acetonitrile
	For CI Reactive Red 194: Gradient method (80/20 (v/v) → 0·5%/min → 75/25)
	For **II** and **III**: Gradient method (80/20 (v/v) → 0·5%/min → 60/40)
Mobile Phase:	(5 mM $(NH_4)_2HPO_4$ + 5 mM $(NH_4)H_2PO_4$)/Methanol
	For CI Reactive Red 3: Gradient method (78/22 → 0·33%/min → 68/32)
Rate of Elution	0·5 ml/min
Column Temperature	30°C
Detector	UV/Vis Detector Wavelength = 534 nm
ε of CI Reactive Red 194 at λ_{max} (534 nm)	
	I: 32,900, **II**: 32,800, **III**: 32,800, **IV**: 32,900 (ε for **I**-**IV**)[10]
	V: 21,80 (obsd.)[a] (Used as correction factors for peak area)
ε of CI Reactive Red 3 at λ_{max} (532 nm)	
	V: 22,000,[a] **VIII** and **IX**: 26,000
Sensitivity	0·01 (Abs.)
Integrator	Chromatopack CR-3A

[a] ε of **V** at λ_{max} (526 nm) = 22,200.

3 RESULTS AND DISCUSSION

3.1 Analysis of reaction products

3.1.1 HPLC of hydrolysis components

According to Abeta *et al.*,[10] CI Reactive Red 194 is hydrolysed to give components, **I–IV**. Besides these components, an unknown red component with a very short retention time was always found in liquid chromatograms of the reaction solution. On the basis of some preliminary experiments, the optimal chromatographic conditions to separate these components were determined as shown in chromatogram (1) for a mixture of model compounds **I–V** (Fig. 1). Chromatograms (2)–(5), obtained by the same procedures, show the progress of hydrolysis for CI Reactive Red 194 under the given conditions (pH 9·96, 50°C). Thus, at an initial reaction time (chromatogram (2), 30 min), the main component **I** is hydrolysed to give **II** and **V**. At an

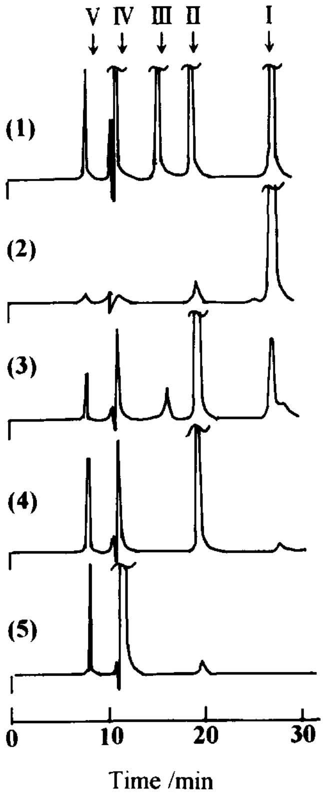


Fig. 1. Liquid chromatograms of (1) a mixture of model compounds **I–V** and the hydrolysis solutions for CI Reactive Red 194 for (2) 30 min, (3) 24 h, (4) 72 h, and (5) 279 h at 50°C and pH 9·96. (Chromatographic conditions: see Table 1.)

intermediate reaction time (chromatogram (3), 24 h), **II** becomes the main component, the hydrolysis of **I** proceeds markedly to give **IV** and **V**, and **III** is also found at this reaction time. When the hydrolysis progresses further (chromatogram (4), 72 h), a small amount of **I** remains, **II** becomes the main component and **IV** and **V** are formed at a molar ratio of about 2:1. After a long reaction time (chromatogram (5), 279 h), a small amount of **II** remains, and the final products **IV** and **V** are formed at the same molar ratio, which remained constant after two weeks under the same conditions.

According to Rys *et al.*,[14–18] 2-chloro-2-hydroxytriazinyl intermediates would be generated as the hydrolysis of MCT groups progresses, since general base catalysis is observed in the reaction of monochlorotriazinyl dyes. The intermediates, however, may revert to **I** or **II** by the neutralization of the hydrolysis solutions of every sampling, although the presence of these intermediates appears to have been proved by Zhu *et al.*[9,19]

3.1.2 Assignment of V

In order to ascertain further the hydrolysis of the imino bridge groups between the chromophore and triazine nucleus, the possibility of hydrolysis of the other imino bridge groups between the *m*-vinylsulfonylphenyl group and the triazine nucleus was also examined (Fig. 2). Under chromatographic conditions which promote the separation of components with shorter retention times, chromatogram (1) shows a good separation for a mixture of model compounds **IV**–**VII**. Chromatogram (2) for the reaction solution of CI Reactive Red 194 (50°C, pH 11·0, 48 h) suggests that the reaction solution contains **V** but no **VI** and **VII**, implying only the hydrolysis of imino bridge groups between the chromophore and the triazine ring.

Separation of the unknown component from the reaction solution by use of an alumina column [eluent: (5 mM $(NH_4)_2HPO_4$ + 5 mM $(NH_4)H_2PO_4$)/ ethanol = 7/6 (v/v)] was made and the mixing test of **V** (cf. Section 2.1.1) and the unknown component separated was also carried out by HPLC, indicating their equivalence. The absorption spectra in the UV and visible regions (200–650 nm) for both the synthesized and the separated **V** were found to be identical.

