Nucleophilic Aromatic Substitution: Effect of Complexation on the Alkaline Hydrolysis of 4-Aminophenylazobenzothiazolium Dyes

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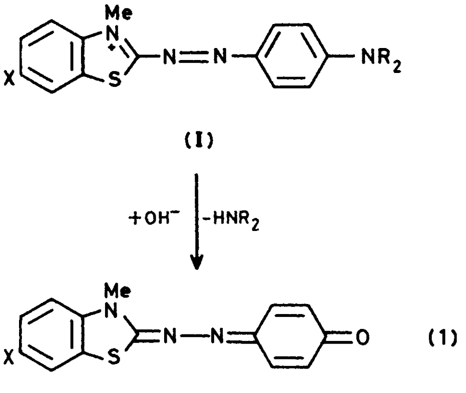
Nucleophilic attack by hydroxide ion on 2-(4-dimethylaminophenylazo)-3,6-dimethylbenzothiazolium iodide to expel the dimethylamino function is inhibited in aqueous solution by aromatic carboxylate, aromatic sulphonate, and phenolate ions. The inhibition is demonstrated to involve complexation of dye with solute to form an unreactive species. The dissociation constant of the complex is relatively insensitive to structure except in the case of phenolate ions where electron-withdrawing substituents favour stability. Both charge transfer and electrostatic effects are necessary for efficient complexing ability of the additive. Complexation of cyclodextrin with the dye is followed by reaction to yield a dye–cyclodextrin covalent species; the intermediate slowly decomposes to give quinone imine, the regular product of dye hydrolysis.

Dyeing of acrylic fibres by cationic dyes is probably due to electrostatic interaction with anionic sites on the fibre introduced in the polymerisation process.[1] Benzothiazolium azo dyes produce a fairly fast colour with acrylic fibres; under alkaline conditions or mild alkali at high temperature the solution of dye fades markedly [equation (1)][2] yet the dye in the fabric is relatively stable. Korolenko[3] noted that the fading rate of some cationic dyes was depressed in the presence of anionic retarders; this is presumably due to some form of complexing with the dye.



(I)

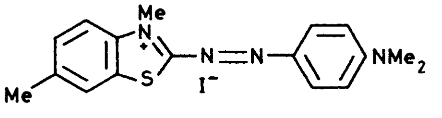
(1)

(II)

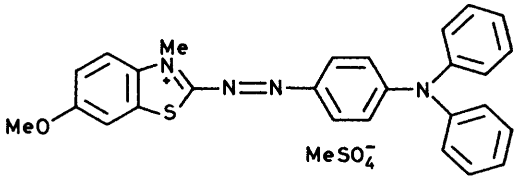
In this report we present the results of a study of the fading reaction (1) as a function of anionic additives in order to provide information on why benzothiazolium azo-dyed fabric is relatively fast to alkali. The results of this study may be useful in the design of conditions for inhibition of fading of cationic dyes in the dyeing bath. We employed dyes (III)—(V) in the investigation.

Experimental

Materials.—Phenols, carboxylic acids, and sulphonic acids were of analytical grade where possible or were purified by recrystallisation or resublimation from bench grade materials. Other chemicals, such as buffer components, were of analytical reagent grade. Water used throughout the investigation was doubly distilled from glass.



(III)



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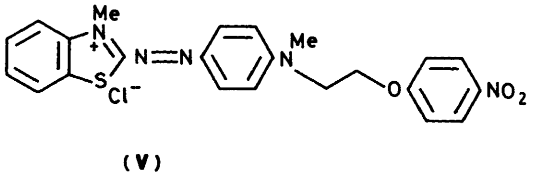


(V)

2-(4-Dimethylaminophenylazo)-3,6-dimethylbenzothiazolium iodide (**III**) and 2-(4-diphenylaminophenylazo)-3-methyl-6-methoxybenzothiazolium methosulphate (**IV**) were from previous work.[2]

