

Role of thermal reactions in photofading of disperse azo dyes on nylon

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ABSTRACT

Disperse azo dyes used for PET especially having nitro groups possess very low light fastness (LF) on nylon 6 (PA). The reason why they have such LF on PA was studied. The photofading of disperse dyes: phenylazo-anilines, -pyridones, -indoles and -quinolone, on PA fabric by exposing to a carbon arc in air was analyzed experimentally by the K/S (Kubelka-Munk parameter) spectra from the reflection spectra within the wavelength range between 250-700 nm. The initial rates of fading on PA correspond to the sum of azo scission (AS)(decrease in the absorption) and nitrosation (NS) of nitro groups (spectral shift). The azo dyes with nitro groups on PA generate hydrazinyl (from azo groups) and hydroxynitrosyl (HNS) radicals (from nitro groups) of dyes by hydrogen abstraction. By the thermal reactions of hydrazinyl radicals with the same or different kinds of monohydrogenated (MHN) dye radicals they undergo AS even when dyes have no nitro groups, while the NS of nitro groups occurs by the reaction of HNS radicals with MHN radicals depending upon their concentrations. The differences in the fading behavior among individual azo dyes can be explained by the energetic restriction of thermal reaction routes of MHN radicals calculating $\Delta_f H^0(\text{gas})$ for reactants, intermediates and products by the PM5 method.

1. INTRODUCTION

Upon exposing disperse dyes on poly(ethylene terephthalate) (PET) to a carbon arc in air, the dyes suffer photo-oxidative fading, while upon exposing on nylon 6 (PA), they suffer photo-reductive fading. It has been known that in general, disperse dyes

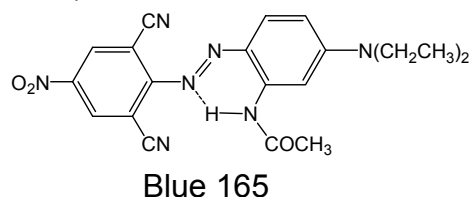
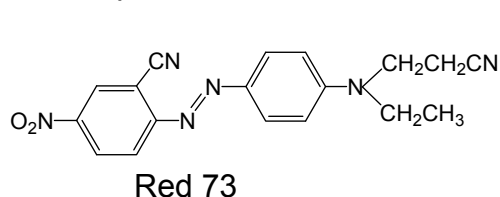
on PET give the highest lightfastness (LF), whilst those on PA give the lowest LF. For example, C.I. Disperse Blue 165 used is a typical azo dye, whose LF is 6 rating on PET and 1 rating on PA. The former decomposition is attributed to the dediazotization via ene and/or [2+2] cycloaddition of $^1\text{O}_2$ toward azo chromophore, while the latter one to the thermal disproportionation reaction of hydrazinyl radicals (as hydrogen acceptor) with monohydrogenated (MHN) azo dye radicals and/or intramolecular hydrogen transfer resulting in azo scission (AS) reaction and to the nitrosation (NS) of nitro groups via the hydrogen abstraction of nitro groups.

In the present study, phenylazo-anilines and phenylazo-indoles: disperse dyes with wide LF ratings are selected and their fading behaviors on PA are examined measuring the K/S spectra of exposed PA fabrics. From the initial rates (K_{PA}) of fading, the fading behaviors of azo dyes are analyzed in terms of some rate constants of basic thermal reactions between MHN radicals in a kinetic equation describing AS and NS.

2. EXPERIMENTAL (Dyes used)

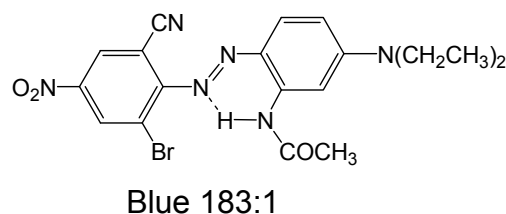
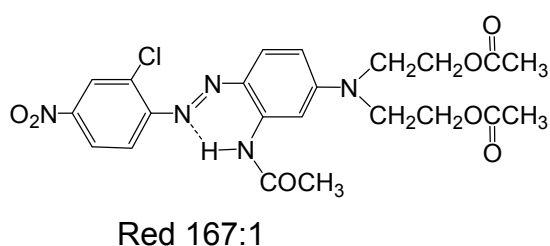
1) C.I. Disperse Red 73, CI 11116, (Red 73), AT

