

The Photofading of Some Aminoazobenzene Dyes on Polyester

Jolanta Sokolowska-Gajda

Institute of Dyes, Technical University (Lodz),
90-924 Lodz, Zwirki 36, Poland

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ABSTRACT

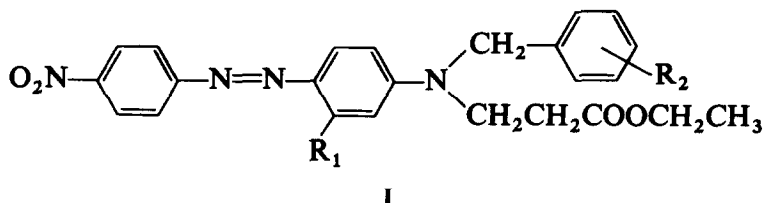
A study of the photofading of some aminoazobenzene disperse dyes derived from N-benzyl-N-phenyl- β -alanine on polyester fabric was carried out. A reasonable linear relationship between the fading rate, measured on the basis of the change of colour parameters ($P\%$, L) as a function of irradiation time, and σ_0 constants of ortho substituents in the phenyl ring of the coupling components was found.

1 INTRODUCTION

One of the most important properties of a dye is its fastness to light, and many efforts have been made to correlate this with the structure of the dye.^{1,2} The majority of published papers have dealt with the influence of different substituents in the diazo components³ or of different terminal amino groups⁴ in coupling components on the photofading of aminoazobenzene dyes. It is well established that the mechanism of photodegradation of dyes in solution is sometimes very different in comparison with their behaviour on fabric. It has also been found that the mechanism of photodegradation of the same dye depends on the dyed substrate, e.g. it is different for polyester and for polyamide fibres.⁵

This paper reports some kinetic measurements of the change of colour parameters ($P\%$, L , C , ΔE) of dyed polyester fabric as a function of irradiation time, and a correlation of the results with the structure of some aminoazobenzene dyes (I) in which some alkyl esters of N-benzyl-N-phenyl- β -alanine were used as coupling components. For this group of

dyes, the photolytic behaviour in ethanolic solution has been previously reported.⁶



<i>Dye</i>	<i>R</i> ₁	<i>R</i> ₂	<i>Lightfastness</i>
Ia	H	H	5
Ib	CH ₃	H	4-5
Ic	OCH ₃	H	4
Id	H	<i>p</i> -CH ₃	5
Ie	H	<i>p</i> -OCH ₃	5
If	H	<i>m</i> -NO ₂	5

The colour of dyed polyester fabric was assessed in terms of tristimulus colorimetry. Values for the chromaticity coordinates (*x*, *y*), luminance factor (*Y*), Helmholtz coordinates (λ_D , λ_C , *P*%) and the position of the colours in the CIELAB colour solid are presented in Table 1.

2 EXPERIMENTAL

The azo dyes used in this study were synthesised as previously described.⁷ 0.5% omf dyeings on polyester of dyes I were used for the determination of the colour parameters (*x*, *y*, *L*, *a*, *b*, *P*%, *C*, ΔE). The fabric samples

TABLE 1
Colour Parameters of the Dyed Polyester Fabric

<i>Dye</i>	<i>Chromaticity coordinates</i>		<i>Luminance factor Y (%)</i>	<i>Helmholtz coordinates</i>			<i>CIELAB coordinates</i>		
	<i>x</i>	<i>y</i>		λ_D	λ_C	<i>P</i> %	<i>L</i>	<i>a</i>	<i>b</i>
Ia	0.58	0.36	15.91	602	490	83.50	46.85	53.25	51.34
Ib	0.57	0.34	11.41	606	491	79.12	40.27	52.37	38.02
Ic	0.56	0.34	13.38	606	491	76.00	43.34	51.74	38.33
Id	0.56	0.36	19.39	600	490	76.53	51.14	51.84	50.37
Ie	0.57	0.36	15.81	603	490	80.41	46.73	50.69	47.61
If	0.56	0.39	25.86	594	491	86.51	57.90	47.52	65.09

were exposed in a Xenotest apparatus (Hanau); the kinetics were followed by measuring colour parameters ($P\%$, L , C , ΔE) with the Bran New Color spectrophotometer at regular intervals of time. The light-fastness was determined according to Polish Standards, which correspond to British Standards.⁸

