# Nucleophilic Aromatic Substitution: Transmission of Substituent Effects in Alkaline Hydrolysis of 4-Aminophenylazobenzothiazolium Dyes

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Alkaline fading of 2'-, 5-, and 6-substituted 2-(4'-aminophenyl)azobenzothiazolium dyes (I) possesses

(I)
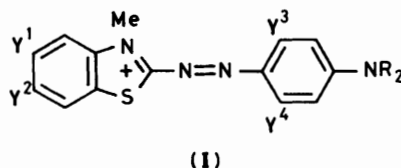
a second-order rate constant (k_{OH}). The value of k_{OH} is shown to predicted by equation (i) where σ_N is

$$\log k_{OH} = 0.76\sigma_N + 0.24\sigma_S + 1.69\sigma^+ + \log[10^{-0.15(pK-9.5)}/(1 + 10^{0.25(pK-9.5)})] + 0.74 \quad (i)$$

σ^+ for 6- and σ for 5-substituents, σ_S is σ^- for 5- and σ for 6-substituents, σ^+ is for 2'-substituents, and the pK is that of the leaving 4'-amine. The dye fading is not very sensitive to substituents in the benzothiazole phenyl ring but the charge is transmitted more effectively through nitrogen than through sulphur.

Phenylazobenzothiazolium dyes bearing a 4'-amino group (I) have useful colour characteristics and can be important in dyeing acrylic materials.[1] These dyes fade in alkaline solution [equation (1)][2] to give the quinone imine (II) necessitating careful pH control during application of the dyes.

In order to design benzothiazolium azo dyes with good fading properties and with particular colours and intensities it is convenient to be able to predict the fading rates as a function of substituents. The effect on k_{OH} [equation (1)] of varying

(I)

$$k_{OH}[OH^-] \downarrow \text{ or } k_B[B]$$

(II)
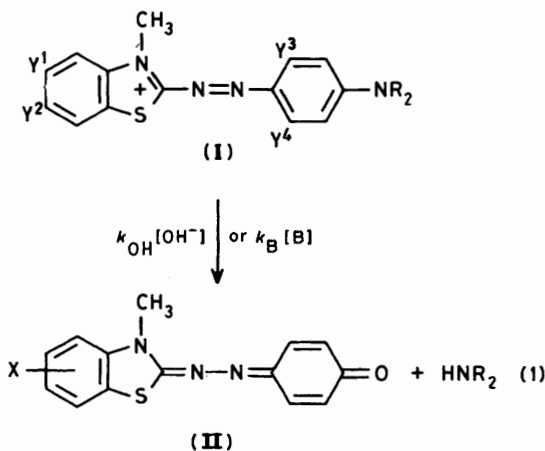
substituents in the leaving amino function and the effect of base structure on the base-catalysed reaction has already been discussed.[2]

We report here a study of substituent effects on k_{OH} for the 2'-, 5-, and 6-positions in the benzothiazolium azo dye (I; R = Me). The work provides an equation to predict the value of k_{OH} as a function of substituents in both aromatic nuclei and on the leaving amine.

Experimental

Materials.—The general methods for preparation of benzothiazole azo dyes by diazo coupling of 2-aminobenzothiazoles and anilines and benzothiazolium azo dyes have been described in a previous report;[2] the iodides of the benzothiazolium azo dyes were precipitated from aqueous solution with KI. The dyes (I; R = Me, X = H; R = Me, X = 6-Me; R = Me, X = 6-MeO) were from a previous study.[2]

2-Amino-6-cyanobenzothiazole was prepared by a modification of the method of Stückwisch.[3] 4-Cyanoaniline did not dissolve appreciably in the normal solvent (acetic acid–water) and dichloroacetic acid was employed as a replacement acid. The yields of the cyanobenzothiazole were nevertheless poor and subsequent synthesis of the 'onium salt was not carried out.

