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The Photofading of Some 3-Amino-5-nitro(2,1)-benzisothiazole-based Dyes on Polyester

Jolanta Sokolowska-Gajda

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

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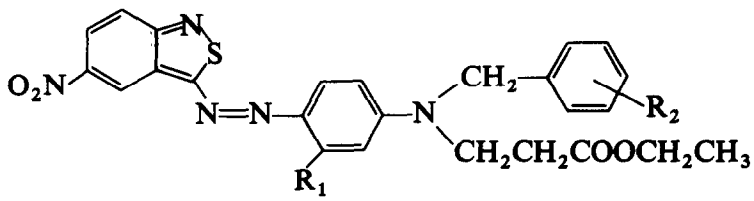
ABSTRACT

*A study of the photodegradation of some 3-amino-5-nitro(2,1)-benzisothiazole-based disperse dyes on polyester fabric is reported. A good correlation between the fading rate, measured from the changes of colour parameters (*P%, L*) as a function of irradiation time, and the electron-impact induced fragmentation of the dyes was found.*

1 INTRODUCTION

Light-stability is one of the most important properties of dyes and many efforts have been made to correlate it with chemical structure.[1,2] Emphasis has been placed on the influence of different substituents in the diazo components,[3] or of the structure of coupling components varied by different substituents in the aromatic ring[4] or by different terminal amino groups.[5] Some analogies between reactions occurring under the influence of heat or light and electron-impact induced fragmentation have been also observed.[6–8]

In the previous paper,[4] some kinetic studies of the photochemical degradation of 3-amino-5-nitro(2,1)-benzisothiazole-based dyes (**I**) in ethanolic solution were reported, and a good linear relation was found between the photofading rates k_0 and the σ_0 constants of the *ortho* phenyl substituents R_1, indicating a photooxidation mechanism.



I

Dye	R_1	R_2
Ia	H	H
Ib	CH_3	H
Ic	OCH_3	H
Id	H	*p*-CH_3
Ie	H	*p*-OCH_3
If	H	*m*-NO_2

It is well established that the mechanism of photodegradation of the dyes in solution is sometimes very different from the photolytic behaviour on textile substrate. This paper reports some kinetic measurements (*P*%, *L*, *C*, ΔE) on polyester fabric dyed with dyes I as a function of irradiation time and a correlation of the results with their electron-impact induced fragmentation. A relationship between photochemical stability and electron-impact fragmentation has been previously described by Mehta and Peters[9] for some aminoazobenzene disperse dyes.

2 EXPERIMENTAL

The azo dyes used in this study were prepared as previously described.[10,11] For the determination of colour parameters (*x*, *y*, *L*, *a*, *b*, *P*%, *C*, ΔE) 0·5% omf dyeings on polyester were used. Fabric samples were irradiated in a Xenotest apparatus (Hanau) and the kinetics followed by measuring the colour parameters *P*%, *L*, *C*, ΔE using a Bran New Color spectro-reflectometer. Lightfastness was determined according to Polish Standards, which correspond to British Standards.[12] The electron-impact mass spectra were recorded on an LKB 2091 spectrometer using an ionising energy of 70 eV.

3 RESULTS AND DISCUSSION

The colour of dyed polyester fabric can be presented in terms of tristimulus colorimetry. Values for the chromaticity coordinates (*x*, *y*), luminance

TABLE 1
Colour Parameters of the Dyed Polyester Fabric

Dye	*Chromaticity coordinates*		*Luminance factor* Y	*Helmholtz coordinates*			*CIELAB coordinates*		
	x	y	*(%)*	λ_D	λ_C	P%	L	a	b
Ia	0·21	0·17	6·23	470	572	55·05	29·99	15·66	−37·64
Ib	0·19	0·16	5·15	470	571	61·92	27·15	12·19	−39·81
Ic	0·19	0·17	4·33	473	573	66·48	24·75	10·44	−35·01
Id	0·20	0·15	3·15	467	572	56·36	20·65	17·16	−35·61
Ie	0·19	0·18	3·76	467	571	61·61	22·85	16·83	−37·44
If	0·23	0·18	4·75	445	568	46·60	26·01	20·59	−31·60

factor (Y), Helmholtz coordinates (λ_D, λ_C, $P\%$) and the position in CIELAB colour solid are reported in Table 1.

The dyed fabric samples were irradiated in the Xenotest for 96 h and the relative values of purity ($\Delta P/P$), lightness ($\Delta L/L$), chroma ($\Delta C/C$) and colour difference ($\Delta E_0 - \Delta E_t/\Delta E_0$) were measured as function of irradiation time. The fading rate curves for the dyes on the fabric may be described by the following equations:

$$\frac{P_0 - P_t}{P_0} = Bt + A \qquad (1)^{13}$$

$$\frac{L_0 - L_t}{L_0} = B't + A' \qquad (2)$$

$$\frac{C_0 - C_t}{C_0} = B''t + A'' \qquad (3)$$

$$\frac{\Delta E_0 - \Delta E_t}{\Delta E_0} = B'''t + A''' \qquad (4)$$

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

Parameters of the resultant correlations are shown in Tables 2–5 and show a very good linear relationship.