2) C.I. Disperse Blue 165, CI 11077, (Blue 165), AT



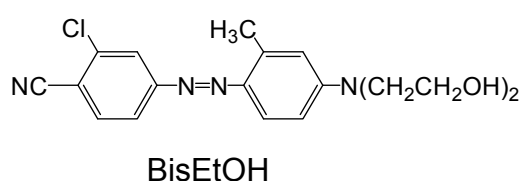
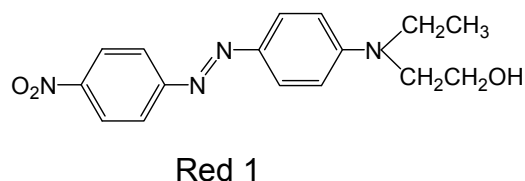
3) C.I. Disperse Red 167:1, C.I. 11338:1, (Red 167:1), AT

4) C.I. Disperse Blue 183:1, C.I. 11078:1 (Blue 183:1), AT



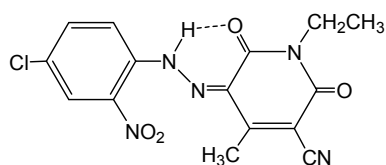
5) C.I. Disperse Red 1, C.I. 11110, (Red 1), AT

6) A NN-bisethanolaniline dye, BisEtOH, AT

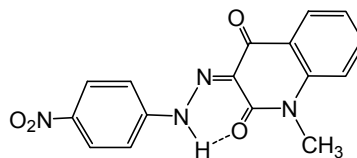


7) C.I. Disperse Yellow 211, CI 12755, (Yellow 211), HT

8) A phenylazo-quinolone dye (Quinolone), HT



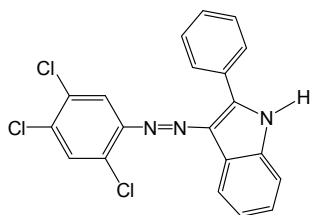
Yellow 211



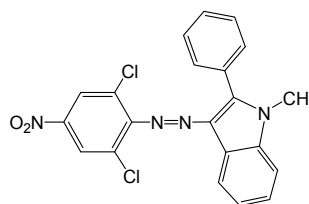
Quinolone

9) An azo dye from phenylindole (Phenylind)

10) An azo dye: dichloronitrophenylazo-phenylindole (Nitrophenylind)



Phenylind



Nitrophenylind

The numbers of atomic sites are listed below Table 2, which are different from those of the usual chemical nomenclature in order to use the common numbers for the corresponding sites.

3. RESULTS AND DISCUSSION

3.1 Fading on nylon substrate

The off-tone fading of Blue 165 and Red 73 on PA is illustrated in Figs. 1 and 2 as the time profiles of the K/S spectra of samples exposed in air. The absorption at λ_{\max} is decreased steadily with time of exposure and a photo-reduced product, a dye with nitroso group for nitro group, is generated. In Fig. 1, the difference spectra of (2) and (3) from which the corresponding spectra of the original dye were subtracted are shown, indicating that the amounts of generation at exposure of 3 and 10 h are nearly same each other. The difference spectra of Red 73 in Fig. 2 indicate that the amounts of generation increased with time of exposure but did not increase after 10 h by long exposure for 40 h. The NS of nitro groups occurs at the initial time of exposure and the dyes with nitroso groups possess considerably high LF.

The two figures suggest that the overlap in the K/S spectra between the dyes with nitroso groups and the original dyes was small, although the overlap certainly occurred and that the effect of the overlap on the K_{PA} values is negligible.

In order to examine the fading behaviors of ten azo dyes by the reflectance spectra of the original and exposed dyed fabrics, the initial slope of fading (K_{PA}) estimated at the λ_{\max} and the λ_{\max} of the product are listed in Table 1. The $(K_{PA}/K_{PET})(k_i/k_{R73})$ values (fading ratio) were calculated to compare the contribution of f_i values to the K_{PA} values.