2-Amino-6-hydroxybenzothiazole was prepared from the 6-methoxy species (10 g) by refluxing with aqueous HBr (500 ml, 48%) for 5 h. The product solution was treated with activated charcoal (1 g), filtered, and cooled. The precipitated crude benzothiazole was then filtered and recrystallised.

4-Substituted 2-nitrophenyl thiocyanates were prepared by the method of Vel'tman.[4] 4-Substituted 2'-nitroaniline (40 mmol) was dissolved in water (80 ml), crushed ice (80 g), and H_2SO_4 (8 ml). The solution was placed in a bath of crushed ice. A solution of $NaNO_2$ (3.5 g) in water (10 ml) was added with stirring and the diazotised mixture kept for 20 min in the ice-bath. The solution was then filtered directly into a chilled flask containing KNCS (4.1 g) in water (20 ml), the mixture was kept at room temperature for two days, and the phenyl thiocyanate filtered and recrystallised. The cyanate was converted into benzothiazole by a modification of the method of Wagner-Jauregg.[5] The new phenyl thiocyanate (7.7 mmol) was added to a solution of $Fe_2(SO_4)_3$ (18 g) in water (45 ml) on a boiling water-bath and ammonia solution (33 ml; 10%) slowly added with stirring. The mixture was kept for 5 h on a boiling water-bath and then water (60 ml) added, the solution was filtered, and the residue washed with more boiling water. The combined filtrates were evaporated to dryness under reduced pressure

Table 1. Alkaline hydrolysis of substituted 3-methyl-(4-dimethylaminophenylazo)benzothiazolium iodides (I)[a]

	Y[2]	Y[1]	M.p. (°C)	σ_S[d]	σ_N[d]	k_{OH}/l mol^{-1} s[-1][g]	pH range	N[f]
1	H	H	b	0	0	0.34[b](0.34)		
2	Me	H	b	−0.07	−0.17	0.24[b](0.24)		
3	MeO	H	b	+0.08	−0.27	0.2[b](0.22)		
4	Cl	H	210—212 (decomp.)	+0.37	+0.23	0.60(0.62)	10.95—12.38	5
5	NO₂	H	190—192 (decomp.)	+0.71	+1.25	3.98(4.5)	10.45—12.5	4
6	OH	H	270 (decomp.)	−0.047	−1.62[e]	0.0069(0.015)	12—13	5
7	H	Me	220—224 (decomp.)	−0.311	−0.07	0.11(0.25)	11—13	4
8	H	MeO	200—204 (decomp.)	−0.778	+0.08	0.25(0.25)	11—13	4
9	H	Cl	200—202 (decomp.)	+0.114	+0.37	0.79(0.69)	11—13	4

[a] 25 °C, ionic strength maintained at 1M with KCl (0.01M in buffer: borate or carbonate). [b] From a previous report.[2] [c] See Experimental section for recrystallisation solvent. [d] Values of σ^+, σ, and σ^- taken from ref. 6. [e] See text for this value of σ^+. [f] Number of data points not including duplicates. [g] Error in parameters is no greater than ±10%; values in parentheses are calculated (see text).

Table 2. Hydrolysis of 3-methyl-6-methoxy-(2-substituted 4'-dimethyl-aminophenylazo)benzothiazolium iodides[a]

2'-Substituent	M.p. (°C)	σ^+[d]	k_{OH}/l mol^{-1} s[-1][e]	pH range	N[c]
H		0	0.2[b](0.22)		
Me	218—220 (decomp.)	−0.311	0.079(0.066)	11.4—14	5
NO₂	218—222 (decomp.)	+0.71	3.98(3.5)	9.95—12	5

[a] 25 °C, ionic strength maintained at 1M with KCl (0.01M buffer: borate or carbonate). [b] From a previous report.[2] [c] Number of data points not including duplicates. [d] From ref. 6. [e] Error in parameters no greater than ±10%; values in parentheses are calculated (see text).

and the amine extracted by boiling with several volumes of ethanol.