An attempt was also made to correlate the obtained values B–B''' (which are the measure of the fading rate of the dye on the fabric) with the ratio of the relative abundance of the daughter ions $\mathbf{I}_{179}/\mathbf{I}_{207}$ (*m/e* 179,

TABLE 2
Regression Data for $P\%/t$

Dye	B$\times 10^3$ *(1/h)*	A$\times 10^3$	*Correlation coefficient* (r)
Ia	3·51	−5·45	0·9891
Ib	4·47	6·35	0·9831
Ic	3·82	25·92	0·9840
Id	4·09	−13·10	0·9960
Ie	4·74	−21·34	0·9951
If	4·85	6·14	0·9915

TABLE 3
Regression Data for L/t

Dye	B'$\times 10^3$ *(1/h)*	A'$\times 10^3$	*Correlation coefficient* (r)
Ia	−2·96	8·59	−0·9856
Ib	−3·81	6·79	−0·9878
Ic	−3·88	41·20	−0·9525
Id	−3·58	42·50	−0·9476
Ie	−4·00	32·04	−0·9697
If	−4·98	9·98	−0·9985

TABLE 4
Regression Data for C/t

Dye	B"$\times 10^3$ *(1/h)*	A"$\times 10^3$	*Correlation coefficient* (r)
Ia	3·46	−2·82	0·9891
Ib	4·41	25·20	0·9785
Ic	3·24	20·28	0·9803
Id	4·46	−16·00	0·9857
Ie	4·64	−0·75	0·9999
If	4·18	11·99	0·9872

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

Dye	$B'''\times10^3$ *(1/h)*	$A'''\times10^3$	*Correlation coefficient (r)*
Ia	16·92	−95·90	0·9893
Ib	21·67	12·34	0·9807
Ic	15·87	28·00	0·9859
Id	19·42	−20·00	0·9897
Ie	21·32	−17·60	0·9990
If	20·40	27·40	0·9941

m/e 207) arising from the cleavage of the C—N bond of the azo group (Table 6).

As shown in Table 6, the lightfastness of dyes **I** on polyester fabric is very similar, and for this reason the values $B-B'''$ appeared to be more useful for correlation of the photostability of the dyes with their electron-impact induced fragmentation.

Using least square analysis of the data, it was found that only in the case of the slope B and B' were the resulting correlations represented by a straight line (Figs 1 and 2), correlation coefficients satisfactorily confirming the linearity (r = 0·93, r = 0·95 for B and B', respectively). As was reported recently for aminoazobenzene compounds,[14] for this group

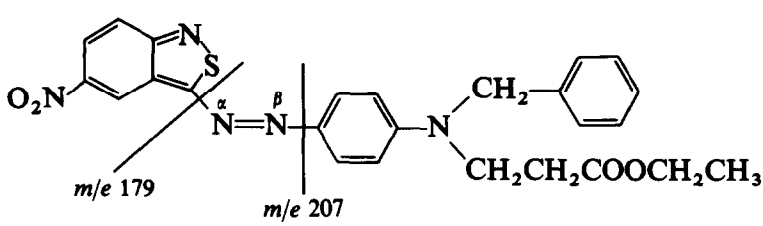


TABLE 6
Lightfastness (LF) and Mass Spectra for Dyes **I**

Dye	*LF of 0·5% dyeings*	*1/LF*	I_{179}/I_{207}
Ia	6	0·1616	0·697
Ib	5	0·2000	0·564
Ic	5–6	0·1818	0·593
Id	5–6	0·1818	0·580
Ie	5	0·2000	0·497
If	5	0·2000	0·390

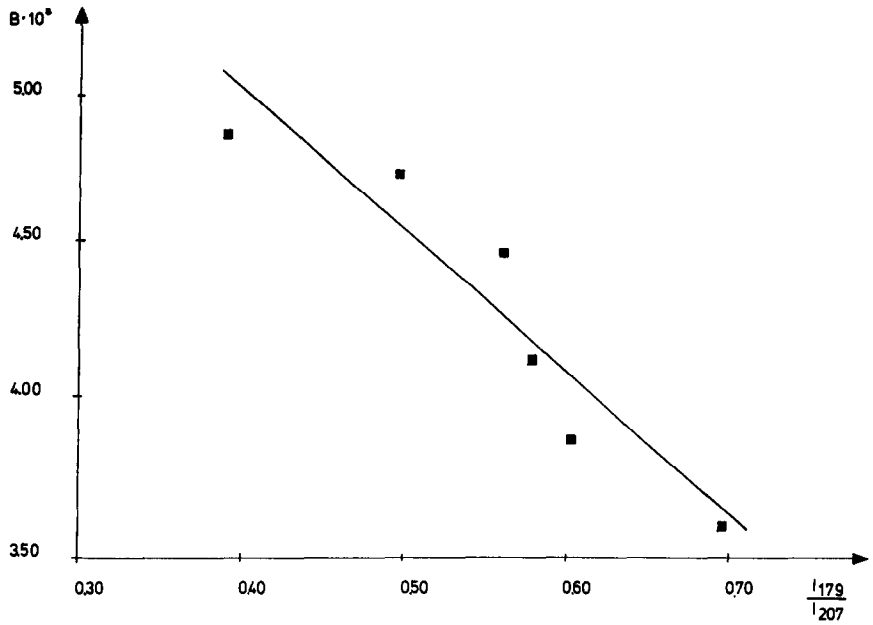


Fig. 1. Relationship between B (slope in eqn (1)) and ratio of relative abundance of fragment ions m/e 179 (I_{179}) and m/e 207 (I_{207}).