3.2 Reaction scheme for CI Reactive Red 194

On adding aqueous sodium hydroxide to an aqueous solution of CI Reactive Red 194, the peak of the sulfatoethylsulfonyl (SES) form disappears very rapidly in the liquid chromatogram. Under weakly alkaline conditions, however, since the conversion of the SES form into **I** occurs slowly,[20]

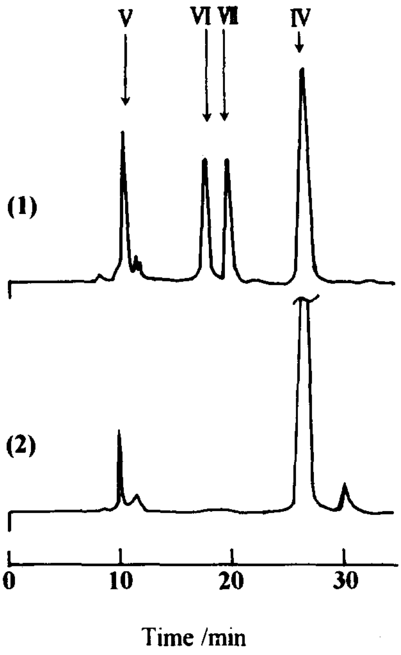
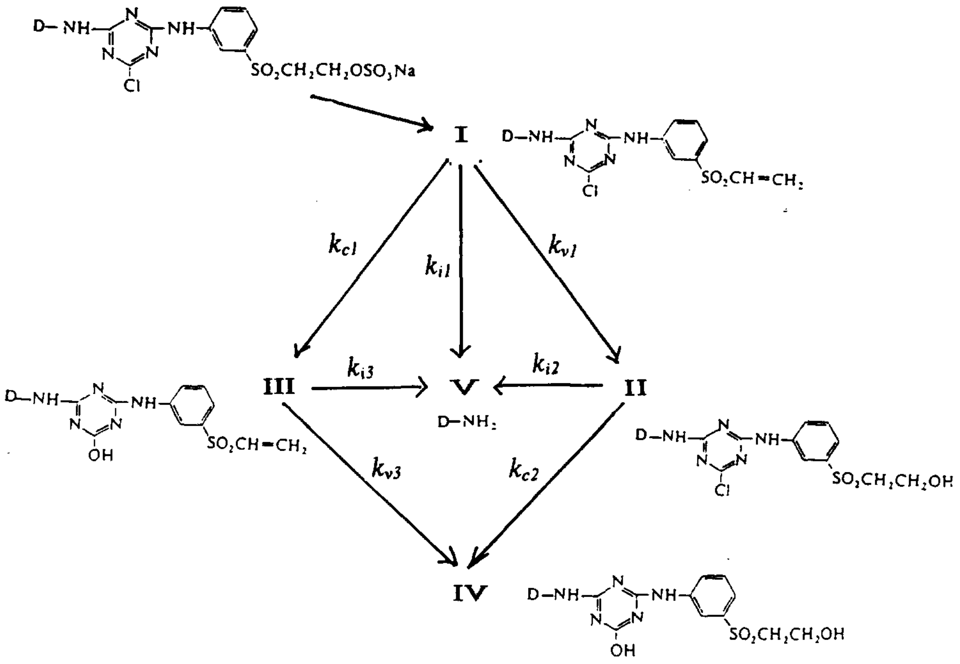


Fig. 2. Liquid chromatograms of (1) a mixture of model compounds **IV–VII** and (2) the hydrolysis solutions for CI Reactive Red 194 at 50°C and pH 11·0 for 48 h. Chromatographic conditions: Column, 250 mm × 6·0 mm i.d. of Asahipack ODP-50; low strength eluent, 5 mM $(NH_4)_2HPO_4$ + 5 mM $(NH_4)H_2PO_4$, high strength eluent, 100% acetonitrile (AN), linear gradient elution from 10%(v/v) AN to 40% AN in 30 min; flow rate, 0·5 ml/min; temperature, 30°C; detection, vis., 534 nm; sensitivity, 0·01 (abs).

sodium hydroxide was added to the dye solution to make it alkaline, and it was then neutralized to make it weakly alkaline (cf. footnote for pH 9·03 in Table 2). The hydrolytic reactions for CI Reactive Red 194 may then be regarded as starting from **I**.

From the HPLC analyses in this present study (cf. Section 3.1), and according to previous studies on the hydrolysis for VS and MCT groups,[9,10] the reaction mechanism of CI Reactive Red 194 may be represented as shown in Scheme 1.

No peaks which corresponded to the bisarylether type dimer[21] were found in the liquid chromatogram of the hydrolysis solutions for CI Reactive Red 194 within the present experimental conditions. As is noted below (cf. Section 3.4), the values of k_{i3} may be smaller than those of k_{i1} and k_{i2}. The components **IV** and **V** were sufficiently stable to detect no decrease of their peak areas in the liquid chromatogram of the highly alkaline aqueous solutions during a long time of hydrolysis reaction. Thus, no arrow is shown linking **IV** to **V** in Scheme 1 (cf. Section 3.5.1).