2-(4-Dimethylaminophenylazo)-6-hydroxybenzothiazole was prepared by diazo-coupling[2] NN-dimethylaniline with 2-amino-6-hydroxybenzothiazole (10 mmol) in water (20 ml) and acetic acid (20 ml). After diazo-coupling was complete NaOAc was added to raise the pH to 5 (raising pH to 7 as previously[2] gave decreased yields for this dye). The precipitate was filtered, washed, and dried. Quaternisation of the hydroxybenzothiazole was carried out by refluxing with methyl iodide. No O-methyl-ation occurs in quaternisation as judged from t.l.c. of the product and comparison of R_F values with that for authentic 6-methoxybenzothiazole azo dye.

The diazo-coupling procedure[2] did not work efficiently for the 6-nitro benzothiazole azo dye preparation. It was found that a better solvent is dichloroacetic acid (20 ml), acetic acid (20 ml), and water (10 ml) for solution of the 2-amino species (10 mmol).

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). Purity was checked routinely by t.l.c. analysis on silica gel plates. Details of new compounds are in Supplementary Publication No. SUP 56696 (3 pp.).*

Other materials were of analytical reagent grade or were recrystallised or redistilled from bench grade reagents. Water used throughout the investigation was doubly distilled from glass.

Methods.—Kinetic procedures were as described previously.[2] Hydrolyses were followed by u.v.-visible spectroscopy with a Pye-Unicam SP800 instrument. Measurements of pH were carried out with a Radiometer PHM 62 digital instrument standardised to ±0.01 pH units with EIL standard buffers.

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* Details of Supplementary Publications are in *J. Chem. Soc., Perkin Trans. 2*, 1987, Issue 1.
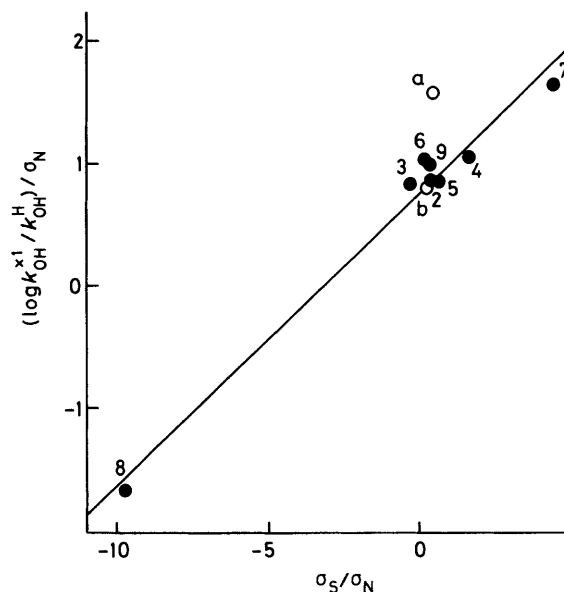
Figure 1. Jaffé-type plot for the alkaline hydrolysis of 5- and 6-substituted benzothiazolium azo dyes (I). Data are from Table 1 and the line is calculated from parameters given in the text and equation (2). Key to points (●) in Table 1; points a and b (○) are those for the 6-O⁻ substituent when σ^+ is taken arbitrarily as −1 and −2 respectively (see Results section)

Results

The benzothiazolium azo dye hydrolysis in alkaline solution obeyed good pseudo-first-order kinetics to over 90% reaction. The rate constants are proportional to the hydroxide ion concentration; second-order rate constants (k_{OH}) were obtained by division by hydroxide ion concentration. The k_{OH} parameters are recorded in Tables 1 and 2 for substituent change in the 5- and 6- and in the 2'-positions. Since we have already thoroughly investigated the pH-dependence of the fading reaction for representative dyes[2] we are able to obtain good data from relatively short pH ranges (see Tables for conditions).