3 RESULTS AND DISCUSSION

To evaluate the photochemical behaviour of dyes I in different media, a study of their photodegradation on polyester fabric was carried out. The object of the work was to examine the potential relationship between the structure of the dyes and the relative changes of the colour parameters of dyed fabric as a function of irradiation time. The dyed fabric samples were irradiated in Xenotest for periods ranging from 0 to 96 h. The colour parameters such as $P\%$ (percentage purity), L (lightness), C (chroma) and ΔE (defined by eqn (1)) of the irradiated samples at regular intervals of time and of nonirradiated samples were measured.

$$\Delta E = \sqrt{(\Delta a)^2 + (\Delta b)^2 + (\Delta L)^2} \quad (1)$$

where Δa and Δb are differences in chromaticity, and ΔL is the difference in lightness.

Attention was focused on the changes of the relative purity $P\%$, relative lightness L , relative chroma C and relative ΔE as a function of irradiation time. As a consequence, this led, according to the method reported by Savarino *et al.*,⁹ to the creation of several fading rate curves of the dyes on the fabric, described by the following equations:

$$\frac{P_0 - P_t}{P_0} = Bt + A \quad (2)$$

$$\frac{L_0 - L_t}{L_0} = B't + A' \quad (3)$$

$$\frac{C_0 - C_t}{C_0} = B''t + A'' \quad (4)$$

$$\frac{\Delta E_0 - \Delta E_t}{\Delta E_0} = B'''t + A''' \quad (5)$$

where P_0 , L_0 , C_0 and ΔE_0 are purity, lightness, chroma and colour difference, respectively, of nonirradiated samples; P_t , L_t , C_t and ΔE_t are purity, lightness, chroma and colour difference, respectively at time t ; t is the time of irradiation (h); B is the slope of the regression line ($1/h$); and A is the intercept of the regression line.

TABLE 2
Regression Data for P^0/t

Dye	$B \times 10^3$ (1/h)	$\lg B$	$A \times 10^3$	Correlation coefficient (r)
Ia	1.905	-2.72	15.36	0.96
Ib	2.870	-2.54	0.54	0.99
Ic	3.847	-2.41	21.56	0.99
Id	1.931	— ^a	1.28	0.92
Ie	1.830	— ^a	-1.16	0.96
If	2.095	— ^a	-4.00	0.98

^a Data not considered.

Parameters for the resultant correlations are presented in Tables 2–5 and confirm in each case an excellent linear relationship, with high values of the correlation coefficient r .

As obtained using eqns (2)–(5), the values of B , B' , B'' and B''' represent the fading rates of the dyes on the polyester fabric. Since it has been found in studies of the photochemical degradation of this groups of dyes in ethanolic solution, that substituents in the coupling components situated *ortho* to the azo linkage, affect the rate of fading (k_0), and that an excellent correlation between $\lg k_0$ and the σ_0 polar constants existed, a correlation of B , B' , B'' and B''' values with the electronic effect of the *ortho* substituents R_1 was attempted.

A satisfactory tendency towards a good linear relationship was achieved for slopes B and B' versus *ortho* polar substituent constants σ_0 . The results are given in Figs 1 and 2.

It should be noted, however, that a similar correlation between slopes B'' and B''' and *ortho* polar substituent constants σ_0 did not exist, and in this case the correlation coefficient values were insufficient to afford a lin-

TABLE 3
Regression Data for L/t

Dye	$B' \times 10^3$ (1/h)	$A' \times 10^3$	Correlation coefficient (r)
Ia	-1.450	3.73	-0.95
Ib	-2.310	2.40	-0.98
Ic	-3.070	15.56	-0.99
Id	-1.530	6.84	-0.99
Ie	-1.880	23.24	-0.97
If	-0.575	5.89	-0.97