Scheme 1. Hydrolysis of CI Reactive Red 194.

3.3 Determination of pseudofirst-order rate constants

Neglecting the rate constants of hydrolysis of the imino bridge groups between the triazine ring and the chromophore for **IV**, since they were estimated to be negligible compared with those for **I**, **II**, and **III** (cf. Section 3.4.2), the kinetic equations for these reaction can be written as follows:

$$\frac{dC_1}{dt} = -(k_{v1} + k_{c1} + k_{i1})C_1 \tag{1}$$

$$\frac{dC_2}{dt} = k_{v1}C_1 - (k_{c2} + k_{i2})C_2 \tag{2}$$

$$\frac{dC_3}{dt} = k_{c1}C_1 - (k_{v3} + k_{i3})C_3 \tag{3}$$

$$\frac{dC_4}{dt} = k_{c2}C_2 + k_{v3}C_3 \tag{4}$$

$$\frac{dC_5}{dt} = k_{i1}C_1 + k_{i2}C_2 + k_{i3}C_3 \tag{5}$$

where C_1–C_5 denote the concentrations of component **I–IV**, and k_{mn} (m = v, c, and i; n = 1–3) the pseudofirst-order rate constants for each reaction, as shown in Scheme 1. The first subscripts, v, c, and i, denote vinylsulfonyl, chloride, and imino groups, respectively, and the second ones components (**I–III**, as 1–3).

Since the initial time of reaction is taken to be that of the first sampling of the reaction solution, some concentrations of **I–V** exist. When their initial concentration is C_n^0 (n = 1–5), the initial conditions for the reaction are:

$$t = 0, \qquad C_n = C_n^0 \qquad (n = 1\text{–}5) \tag{6}$$

During the hydrolysis reaction of VS and MCT groups, the chromophore for **I–IV** underwent little spectral change, but the occurence of **V** gave some variations in the visible and UV regions. It could be considered, however, that the sum of the concentrations of the various species for CI Reactive Red 194 remained constant during the reaction. When percentage occurrences were estimated from the peak area of the liquid chromatogram, it was necessary to make a modification for **V**, and small ones for the other components, by use of the correction factors shown in Table 1. When this was done, the constancy of the total concentration of the five species was confirmed as being maintained, within experimental error. Then, the boundary conditions are given by:

$$t > 0, \qquad C_0 = \sum_{i=1}^{5} C_i \tag{7}$$

By use of the initial and boundary conditions, eqns (1)–(5) can be analytically integrated to give the exponential function (cf. Appendix A1).

These equations, giving the solutions of eqns (1)–(5), describe the reaction behaviour of each species. The values of k_{mn} may be determined so as to fit the calculated profiles with the corresponding experimental ones (cf. Appendix A2). Such an example for the hydrolysis behaviour of CI Reactive Red 194 at pH 9·96 and 50°C is shown in Fig. 3. The plots are the experimental ones, and the curves are drawn from the analytical solutions using the set of parameters of k_{mn} given in Table 2.

3.4 Reaction mechanism of CI Reactive Red 194

3.4.1 Hydrolysis of II

In order to confirm the reaction scheme in more detail, the reaction behaviour of **II** was examined. As shown in Fig. 4(a), **II** underwent the hydrolysis of MCT groups to give **IV**, as well as of the imino bridge groups between the chromophore and the triazine ring to give **V**.

TABLE 2

Values of k_{mn} (min^{-1}), Pseudofirst-Order Rate Constants of Hydrolysis of Various Components for CI Reactive Red 194 at 50°C

pH	*Activity of OH$^-$* [a]	$10^3\,k_{v1}$	$10^3\,k_{v3}$	$10^4\,k_{c1}$	$10^4\,k_{c2}$	$10^4\,k_{i1}$	$10^4\,k_{i2}$	$10^4\,k_{i3}$
CI Reactive Red 194								
9·03[c]	$5\cdot85 \times 10^{-5}$	0·119	0·060	0·13	0·30	0·07	0·11	—[b]
9·96[d]	$4\cdot98 \times 10^{-4}$	1·01	0·56	1·2	1·7	0·5	0·60	—[b]
10·62[e]	$2\cdot28 \times 10^{-3}$	5·05	3·0	8·0	10·0	2·0	4·8	—[b]
10·73[f]	$2\cdot94 \times 10^{-3}$	5·32	2·0	7·6	8·8	2·5	3·6	—[b]
11·44[g]	$1\cdot51 \times 10^{-2}$	25·6	19·0	30·0	49·0	6·0	21·0	—[b]
12·40[h]	$1\cdot38 \times 10^{-1}$	261·0	$1\cdot8 \times 10^{2}$	70·0	$2\cdot0 \times 10^{2}$	40·0	66·0	—[b]
Model compound II								
9·96[d]	$4\cdot98 \times 10^{-4}$	—	—	—	1·49	—	0·460	—
10·62[e]	$2\cdot28 \times 10^{-3}$	—	—	—	9·74	—	3·88	—
11·44[g]	$1\cdot51 \times 10^{-2}$	—	—	—	48·8	—	15·2	—
Model compound III								
9·96[d]	$4\cdot98 \times 10^{-4}$	—	0·51	—	—	—	—	0·06
10·62[e]	$2\cdot28 \times 10^{-3}$	—	3·10	—	—	—	—	0·29
11·44[g]	$1\cdot51 \times 10^{-2}$	—	18·6	—	—	—	—	1·5

[a] Mol dm^{-3}.