The values of k_{OH} for the 5- and 6-substituents fit an excellent Jaffé equation (2); σ_N for the 6-position (*para*) are σ^- and σ_S for

$$\log k_{OH}^x = 0.76 \pm 0.01 \, \sigma_N - 0.47 \pm 0.01 \, \sigma_S \, (r \, 0.993) \quad (2)$$

the 5-position (*para* to S) are σ^+. Other values ($\sigma_{N(meta)}$ and $\sigma_{S(para)}$) are regular Hammett σ values. The values of σ, σ^+, and σ^- are taken from the work of Chapman and Shorter[6] and the rationale of the use of the exalted σ values rather than the regular Hammett σ is discussed later. The correlation coefficient

between the σ_N and σ_S for the substituents employed is 0.647 and satisfies Jaffé's criterion ($r < 0.900$ for the correlation coefficient between σ values for both transmission routes) for the application of his two-parameter equation.[7]

There appears to be no literature value of σ^+ for the 4-O$^-$ group. This value must be considerable larger than σ^+ for 4-OH (-0.92) and also than σ for 4-O$^-$ (-0.81). 4-NH$_2$ and 4-NMe$_2$ have values of σ^+ of, respectively, -1.3 and -1.7 and are approximately double the value of the regular σ values (-0.66 and -0.83). We employ a value of σ^+ for 4-O$^-$ (-1.62) which is twice that of the regular Hammett σ value for this substituent. Figure 1 illustrates points for the 4-O$^-$ substituent when values of σ^+ of -1 and -2 are taken; the value of σ^+ for 4-O$^-$ is not critical within the reasonable range chosen and we therefore believe that the value of -1.62 is a satisfactory approximation.

The hydrolysis of the benzothiazolium azo dyes with variation of substituents in the 2'-position obeys the Hammett equation (3).

$$\log k^x_{OH}/k^H_{OH} = 1.69 \pm 0.12\,\sigma^+ - 0.63 \pm 0.06\,(r\,0.997) \quad (3)$$
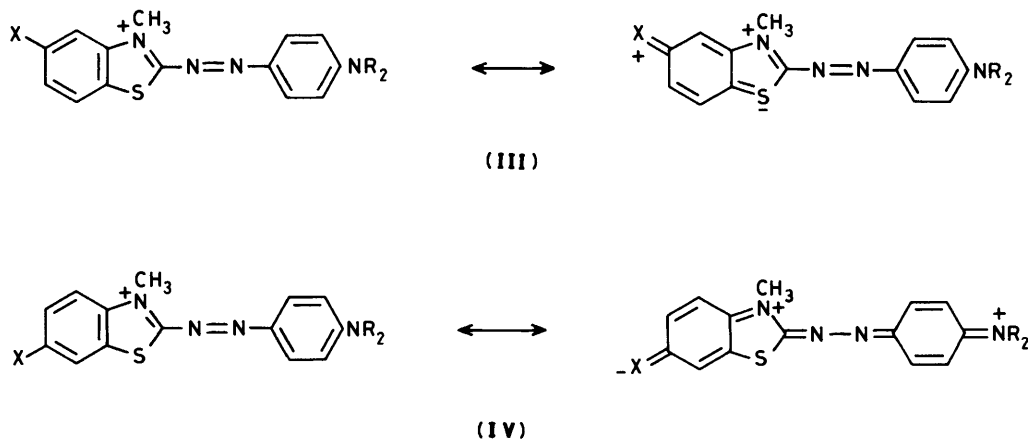
Equations (2) and (3) can be combined with equation (8) of the previous report[2] to yield equation (4) which predicts the rate constant (k_{OH}) for 4'-aminophenylazo-3-methylbenzothiazolium dyes substituted in the 2'-, 5-, and 6-position and in the 4'-amino group. The values of σ are as described above

$$\log k_{OH} = \log [10^{-0.15(pK-9.5)}/(1 + 10^{0.25(pK-9.5)})] + 0.74$$
$$+ 0.24\sigma_S + 0.76\sigma_N + 1.69\sigma^+ \quad (4)$$

and pK is the pK of the leaving amine. The fit of the data to equation (4) is illustrated in Tables 1 and 2 where values in parentheses are calculated from equation (4).