2-{4-N-*Methyl*-N-[2-(4-*nitrophenoxy*)*ethyl*]*aminophenylazo*}-3-*methylbenzothiazolium chloride* was prepared by the method of Hunig.[4] 3-Methylbenzothiazolin-2-one hydrazone hydrochloride monohydrate (2.33 g, 10 mmol) in water (100 ml) was treated with iron(II) sulphate $FeSO_4 \cdot 7H_2O$ (3 mg) and *N*-methyl-*N*-[2-(4-nitrophenoxy)ethyl]aniline (2.72 g) in acetone (20 ml) with HCl (aqueous 1M; 20 ml). The mixture was stirred and H_2O_2 (10 ml; 20% w/v) added. The solution was then maintained at 80 °C and formic acid (30 ml) added. The deep blue-red solution was filtered hot and allowed to cool. Crystals of the dye were precipitated with saturated NaCl, filtered, washed with a little water and dried; they had m.p. 198—200 °C (decomp.) (Found: C, 49.7; H, 5.2; N, 12.6. $C_{23}H_{22}ClN_5O_3S \cdot 5H_2O$ requires C, 49.7; H, 5.4; N, 12.6%). The crystals were homogeneous as judged from a single spot on t.l.c. with silica gel (Kieselgel 60 on

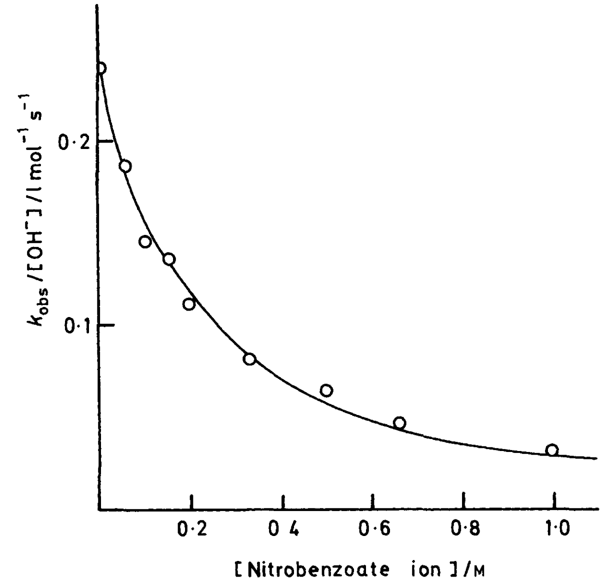


Figure 1. Hydrolysis of (III) in the presence of 4-nitrobenzoic acid at pH 12.0. Conditions as in the Table. Line is calculated from equation (2) and the parameters in the Table (assuming k'_{OH} 0)

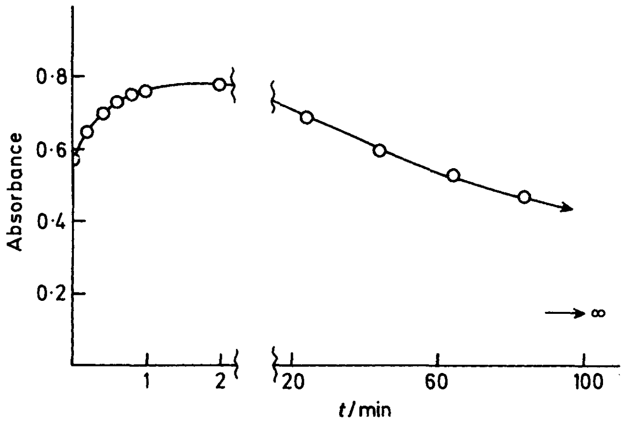


Figure 2. Absorbance at 500 nm of a solution of (III) in β-cyclodextrin (1mM) as a function of time at 25 °C, ionic strength maintained at 1M with KCl and pH 12.0. Absorbance after 'infinite' time is indicated by the arrow

alumina foil from Merck) and 1:1 MeOH–$CHCl_3$ as eluant.