[b] See Appendix A2.2 for k_{i3} obtained from the hydrolysis of **I**.

[c] After the dye sample ($2\cdot0 \times 10^{-4}$ mol dm^{-3}) was kept in 0·01 M NaOH soln at 50°C for 5 min, buffer soln (0·01 M H_3PO_4, 0·086 M $Na_2B_4O_7$, and 0·0164 M KH_2PO_4) of equal volume was added.

[d] Aq. soln of Na_2CO_3 and $NaHCO_3$ of equal conc. ($1\cdot25 \times 10^{-2}$ M).

[e] Aq. soln of Na_3PO_4 ($5\cdot0 \times 10^{-3}$ M) and Na_2HPO_4 ($2\cdot0 \times 10^{-2}$ M).

[f] Aq. soln of NaOH ($5\cdot0 \times 10^{-3}$ M).

[g] Aq. soln of Na_3PO_4 ($2\cdot24 \times 10^{-2}$ M) and Na_2HPO_4 ($8\cdot3 \times 10^{-4}$ M).

[h] Aq. soln of 0·20 M NaOH.

From the reaction behaviour of **II**, the values of the kinetic parameters, k_{c2} and k_{i2}, were determined by use of eqns (4) and (5). In order to determine the optimal combination of parameters, their values were determined by the least-squares method to give the best fit between observed and calculated concentrations (cf. Appendix A2.1).

3.4.2 *Hydrolysis of III*

The reaction behaviour of **III** (Fig. 4(b)) shows that the sample of model compound **III** contained some **V**, and that the concentration of **V** increased very slowly as the reaction proceeded, in addition to the hydrolysis of VS groups. Thus, the rates of the hydrolysis for the imino bridge groups were very small compared with those for **I** and **II**. It was also confirmed that no hydrolysis of **IV** was observed at 50°C below pH 11.

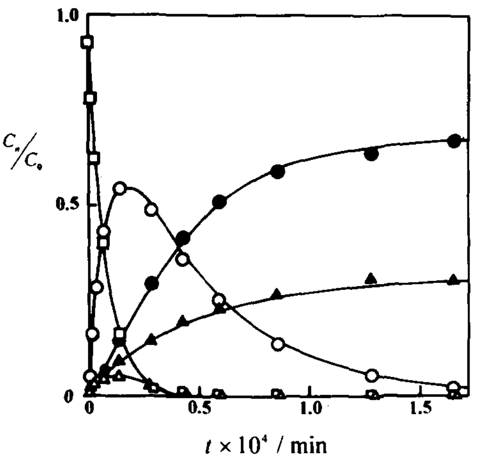


Fig. 3. Hydrolysis behaviour for CI Reactive Red 194 at pH 9·96 and 50°C: Mole fraction, C_n/C_0, for each component, (□) **I**, (○) **II**, (△) **III**, (●) **IV** and (▲) **V** obtained by the HPLC analysis (cf. Table 1) of the hydrolysis solutions. Solid lines are the calculated profiles for each component, which are described by eqns (1)–(5) or their analytical solutions such as eqns (A1) and (A3) by use of k_{mn} shown in Table 2.

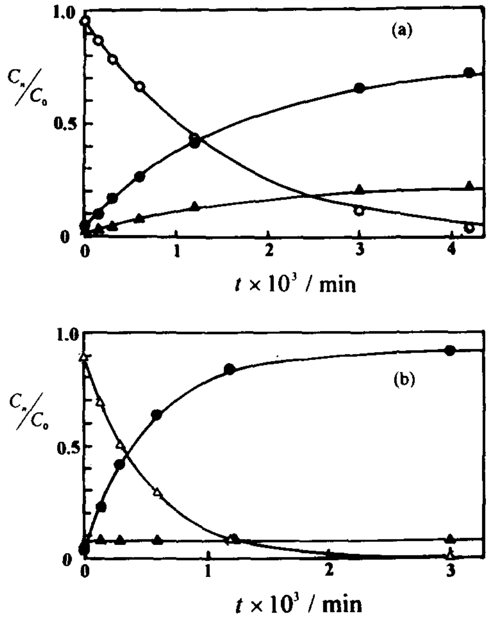


Fig. 4. Hydrolysis behaviour for (a) **II** and (b) **III** at pH 11·44 and 50°C: Mole fraction, C_n/C_0, for each component, (○) **II**, (△) **III**, (●) **IV** and (▲) **V** obtained by HPLC analysis of the hydrolysis solutions. Solid lines are the calculated profiles for each component, which are described by the same equations as in Fig. 3 by use of k_{mn} shown in Table 2.