Discussion

Transmission of substituent effects from the phenyl ring of the benzothiazolium nucleus to the 4'-position involves two pathways, through S or through N, the ρ values of which are designated ρ_S and ρ_N for the Jaffé analysis.[7] Regular Hammett σ constants give a poor correlation of the data of Table 1 because some substitutents can interact mesomerically with the reaction centre at position 4' in the phenylazo ring. Regular σ constants are employed for both σ_S and σ_N when the substituent is *meta* to the sulphur (6-) or nitrogen (5-). Substituents in position 5 can

Figure 2. Hammett dependence on σ^+ of the alkaline hydrolysis of quinone di-imines. Data are from ref. 13 and the key to the points is: 1, 4-MeO; 2, 4-Me; 3, H; 4, 4-Cl. The unfilled circles represent the correlation if the regular σ constant is employed

The values of ρ_S and ρ_N are consistent with significant transmission through the sulphur atom which carries about a quarter of the total effect. So far as we are aware there has been no study of substituent effect transmission with benzothiazolium ions reported in the literature. Work on the dual transmission pathway for benzothiazole appears to favour the nitrogen route. Dissociation of the conjugate acids of 2-aminobenzothiazoles possesses ρ_N 1.47 and ρ_S 1.1[8,9] for substituents in the fused phenyl ring. Other workers have indicated that sulphur transmits the substituent effect only weakly compared with nitrogen in reactions through position 2 in benzothiazole systems [attack of methoxide ion on 2-chlorobenzothiazoles and oxidation of 2-(methylthio)benzothiazoles to sulphoxides];[10,11] Jaffé, however, noted that ρ_S in these systems was close to its uncertainty value.[9] Rate constants for proton transfer at C-2 in benzothiazoles have ρ_N 0.985 and ρ_S 1.315.[12] Asymmetric and symmetric stretching vibrations of the 2-amino group in 2-aminobenzothiazoles have been proposed to involve transmission mainly through the nitrogen;[13] however, only substituents in the 6-position were employed and, since σ_N and σ_S for these substituents correlate

(III)

(IV)

mesomerically donate electrons to the sulphur (III) and σ_S for this position is therefore σ^+. Substituents in position 6 can mesomerically withdraw electrons from the 4'-position (IV) and σ_N is thus σ^- for this position.
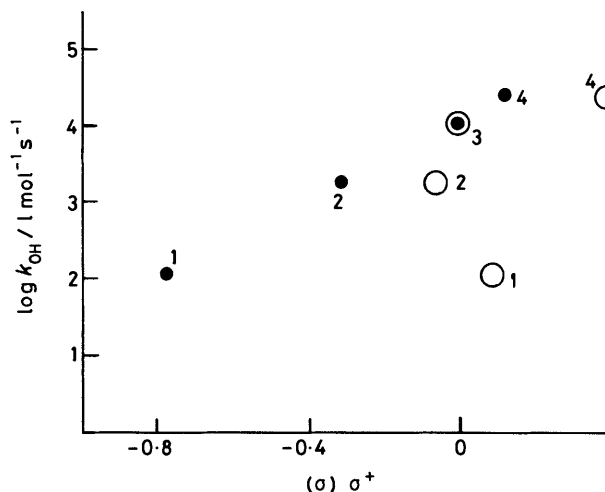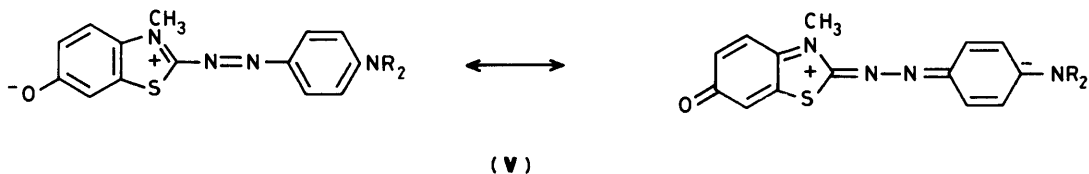
with each other (r 0.947), it is difficult to make a conclusion concerning the relative transmission propensities, bearing in mind Jaffé's dictum.[7] Similar criticisms may be levelled at conclusions drawn from the other data.[8,10–12] An excellent,