The factor of (k_i/k_{R73}) was employed to eliminate the effects of $k_{0,i}$ from the K_{PET} (the initial slope of fading on PET) values [1,2]. The K_{PA} values are 0.1 - 7 times as large as those on PET, while the fading ratios are 0.3 - 130 times larger than those on PET. Although the range of f_i values for the dyes examined is narrow, the effect of f_i values to the K_{PA} values can be confirmed in a series of these studies including the present study. (The wide range of fading ratio may be semi-quantitatively explained in terms of five terms in the right hand side (rhs) of Eq. (1); or multiple reaction route, as mentioned below.)

3.2 Reaction kinetics of AS and NS of nitro groups

The K_{PA} values at the λ_{max} correspond to the sum of AS (decrease in the absorption) and NS of nitro groups (shift in the absorption) as was confirmed in Figs. 1 and 2. The excited states of azo dyes with nitro groups abstract hydrogen to generate hydrazinyl (from azo groups) and hydroxynitrosyl (HNS) radicals (from nitro groups). The AS via the thermal reactions between the dye radicals was reported by van Beek et al. [3-7]. The hydrazinyl radicals cause the AS of hydrogen acceptor (HA), while the HNS radicals the NS of nitro groups. These reactions are illustrated in Scheme 1. When N7- or N8-radicals (as the hydrogen acceptor) abstract hydrogen at the N8- or N7-site of next highest reactivity, disproportionation reaction occurs resulting in the AS accompanied with the generation of the corresponding amines and iminyl-biradicals, depending upon whether or not the reaction route is energetically favorable (cf. Tables 2-4). Assuming that a homogeneous reaction system of dye fading in PA fabric holds in the initial time of exposure, the kinetic equation of the photo-reduction via disproportionation between MHS radicals and the NS of HNS radicals can be written by:

$$-\frac{d[D]}{dt} = k_{AS}^{N7} [N7][MHN] + k_{AS}^{N8} [N8][MHN] + k_{NS}^{HNS} [HNS][MHN] + k_{IM}^{N7} [N7] + k_{IM}^{N8} [N8] \quad (1)$$

D is dye; HNS is HNS radical from nitro group; brackets denote the concentration; k_A^{Rad} ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) is the second-order rate constant of disproportionation between MHN radicals where subscript denotes the type of reaction: AS and NS and superscript the hydrogen acceptor (reactant): N7-, N8- and HNS radicals. Their values are thermochemically estimated in terms of the heat released. [MHN] is generated so as to be proportional to the quantum yields of the T_1 for the azo and nitro groups but just after the generation rearrangement occurs to attain thermal equilibration. [N7], [N8] and [HNS] are generated from T_1 state of azo and nitro groups, but change depending upon their stability; k_{IM}^{N7} and k_{IM}^{N8} (s^{-1}) are the first-order rate constants of intramolecular hydrogen abstraction of N7- and N8-radicals, respectively. Since the k_{NS}^{HNS} val-

ues for all the dyes are regarded as large due to the positive heat released, no difference may exist between dyes thermochemically. No generation of nitrogen dihydroxide groups are produced due to consumption of HNS radicals by the reaction with N7- and/or N8-hydrazinyl radicals of higher concentrations [3-7].

Only the corresponding radical acts as the hydrogen acceptor, while the total MHN radical isomers as the hydrogen donor. Here, it is assumed that the total rate of fading is the sum of five terms in the rhs of Eq. (1). Applying the same procedure of the thermochemical analyses to the AS and the NS of nitro groups in terms of $\Delta_f H^0(\text{gas})$ for the reactants, intermediates and products, what reaction routes of AS and NS of nitro groups are allowed is examined. The energetics for the reactions of N7- and N8-radicals as hydrogen acceptor is listed in Tables 2 and 3 (Analyses of k_{AS}^{N7} and k_{AS}^{N8} , respectively), as two examples and the analyses of all the rate parameters are summarized in Table 4.