TABLE 4
Regression Data for C/t

Dye	$B'' \times 10^3$ (1/h)	$A'' \times 10^3$	Correlation coefficient (r)
Ia	2.195	88.00	0.99
Ib	2.260	-4.56	0.99
Ic	3.640	-10.18	0.99
Id	2.740	-14.09	0.99
Ie	2.080	-13.60	0.96
If	2.430	5.53	0.97

ear relationship. It was also found that $\lg B$ gave a very good linear relationship with the electronic effects of the *ortho* substituents σ_0^{10} and this is demonstrated in Fig. 3. A similar relationship between $\lg B''$ and $\lg B'''$ versus σ_0 did not provide satisfactory results. It is also clear from Figs 1-3 that the slopes B or $\lg B$ and B' versus σ_0 are negative and positive, respectively; this indicates, in contrast to results obtained in ethanolic solution, an oxidative degradation of dyes I or polyester fabric. For dyes I correlation was made between the resulting slope B with the reciprocal of the lightfastness (Fig. 4), according to a suggestion made by Savarino *et al.*⁹ Least square analysis of the data gave an excellent relationship.

It is apparent from these results that the relative $P\%$ as a function of irradiation time was the only representative parameter which showed a good relationship versus σ_0 and the reciprocal of the lightfastness. Surprisingly, the relative changes of ΔE as a function of irradiation time (which is usually regarded as giving an impression of the total magnitude of the colour difference observed) did not show a satisfactory relationship either with lightfastness or its reciprocal.

TABLE 5
Regression Data for $\Delta E/t$

Dye	$B''' \times 10^3$ (1/h)	$A''' \times 10^3$	Correlation coefficient (r)
Ia	18.220	9.99	0.99
Ib	17.810	-11.59	0.99
Ic	25.280	-46.79	0.99
Id	21.300	-1 000.00	0.99
Ie	17.750	-64.00	0.98
If	19.860	45.00	0.99

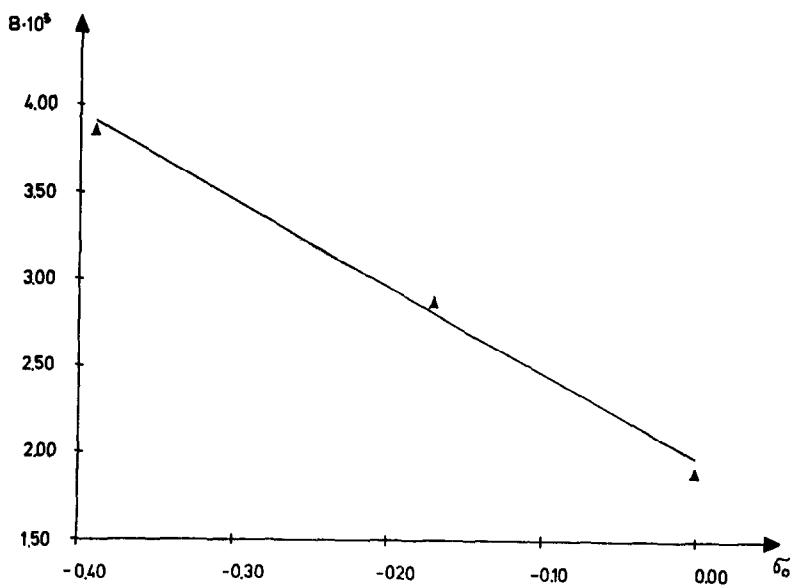


Fig. 1. Relationship between B (slope in eqn (2)) and the electronic effect of the substituent.