Identities of materials synthesised were confirmed by i.r. (Perkin-Elmer 297 instrument) and n.m.r. spectroscopy (JEOL 100 MHz instrument) and by elemental analysis (Mr. A. J. Fassam, this laboratory).

Methods.—Kinetics of reaction and measurements of spectra and pH were carried out as previously described.[2,5]

Results

Rates of hydrolysis of dyes obeyed excellent pseudo-first-order kinetics up to *ca.* 90% of the total reaction. Previous work[2] has shown that the rate law is first order in hydroxide ion concentration and division of the first-order rate constants by the latter concentration gives the second-order rate constant (k_{OH}) for attack of hydroxide ion on the dye.

The presence of added anionic species (phenolate, benzoate, and sulphonate ions) retarded the dye hydrolysis rate. A typical concentration dependence of the rate constant for hydrolysis is given in Figure 1 for the 4-nitrobenzoate ion and (III). The pseudo-first-order rate constants follow the rate law (2) which is associated with the mechanism given in equation (3). The

$$(k_{OH} - k'_{OH}) = (k_{OH} - k_{obs}/[OH^-])(1 + K_{eq}/[A]) \quad (2)$$

$$\begin{tikzcd} \text{Dye} + \text{A} \arrow[r, shift left, "K_{eq}"] \arrow[d, "k_{OH}[OH^-]"] & \text{Dye}\cdot\text{A} \arrow[l, shift left] \arrow[d, "k'_{OH}[OH^-]"] \\ \text{product} & \text{product} \end{tikzcd} \quad (3)$$

quantity K_{eq} is a dissociation constant of the dye–addend complex and is essentially the concentration of addend (A) for half-complex formation at equilibrium. Equation (2) governs

Table. Equilibrium constants for the interaction of dye (III) with various agents in water[a]

Addend	K_{eq}/mol l^{-1} [g]	[A]/M [c]	N [d]
Benzoate ions			
4-Nitro	0.17	0.05—1.0	9
3-Nitro	0.33	0.1—0.67	7
3-Chloro	0.36	0.1—0.7	6
4-Chloro	0.32	0.05—1.0	7
Parent	0.35(0.36)[b]	0.1—1.0	12 (7)
4-Carboxylate	0.18	0.04—0.3	5
3-Methyl	0.15	0.05—0.6	8
4-Methyl	0.83	0.1—0.67	7
4-Methoxy	0.25	0.1—1.0	7
4-Oxy-anion	0.2	0.1—0.3	7
Benzenesulphonate ions			
4-Methyl	0.18	0.05—0.5	6
Parent	0.36	0.03—0.5	5
4-Nitro	0.4	0.16—0.5	5
Phenolate ions			
3-Nitro	0.057	0.01—0.2	9
4-Cyano	0.23	0.08—0.5	7
3-Chloro	0.22	0.05—0.5	6
Parent	1.5	0.17—0.5	5
Benzene derivatives[i]			
Anisole	2.3	0.3—9	8
Toluene	3.2	0.31—9.4	9
Benzene	10	1.0—11.0	7
Chlorobenzene	19	0.98—9.8	7
Nitrobenzene	8.3	0.98—9.8	7
NNN-Trimethylammoniobenzene iodide	0.11[e]	0.025—0.5	7
Other addends[h]			
1-Carboxynaphthalene[j]	0.069	0.05—1.0	6
2-Carboxymethylnaphthalene[j]	0.022	0.01—0.2	8
Cyclohexanecarboxylic acid[j]	2.2	0.33—1.0	4
2-Picoline	0.28	0.05—0.5	7
Cyclodextrin	0.0068[f]	0.00033—0.01	8
Pyridine	3.4	0.1—1.0	4