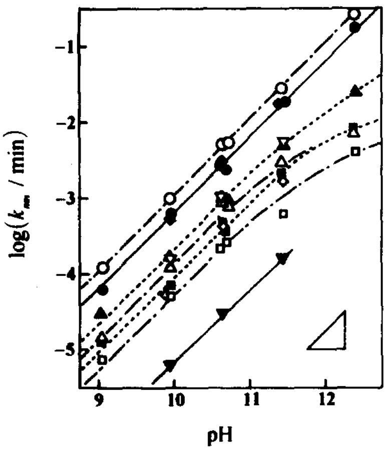


Fig. 5. Relationships between log k_{mn} and pH for the various components of CI Reactive Red 194 at 50°C. Symbols are shown below (k_{mn}: pseudofirst-order rate constants (min^{-1}), $m = v$, c, or i; n = 1–3 which correspond to I–III; cf. Scheme 1).

k_{mn}	k_{v1}	k_{v3}	k_{c1}	k_{c2}	k_{i1}	k_{i2}	k_{i3}	*Lines*
Estd from I	○	●	△	▲	□	■		— — —
Estd from II				▽		◇		- - - - - -
Estd from III		◆					▼	———

3.5 pH-Dependence of rate constants

3.5.1 Hydrolysis for II and III

The hydrolysis behaviour of **II** and **III** was examined at different pH values. The values of k_{c2} and k_{i2} for **II** and those of k_{v3} and k_{i3} for **III** were determined by use of the methods mentioned in Appendix A2.1 (Table 2 and Fig. 5).

Figure 5 shows that plots of the logarithms of k_{c2}, k_{i2}, k_{v3}, and k_{i3} against pH have a slope of unity for VS groups over all the pH range examined, and for MCT and imino groups at pH ≤ 10·62. The activity of hydroxide ions was estimated by the value of the ionic product of water at 50°C and the pH values measured at that temperature. Although the hydrolyses were carried out under conditions of constant pH, these reactions must be of second order, and the rate constants for these, k'_{mn} (dm^3 mol^{-1} min^{-1}), can be obtained from the values of k_{mn} divided by the activity of hydroxide ions. The values of k_{mn} and k'_{mn} are discussed in Section 3.6.2.

3.5.2 Hydrolysis of CI Reactive Red 194

The hydrolyses of CI Reactive Red 194 were carried out in the pH range between 9 and 12·4. The values of seven kinds of k_{mn} were determined by

TABLE 3
Second-Order Rate Constants of Hydrolysis, k'_{mn} (dm^3 mol^{-1} min^{-1}), for CI Reactive Red 194 at 50°C and Various pH Values

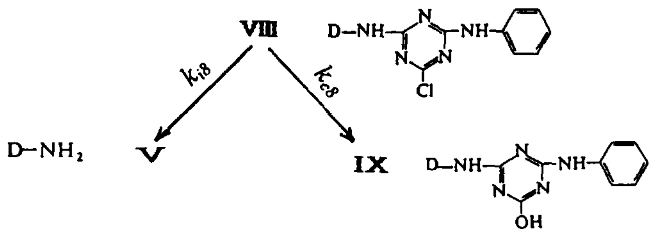
pH Range	k'_{v1}	k'_{v3}	k'_{c1}	k'_{c2}	k'_{i1}	k'_{i2}	k'_{i3}
≤10·62	1·95±0·17	1·09±0·21	0·27±0·05	0·39±0·08	0·090±0·005	0·15±0·04	0·011±0·002
11·44	1·95±0·17	1·09±0·21	0·20	0·32	0·04	0·12	—

the least-squares method so as to fit the calculated profiles to those of the corresponding experimental profiles for five species (cf. Appendix A2). The results are summarized in Table 2.

The values of k_{mn} ($n = 2$ and 3) estimated from the hydrolysis of **I** agreed with the corresponding values of k_{mn} from the hydrolysis of **II** and **III** within experimental error.

The experimental plots of the logarithms for seven kinds of k_{mn} against pH are shown in Fig. 5. These plots for k_{v1} and k_{v3} were linear and had a slope of unity over all the pH range examined, while those for k_{cn} and k_{in} ($n = 1$, 2, or 3) gave similar results at pH $\leq$ 10·62 but the slope became smaller than unity at pH > 11. These plots against pH for different n did not agree with each other. Thus, the reactivities of VS, MCT, and imino bridge groups are altered by the reaction of another reactive group, although Abeta *et al.*[10] postulated that $k'_{v1} = k'_{v3}$ and $k'_{c1} = k'_{c2}$ in the estimation of k_{mn}.

As in the case of **II** and **III**, the values of k'_{mn} can be also determined from the hydrolysis of **I** (Table 3). The values of k'_{mn} ($m = c$ or i) were affected by change in pH in the high pH region. The pH-variation of k'_{cn} for MCT groups has been explained by Horrobin[22] in terms of the ionization of imino bridge groups. The results of this work show that the imino bridge groups take on the same promoting effect on the reactivity as MCT groups by the introduction of VS groups. However, the reactivities of the two kinds of groups are dependent upon the intrinsic chemical structure, and



Scheme 2. Hydrolysis of CI Reactive Red 3.