simple Hammett correlation between the energy of the absorption of benzothiazole azo dyes and substituents in the 6-position does not, however, enable us to dissect the relative transmissions of sulphur and nitrogen.[14]
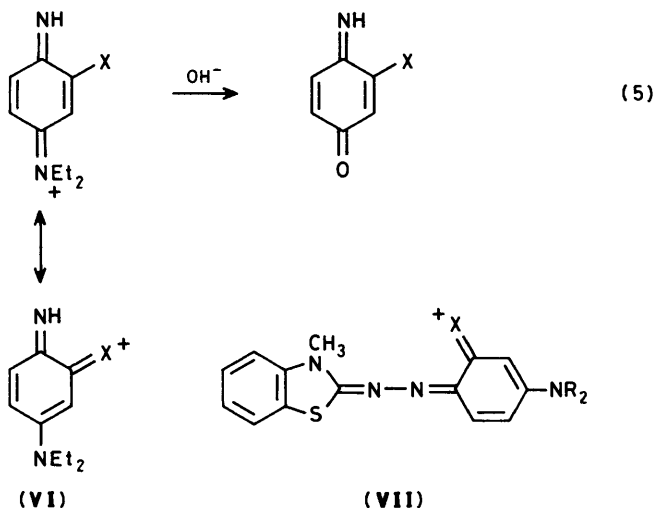
The ability of nitrogen to transmit charge mesomerically to the azophenyl ring (IV) in the dye-fading reaction may be the cause of the higher transmitting ability compared with sulphur. Although the sulphur interacts mesomerically with a suitable 5-substituent (III) the effect is not projected further into the phenylazo ring except by induction. It is not expected that inductive transmission through S or N is significant.

The very low reactivity of the 6-hydroxy species is due to the ionisation of hydroxy to give oxy anion at the high pH involved in the hydrolyses; we must therefore employ σ_N and σ_S appropriate to the oxy anion and not the parameters corresponding

hydrolysis of quinone di-imines [equation (5)];[15] we have analysed the data according to the Hammett σ^+ dependence and the fit is shown in Figure 2. The dependence could arise due to the importance of resonance canonical structures such as (VI) and in the dye hydrolysis a canonical structure (VII) is presumably responsible.

Perusal of Tables 1 and 2 indicates good fit of the data to the empirical equation (4). There are not sufficient data to test for any interaction between the substituent effects in the benzothiazole ring but this is unlikely.[16] It is probable that the Hammett ρ values will depend on the amine substituent and the β value for the effect of variation of the amine on k_{OH} will depend on the ring substituents;[17] this cross-interaction problem is not addressed here but we do not expect it to be serious enough to invalidate the equation for use in technical applications.

(V)

to the hydroxy group. Undoubtedly, the low reactivity of the 6-hydroxy species (present as the zwitterion) is due to mesomeric transmission of charge through the nitrogen as illustrated in (V).

Substitution at the 2'-position in the phenylazo ring (I) gives rise to a set of rate constants for alkaline hydrolysis governed by a Hammett σ^+ dependency [equation (3)]. The application of a σ^+ dependence to a system with attack *meta* to the substituents requires some explanation. A similar σ^+ dependency holds for *meta* substituents in the alkaline

(5)

(VI)   (VII)

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