[a] Conditions except where stated: 25 °C, ionic strength maintained at 1M with KCl, wavelength for kinetic study 600 nm, pH 12.00 ± 0.05. The value of k_{OH} is 0.24 l mol^{-1} s^{-1}; except where stated k'_{OH} is negligible (see text). [b] Measured spectrophotometrically from the change in absorbance at 670 nm, pH 7.95. [c] Concentration range of addend. [d] Number of data points not including duplicates. [e] Value of k'_{OH} 0.45 l mol^{-1} s^{-1}; conditions as under footnote *a*. [f] Value of k'_{OH} 2.2 l mol^{-1} s^{-1}. [g] Error in the dissociation constant no greater than 10%. [h] The following species at pH 12.00 and at the concentrations indicated had no effect on the fading rate of (III): KCl (1M), KOAc (1M), and K_3citrate (0.17M). [i] Conditions: 25 °C, ethanol solvent, wavelength used for absorption measurements: 640 nm; except for the cationic addend, the value of K_{eq} was determined spectroscopically. [j] Values are for the conjugate bases.

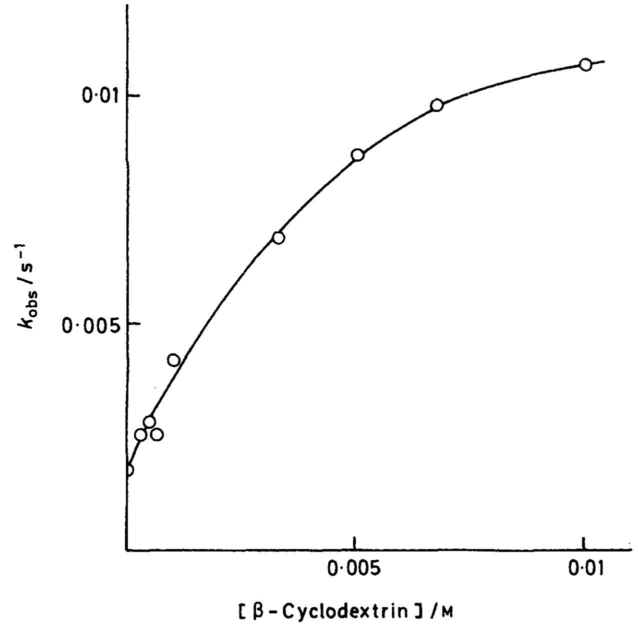


Figure 3. Rate constant for formation of intermediate between β-cyclodextrin and (**III**) as a function of cyclodextrin concentration. Conditions as in the Table. Line is calculated from equation (2) and parameters given in the Table

the general case where the complex and dye can react faster or slower with hydroxide ion than the uncomplexed dye. The value of k'_{OH} can also be negligible compared with k_{OH}.

Values of K_{eq} and k'_{OH} are given in the Table; k'_{OH} is less than 10% of k_{OH} except where noted and this value is below the error limits for its measurement. Only in the case of the *NNN*-trimethylammoniobenzene cation is $k'_{OH} > k_{OH}$.

The absorption maximum in the spectrum of the dye (**III**) shifts to longer wavelengths in the presence of aromatic anions. This shift is probably due to the different absorption of a complex rather than specific solute effects because the absorption at a particular wavelength in the presence of addend (A) varies according to equation (4) where Abs_0 is the absorption of

$$\text{Abs} - \text{Abs}_0 = [\text{Dye}_{tot}]\Delta\varepsilon/(1 + 1/K_{eq}[\text{A}]) \qquad (4)$$

the solution at zero addend concentration. The quantity $\Delta\varepsilon$ is the difference in molar extinction coefficients between dye and complex at the wavelength in question. The value K_{eq} was found to be 0.36 mol l^{-1} compared with the kinetically determined value (0.35 mol l^{-1}) for interaction of benzoate ion with dye (**III**) at 25 °C, aqueous solution with ionic strength maintained at 1M with KCl. The spectra have an excellent isosbestic wavelength at 600 nm and a bathochromic shift of the maximum from 595 to 650 nm for the benzoate–dye (**III**) system. Other addends altered the spectrum of (**III**) and the resultant values of K_{eq} are recorded in the Table.