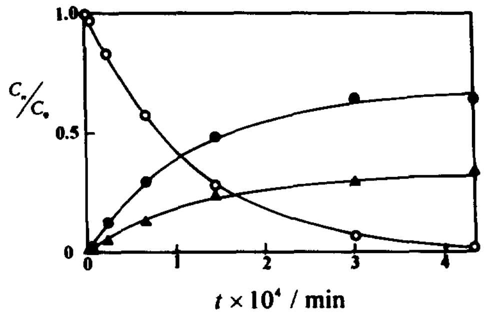


Fig. 6. Hydrolysis behaviour for CI Reactive Red 3 at pH 10·63 and 50°C: Mole fraction, C_n/C_0, of each component, (▲) V, (○) VIII, and (●) IX, obtained by HPLC analysis of the hydrolysis solutions. Solid lines are the calculated profiles for each component, which are described by the same equations as in Fig. 3 by use of k_{m8} shown in Table 4.

also upon partial modification of the structure. The variations of k'_{mn} with change in the chemical structure are discussed in Section 3.6.2.

3.5.3 Hydrolysis of CI Reactive Red 3

The hydrolysis behaviour of CI Reactive Red 3 at pH 10·63 and 50°C is shown in Fig. 6. Scission of the imino bridge groups between the chromophore and the triazine nucleus was also observed. The formation of **V** from CI Reactive Red 3 (**VIII**) was confirmed by HPLC, while no **V** was formed from the hydrolysed product **IX** under the experimental conditions examined. The absence of formation of **VI** and **VII** from CI Reactive Red 3 and **IX**, as well as none of **VII** from **IX**, were also confirmed. From this hydrolysis behaviour, the reaction scheme of the hydrolysis of CI Reactive Red 3 may be described as shown in Scheme 2. If the hydrolysis solutions were kept at constant pH, all the reactions may be regarded as being of pseudofirst-order. The reaction equations for the hydrolysis of CI Reactive Red 3 may then be written by:

$$\frac{dC_8}{dt} = -(k_{c8} + k_{i8})C_8 \tag{7}$$

$$\frac{dC_9}{dt} = k_{c8}C_8 \tag{8}$$

$$\frac{dC_5}{dt} = k_{i8}C_8 \tag{9}$$

where the pseudofirst-order rate constants, $k_{m8}(m = c \text{ or } i)$ are shown in Scheme 2.

Since these simultaneous differential equations can be easily integrated,

TABLE 4

Pseudofirst-Order Rate Constants, k_{m8} (m = c or i), and Second-Order Rate Constants, k'_{m8} (m = c or i), of Hydrolysis for CI Reactive Red 3 at 50°C

pH	*[OH⁻] (mol dm⁻³)*	k_{c8} *(min⁻¹)*	k_{i8} *(min⁻¹)*
9·87[a]	$4{\cdot}06 \times 10^{-4}$	$8{\cdot}10 \times 10^{-5}$	$4{\cdot}50 \times 10^{-5}$
10·25[b]	$9{\cdot}74 \times 10^{-4}$	$2{\cdot}44 \times 10^{-4}$	$1{\cdot}22 \times 10^{-4}$
10·63[c]	$2{\cdot}34 \times 10^{-3}$	$5{\cdot}85 \times 10^{-4}$	$2{\cdot}83 \times 10^{-4}$
11·18[d]	$8{\cdot}29 \times 10^{-3}$	$1{\cdot}23 \times 10^{-3}$	$5{\cdot}80 \times 10^{-4}$
11·48[e]	$1{\cdot}65 \times 10^{-2}$	$2{\cdot}61 \times 10^{-3}$	$1{\cdot}00 \times 10^{-3}$
12·12[f]	$7{\cdot}22 \times 10^{-2}$	$1{\cdot}72 \times 10^{-2}$	$3{\cdot}70 \times 10^{-2}$
k'_{c8} (mol dm^{-3} min^{-1})	at all pH values	0·208 ± 0·042	
k'_{i8} (mol dm^{-3} min^{-1})	pH ≤ 10·63	0·119 ± 0·006	
	pH 12·12	0·051	

[a] The same soln as *d* in Table 2.

[b] Aq. soln of Na_2CO_3 ($2{\cdot}00 \times 10^{-2}$ M) and $NaHCO_3$ ($4{\cdot}8 \times 10^{-3}$ M).

[c] The same soln as *e* in Table 2.

[d] 0·010 M NaOH.

[e] 0·020 M NaOH.

[f] 0·10 M NaOH.

the values of the kinetic parameters, k_{c8} and k_{i8}, can be determined so as to fit the calculated profiles with the corresponding experimental ones by the least squares method, as in the case of CI Reactive Red 194 (cf. Appendices A1 and A2). The results obtained are summarized in Table 4, and an example of the good coincidence between the experimental and calculated profiles is shown in Fig. 6.

The plots of logarithms for k_{m8} (m = c or i) against pH are shown in Fig. 7. The values of the second-order rate constants, k'_{c8}, were constant over all the pH range examined, while those of k'_{i8} became smaller with an increase in pH at pH > 11 (cf. Table 4). In a previous paper,[11] the present authors estimated the value of k_{c8} at 40°C from that at 80°C; this value may be too small due to the use of a larger value of the activation energy.