3.3 Thermochemical analyses of reaction rate constants

3.3.1 Blue 165 and Red 167:1

As explained above, the photo-reductive fading is described by the sum of five terms in the rhs of Eq. (1). The order of k_{AS}^{N7} values for N7-radicals for ten dyes as hydrogen acceptor is illustrated by the number in parentheses, while the k_{AS}^{N8} values of N8-radicals are exceptional for two dyes and are negligible for the other dyes. The k_{AS}^{N7} and k_{IM}^{N7} values for Red 167:1 are largest among ten dyes examined, although the reaction ratio is the next largest. The contribution of N8-radicals to the reaction ratio may be very small, since the k_{AS}^{N8} and k_{IM}^{N8} values are very small. The largest reaction ratio of Blue 165 is attributed to the largest generation of hydrazinyl and HNS radicals and large k_{AS}^{N7} value. Since the generation of both the radicals for Red 167:1 is considerably smaller than that of Blue 165, the reaction ratio of Red 167:1 becomes the next largest. The energetics of NS indicates that the k_{NS}^{HNS} values for all the dyes with nitro groups are very large. But Blue 165 exhibits marked NS of nitro groups, while Red 167:1 small one. Since the small generation of HNS radicals for Red 167:1 is consumed by the reaction with hydrazinyl radicals resulting in small NS, while the former large generation for Blue 165 is attributed to the very large generation of HNS radicals resulting in large NS due to the activation of two cyano groups.

3.3.2 Blue 183:1, Red 73 and Red 1

Blue 183:1 and Red 73 possess the thirdly largest k_{AS}^{N7} value and the smallest k_{AS}^{N7} value, respectively, as the dominant factor in Eq. (1), although the stability of N7-radicals is lower than that of N8-radicals. This fact explains the order of fading ra-

tios: Blue 183:1 > Red 73.

Red 1 exhibited a fading ratio smaller than those of above two dyes, which is attributed to the smallest k_{AS}^{N7} value and the very small generation of HNS radicals as the dominant factor.

3.3.3 Nitrophenylind and Phenylind

These dyes are phenylazoindoles: the former contains nitro group and possesses excellent LF on PET. On PA, however, the former exhibit off-tone fading and have a little larger k_{AS}^{N7} value than that of the latter as the predominant factor in Eq. (1). Nitro groups in Nitrophenylind may generate HNS radical and activate the azo chromophore to increase the generation of hydrazinyl radicals resulting in the larger values of the former dye.

3.3.4 Effect of nitro groups

Azo dyes with no nitro groups exhibited the smallest and the next fading ratios, respectively, and are listed in Table 1. It is evident that nitro groups increase the fading ratios on PA. Among dyes with nitro groups, *o,o'*-dicyano groups may activate the action of nitro groups following by *o*-cyano group.

These nitro groups cause the increased generation of MHN radicals. As explained by some examples, the thermal reactions between MHN radicals controlled the rates of reaction.

4. REFERENCES

1. Okada Y, Hihara T, Morita Z. Dyes and Pigments, In press. (Catalytic fading of pyridone dyes).
2. Okada Y, Hihara T, Morita Z. Dyes and Pigments, Accepted (Photofading azo dyes on PET).
3. van Beek HCA et al. Journal of the Society of Dyers and Colourists, 1971; 87(3): 87-92.
4. van Beek HCA et al. Journal of the Society of Dyers and Colourists, 1971; 87(10): 342-8.
5. van Beek HCA et al. Journal of the Society of Dyers and Colourists, 1973; 89(11): 389-96.
6. Heijkoop G, van Beek HCA. Recueil Travaux Chimiques des Pays-Bas, 1976; 95(1): 6-10.
7. Heijkoop G, van Beek HCA. Recueil Travaux Chimiques des Pays-Bas, 1977; 96(2): 83-5.
8. Okada Y, Hihara T, Morita Z. Dyes and Pigments, submitted (Photoreduction on PA).