The hydrolysis of (**V**) in alkaline solution (30% v/v EtOH/-water; 25 °C) gave a value of k_{OH} 1.7 l mol^{-1} s^{-1} and that of the parent (**I**; X = H, R = Me) has a value 0.34 l mol^{-1} s^{-1}.[2]

Repetitive scanning of the visible spectrum of a solution of dye (**III**) and β-cyclodextrin at pH 12.0 indicated an initial rapid change to an intermediate with an absorption maximum at 520 nm; the intermediate slowly decays to a product with absorption maximum at 448 nm (isosbestic wavelength for the decay is 460 nm). The absorption maximum of the quinone imine (**II**; X = Me) prepared previously[2] changed from 432 to 448 nm in the presence of β-cyclodextrin.

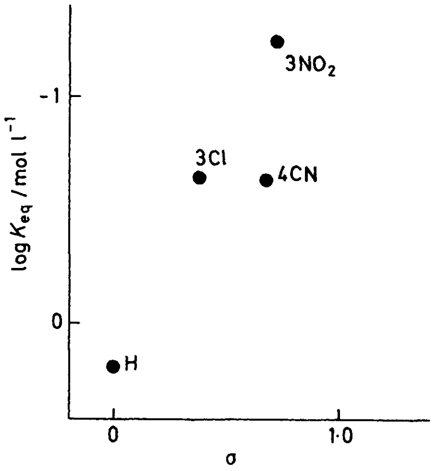


Figure 4. Hammett dependence of K_{eq} for phenolate ions. Data from the Table and σ values from H. Maskill, 'The Physical Basis of Organic Chemistry,' Oxford University Press, Oxford, 1985

Discussion

Simple anions such as acetate or citrate do not bind appreciably to benzothiazolium azo dyes and non-ionic arenes complex an order of magnitude less efficiently than do the corresponding anionic species. The mechanism of binding of dye with addend is not due to a single interaction between dye and agent; this is confirmed by the absence of substituent effect on K_{eq} for benzenesulphonate and benzoate anions. It is proposed that benzenesulphonate and arenecarboxylate anions bind with dye (**III**) *via* an electrostatic and a charge-transfer interaction of the type illustrated in (**VI**). The dye acts as a π-donor and the cancellation of the two electronic effects gives zero substituent effect for the dissociation constants of the complexes with sulphonate and carboxylate. The very low values for k'_{OH} for the complexes indicate that the complexed agent is very close to the reactive 4′-centre as in (**VI**). The bound anionic group effectively lowers the reactivity at position 4′ electrostatically. Presumably the positive charge of the bound *NNN*-trimethylammoniobenzene augments the reactivity of the 4′-position because $k'_{OH} > k_{OH}$. The dramatic effect of the addend on the hydrolysis rate would indicate that the binding occurs with the phenylazo group rather than with the benzothiazolium part of the dye.

We have excluded the possibility that simple anions such as acetate or chloride bind at a part of the dye molecule remote from the centre of reaction since there is no change in visible spectrum on addition of these species. The absence of an effect even with a trianion (citrate) is strong evidence that a dual interaction mechanism must operate. That the binding interaction does not include a simple hydrophobic force is confirmed by the weak binding between cyclohexanecarboxylate anion, which does not possess π-acceptor ability, and dye (**III**). The donation from the π-system of the dye to the acceptor arene presumably extends the conjugated system and the absorption maximum is shifted to longer wavelengths than in the free dye. Carboxylate derivatives of naphthalene are the most strongly bound anions.

The dissociation constants for caffeine–benzoate anion complexes[6] are smaller for electron-releasing substituents in the benzene ring indicating that benzoate anions can act as π-acceptors despite their possessing negative charge. The problem with postulating a cationic π-donor is presumably alleviated by electrostatic interaction of the positive charge with the benzoate anion.