3.6 Variations of k'_{mn} with chemical structure

3.6.1 Comparison between CI Reactive Red 194 and CI Reactive Red 3

CI Reactive Red 194 is a *m*-sulfatoethylsulfonyl-substituted derivative of CI Reactive Red 3. With the introduction of VS groups, the values of k'_{c1} became larger than k'_{c8} by a factor of 1·3, and of k'_{i1} smaller than k'_{i8} by a factor of 0·75, a reverse effect. The VS groups introduced into CI Reactive Red 3, or the VS groups in CI Reactive Red 194, have a reactivity larger by a

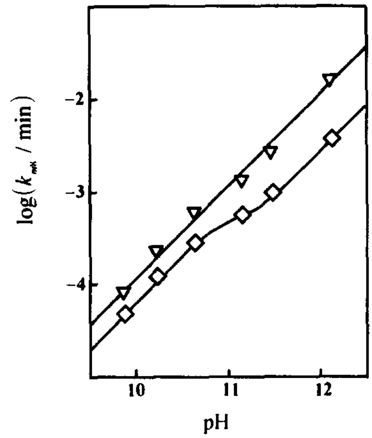


Fig. 7. Relationships between k_{m8} ($m = c$ (∇) or i (◇)) and pH for CI Reactive Red 3 at 50°C (cf. Scheme 2).

factor of 1·3 compared with those of the VS groups in CI Reactive Orange 7, a reactive dye which exhibits the highest reactivity among ordinary VS dyes.[20,23] Thus, the introduction of VS groups into MCT dyes proves to be an excellent structural modification of reactive dyes. As a result of the increase in reactivity, CI Reactive Red 194 can be applied at 50°C.

The introduction of 2-hydroxyethylsulfonyl groups into CI Reactive Red 3, on the other hand, made the values of k'_{c8} and k'_{i8} larger by factors of 1·9 and 1·3, respectively, a substituent effect different from that of VS groups.

3.6.2 Comparison between the values of k'_{mn}

He *et al.*[9] estimated the ratios of k_{v1}/k_{c1} for four model compounds of bifunctional reactive dyes to be 3·5–4·2 at very high pH, while the value of k'_{v1}/k'_{c1} for CI Reactive Red 194 in the present study was 7·2 at pH < 11, implying that the ratio may depend upon the chemical structure of the chromophore.

The value of k'_{i1}/k'_{c1} for CI Reactive Red 194 was measured to be 0·33, while that of k'_{i8}/k'_{c8} for CI Reactive Red 3 was 0·57. After the hydrolysis of VS groups in CI Reactive Red 194, the k'_{i2}/k'_{c2} value was estimated to be 0·04, and by the further hydrolysis of MCT groups the value of k'_{i4} became negligible. The values of k'_{in} (n = 1, 2, 3, or 8) were smaller than those of the corresponding values of k'_{vn} and k'_{cn}, and the reactivity of the imino groups was estimated to decrease as the hydrolysis of VS and MCT groups progressed. Since the scission of imino bridge groups between the triazine group and the chromophore may, however, have a serious influence on the wet fastness of reactive dyeings, the reaction of both the VS and MCT groups in bifunctional dyes should be completed in the dyeing process.

3.6.3 *Variation of k'_{mn} with partial modification of structure*

After the hydrolysis of VS groups, the rates of hydrolysis for MCT and imino groups became larger by factors of 1·4 and 1·7, respectively, than those for CI Reactive Red 194. The ratios of k'_{i2}/k'_{c2} became 0·04 due to mutual variations in the reactivity, while those of k'_{i1}/k'_{c1} were 0·33. The values of k'_{v3} were smaller than those of k'_{v1}, while those of k'_{c2} were larger than those of k'_{c1}. By the hydrolysis of either the VS or MCT group, the rates of hydrolysis for the other MCT or VS groups in mixed-bifunctional dyes are affected, the rates of VS groups becoming smaller and, conversely, those of MCT groups larger. The value of k'_{i1} becomes larger by hydrolysis of VS groups, much smaller by hydrolysis of MCT groups, and negligible by hydrolysis of both the groups.

The essential reason why bifunctional reactive dyes show such large and complex variations in the reactivity after either one reactive group has reacted remains to be examined.

4 SUMMARY

The reaction mechanism of the hydrolysis of CI Reactive Red 194 has been elucidated, as well as the formation of byproduct. The pseudofirst-order and second-order rate constants of the reaction for the VS and MCT groups of CI Reactive Red 194, and the reaction intermediates, as well as for the hydrolysis of the imino bridge group between the chromophore and the triazine nucleus, have been determined over a wide pH range at 50°C.

The imino bridge groups between the chromophore and the *s*-triazine group are extensively hydrolysed under alkaline conditions. The hydrolysis of the imino bridge groups between the chromophore and the triazine nucleus may be the greatest defect of this dye, since at least some proportion of dye may lose its reactive system before reacted with cellulose during dyeing, and dyes which react with cellulose via VS groups without any reaction of MCT groups have the possibility of being split off from the fibre, resulting in bleeding, if the dyed fabrics are exposed to an alkaline environment. In the dyeing process, an effort to minimize this defect should be made, for example, by complete fixation under high alkaline conditions after the exhaustion dyeing.