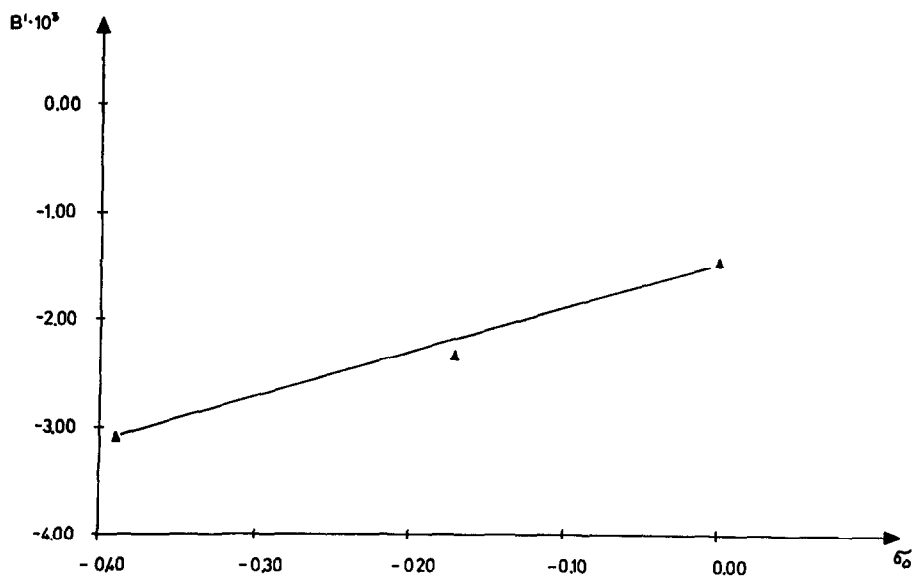


Fig. 2. Relationship between B' (slope in eqn (3)) and the electronic effect of the substituent.

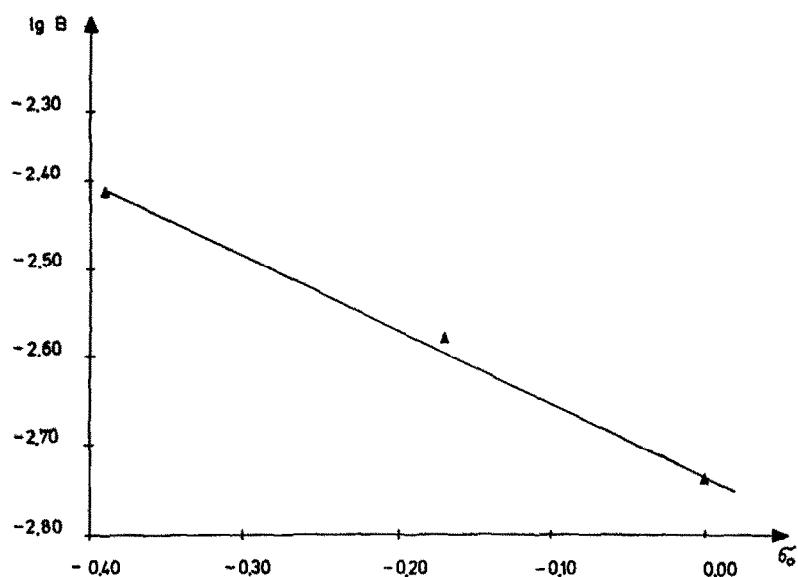


Fig. 3. Relationship between $\lg B$ (slope in eqn (2)) and the electronic effect of the substituent.

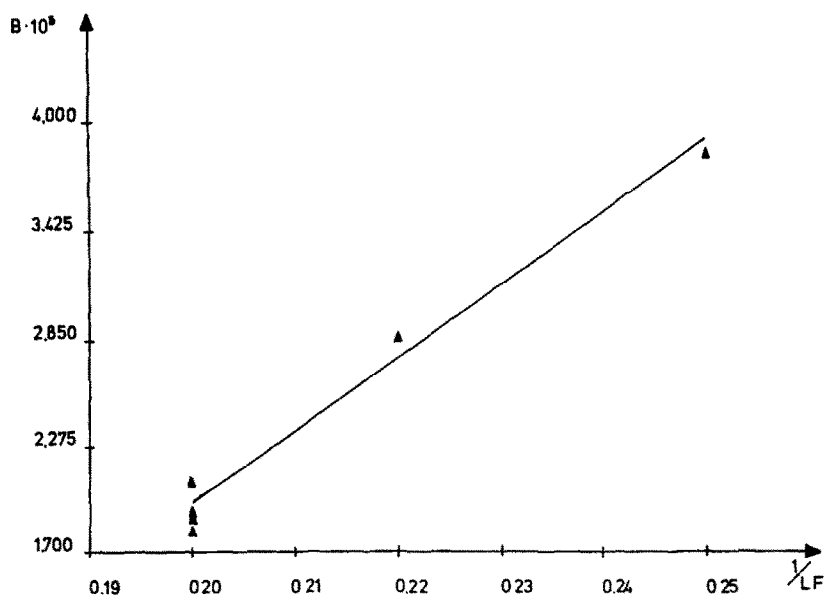


Fig. 4. Relationship between B (slope in eqn (2)) and the reciprocal lightfastness.

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