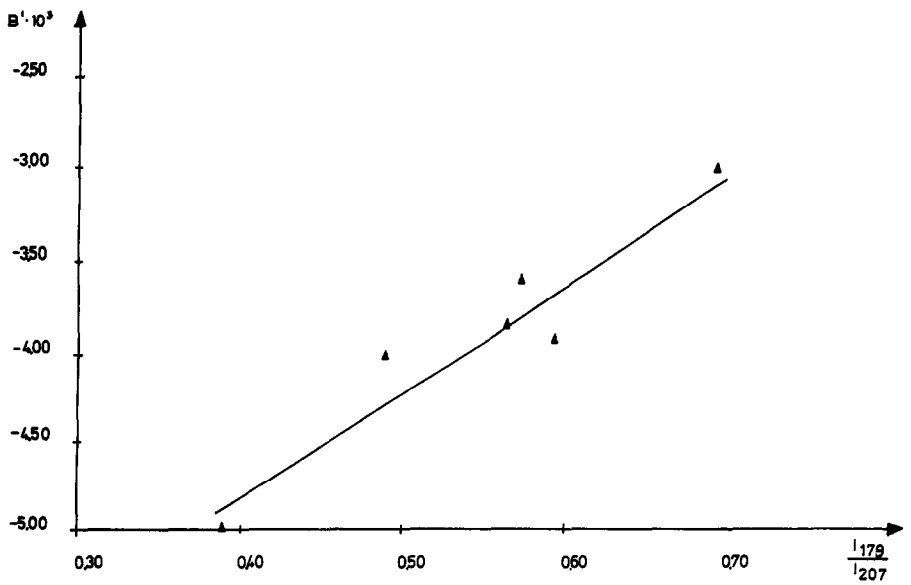


Fig. 2. Relationship between B' (slope in eqn (1)) and ratio of relative abundance of fragment ions m/e 179 (I_{179}) and m/e 207 (I_{207}).

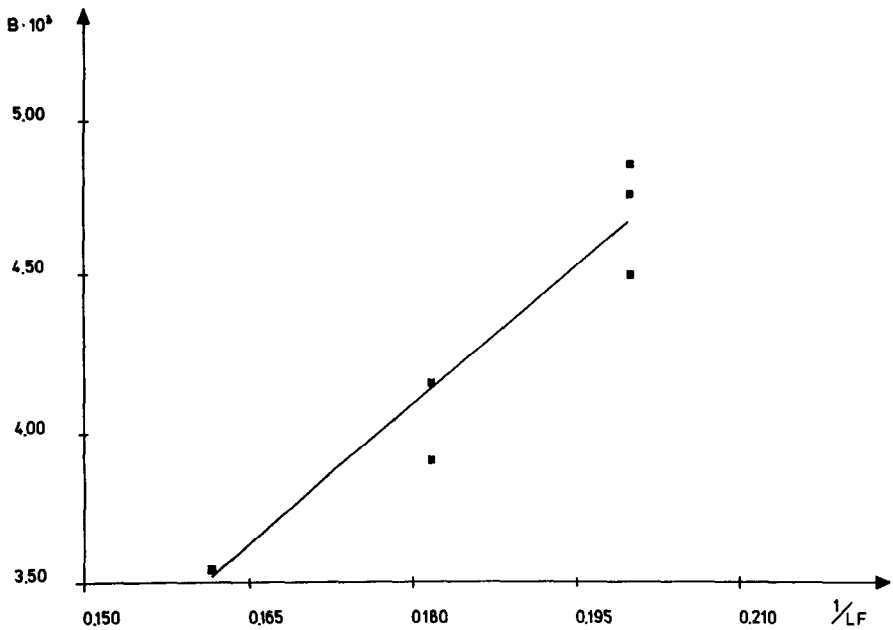


Fig. 3. Relationship between B (slope in eqn (1)) and reciprocal of lightfastness.

of dyes also a fair correlation (r = 0·94) between the slope B and the reciprocal of the lightfastness was achieved (Fig. 3).

It is thus apparent from previous[4] and present investigations that the photodegradation of the same dye depends on experimental conditions and is sometimes unpredictable. Although for 3-amino-5-nitro(2,1)-benziso-thiazole-based dyes[14] an oxidative mechanism of photodegradation in ethanolic solution was found, the results obtained on polyester fabric clearly indicate a strong relationship between their lightfastness and electron-impact induced fragmentation.

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