In the case of CI Reactive Red 194, the problem may be eliminated by thorough reaction of both the VS and MCT groups with cellulose. Thus CI Reactive Red 194, which combines with cellulose via VS groups, has more active MCT groups than the original dye. The imino bridge groups of the dye which combines with fibre via both VS and MCT groups are very stable to hydrolysis, if these variations in reactivity hold for the reaction with the hydroxyl groups of cellulose. In CI Reactive Red 194, this is an excellent property to improve any inferior quality due to the hydrolysis of imino bridge groups.

The reactivities of mixed-bifunctional reactive dyes containing both VS and MCT groups are changed after the reaction of either the VS or MCT group. The variations in the reactivity of the reactive groups, and the chemical structure of the chromophore, are complex factors when analyzing the reactivity–structure relationships, and a fuller rationalisation of this problem remains to be elucidated.

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APPENDIX:
ANALYTICAL SOLUTIONS OF REACTION EQUATIONS

A1 Solution of reaction equations

Equation (1) may be integrated by the method of the separation of variables under the initial conditions (6) as follows:

$$C_1 = C_1^0 \exp(-f_1 t) \tag{A1}$$

where $f_1 = k_{v1} + k_{c1} + k_{i1}$.

When eqn (A1) is substituted into eqn (2) for C_1, eqn (2) becomes a linear differential equation of the first order.

$$\frac{dC_2}{dt} = k_{v1} C_1^0 \exp(-f_1 t) - f_2 C_2 \tag{A2}$$

where $f_2 = k_{c2} + k_{i2}$. Then, the solution of eqn (A2) may be given by:

$$C_2 = \frac{k_{v1} C_1^0}{-f_1 + f_2} \{\exp(-f_1 t) - \exp(-f_2 t)\} + C_2^0 \exp(-f_2 t) \tag{A3}$$

Equations (3), (4), and (5) may be solved by the same method.

A2 Methods of estimation for kinetic parameters

A2.1 Rate parameters for II and III

In this case, $k_{c1} = 0$ and $k_{v1} = 0$. Equations (2) and (3) can be simply expressed by the form of eqn (A1):

$$C_n = C_n^0 \exp(-f_n t) \qquad (n = 2, 3) \tag{A4}$$

where $f_3 = k_{v3} + k_{i3}$.

Here, eqns (4) and (5) may be integrated like eqn (A3) as follows:

$$C_h - C_h^0 = -\frac{k_{mn}C_n^0}{f_n}\exp(-f_n t) \qquad (h = 4, 5;\ n = 2, 3;\ m = \mathrm{v, c}) \quad \text{(A5)}$$

where f_n can be calculated from eqn (A4):

$$f_n = -\frac{1}{t}\ln\frac{C_n}{C_n^0} \quad \text{(A6)}$$

The mean values of f_n and k_{mn} were at first determined from the experimental profiles of C_n. By use of the hydrolysis behaviour of **II** (e.g., Fig. 4(a)), the approximate values of k_{c2} and k_{i2} were estimated from the experimental profiles for **II**, **IV**, and **V**. Those for k_{c2} and k_{i2} were also estimated from the experimental profiles for **II**, **IV**, and **V**, which were obtained from the hydrolysis behaviour after the reaction time when components **I** and **III** disappeared. The approximate values for k_{v3} and k_{i3} were estimated from the profiles for **III**, **IV**, and **V**, which were obtained from the hydrolytic behaviour for **III** (e.g. Fig. 4(b)).

The optimum values of k_{c2}, k_{i2}, k_{v3}, and k_{i3} were determined by the least-squares methods by using their approximate values as the initial ones.[22] Although the values for k_{i2} and k_{i3} are, respectively, considerably smaller compared with those for k_{c2} and k_{v3}, their kinetic parameters could be estimated to three significant figures except for k_{i3} whose ones were estimated at best to two significant figures, because the amount of product for the component was small (cf. Table 2).

*A2.2 Rate parameters for **I***

According to the hydrolysis behavior (e.g. Fig. 3), the approximate values of f_1 were determined by the initial rate of decrease for **I**. The values of k_{c2} and k_{i2} obtained from the hydrolysis of **II** were used as their initial values for the calculation of the optimum values of kinetic parameters and the other initial values were set as: $k_{c1} = k_{c2}$, $k_{i1} = k_{i2}$ and $k_{v1} = f_1 - (k_{c1} + k_{i1})$.

The optimum values of rate parameters for the hydrolysis of **I** were determined by the least-squares method so as to minimize the variance between the experimental and calculated reaction profiles.[24]

From the hydrolysis behaviour of **I**, the seven values of parameters, k_{mn}, must be simultaneously determined. The optimum values of parameters having relatively larger values compared with those having smaller ones could be estimated to three significant figures, while the latter parameters were estimated at best to two significant figures. No precise values of k_{i3} could be estimated from the reaction profiles of **I**, because they were estimated to be negligible. There was found to be no significant difference between the variance when k_{i3} of the initial value and k_{i3} of zero were used (cf. Table 2).