The complexing of dye with phenolate anions exhibits sig-

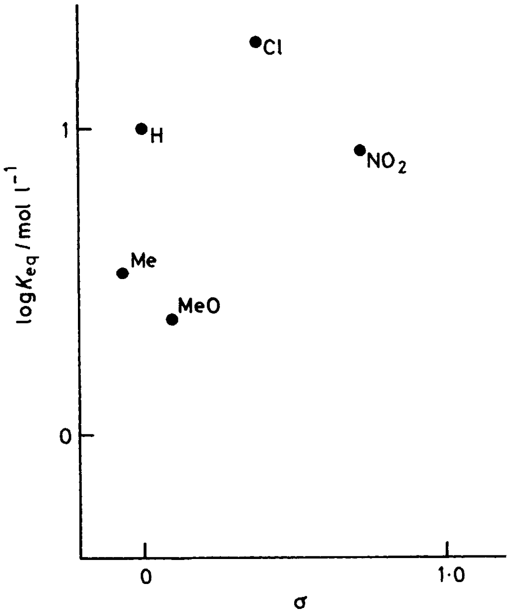


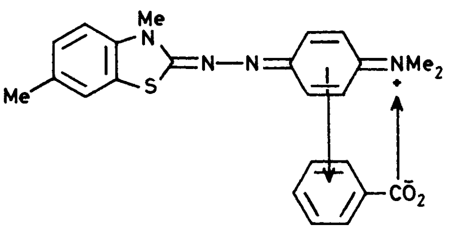
Figure 5. Hammett dependence of K_{eq} for benzene derivatives. Data from the Table and σ values as in Figure 4

nificant substituent effect (Figure 4) indicating donation of charge *from* the dye. The correlation is not perfectly linear probably consistent with charge delocalisation in the anion acceptor which may not occupy a single configuration in its binding at the phenylazo group. It is likely that the sulphonates and carboxylates, with their fixed charge, have (VI) as their major configuration for binding in the complex.

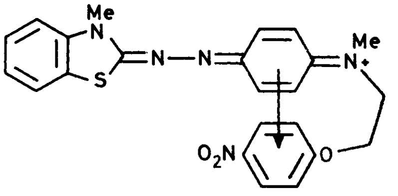
Arenes and pyridine complex with (III) to a weaker extent than do the corresponding sulphonate and carboxylate anions and there is a non-linear substituent effect (Figure 5). It is not possible to decide whether the agent is acting as donor or acceptor and the non-linearity is probably due to several optimal positions of the agent in the complex. The presence of an anionic side chain on the arene ring would stabilise one of these positions by electrostatic interaction with the positive charge on the dye. It was not possible to test the reactivity of the complexes to hydrolysis because the binding experiments were carried out in ethanol solvent.

Dye (V) shows a slight enhancement in rate of hydrolysis over the parent species probably because of an internal complexation as in (VII) which activates position 4′.

The benzothiazolium azo dye (III) complexes with β-cyclodextrin and appears to react with it (Figure 2). The rate constant for disappearance of the dye corresponding to the first of the consecutive steps depends on the cyclodextrin concentration according to the complexation law (2). The value of K_{eq} is close to that for complexing of other agents with cyclodextrins;[7] the dye binds within the cyclodextrin torus[8] because the complexation is reduced by the calculated amount by addition of iodide ion. Further evidence that binding is within the torus is that the hydrolysis of the hindered dye (IV) is not affected by added cyclodextrin.



(VI)



(VII)

The value of k'_{OH} is very much enhanced over the uncomplexed rate constant (k_{OH}) and this is consistent with reaction of the dye with alkoxide formed by ionisation of one of the sugar hydroxy functions. It is difficult, otherwise, to see how simple hydroxide ion attack on the bound dye could exceed that of the free. Moreover, the initial reaction is not to form the quinone imine (II) as judged from the initially formed spectrum. The intermediate slowly decomposes to quinone imine (Figure 2) as evidenced by the spectrum of the final product.

The results of this study indicate that the structure of the arene anion is not particularly critical with regard to its potential in protecting the dye against hydrolysis.

The studies with cyclodextrins indicate that there could be a problem of fastness in dyes bound to carbohydrate-containing fibres.

Acknowledgements

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