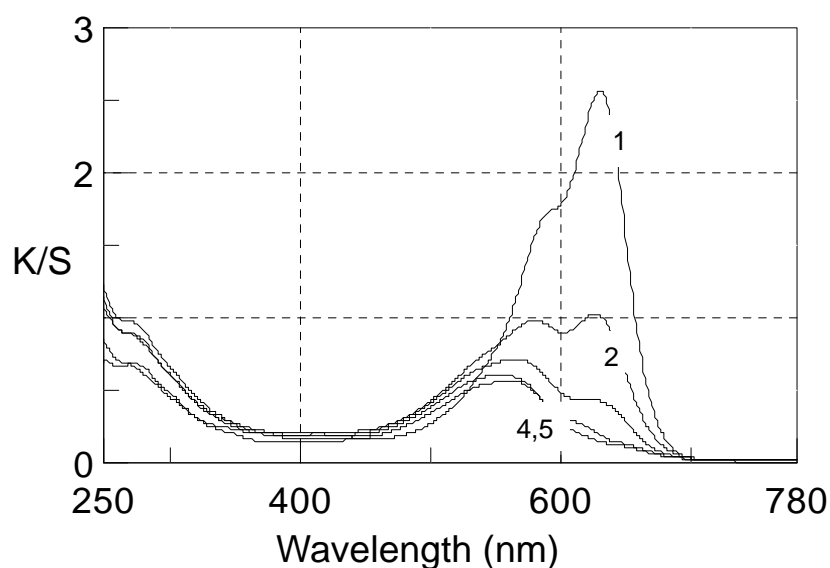


Fig. 1. K/S spectra of Blue 165 on PA exposed to a carbon arc for: (1) 0 h (Original); (2) 3 h; (3) 10 h; (4,5) K/S spectra of the dyes with nitroso groups: Difference spectra of (2) and (3) from which the corresponding spectra of original dye were subtracted. (Spectrum 3 is illustrated in order between 2 and 4,5.)

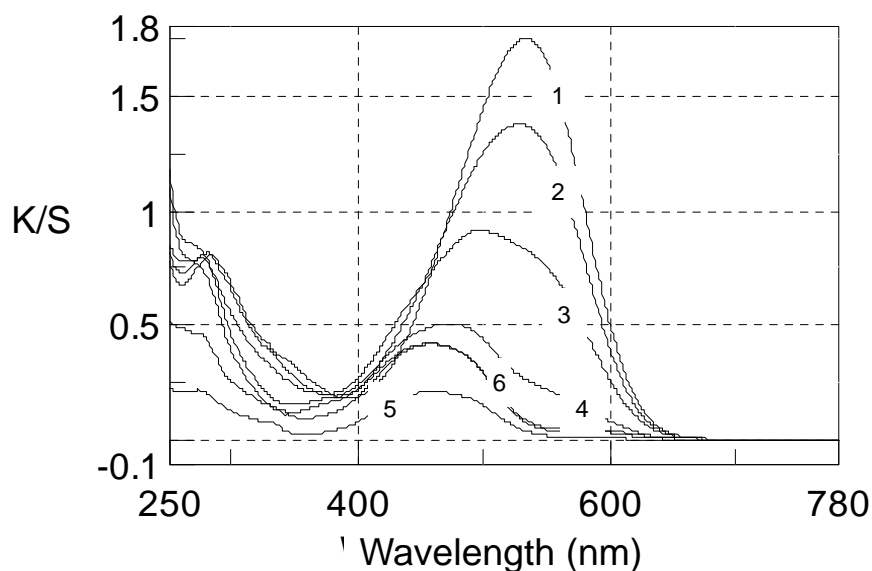
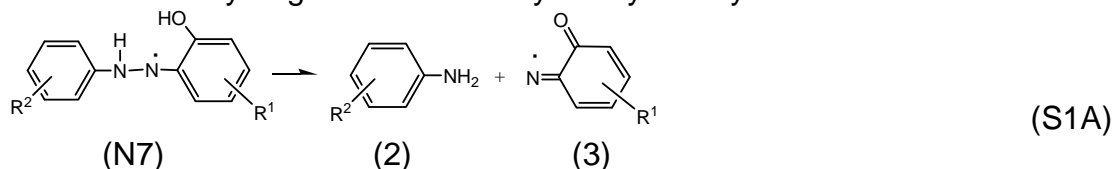


Fig. 2. K/S spectra of Red 73 on PA exposed to a carbon arc for: (1) 0 h (Original); (2) 3 h; (3) 10 h; (4) 40 h; (5) and (6): Difference spectra of (2) and (3), respectively, from which the corresponding spectra of original dye were subtracted. (Difference spectrum corresponding to (4) coincided completely with that of (3).)

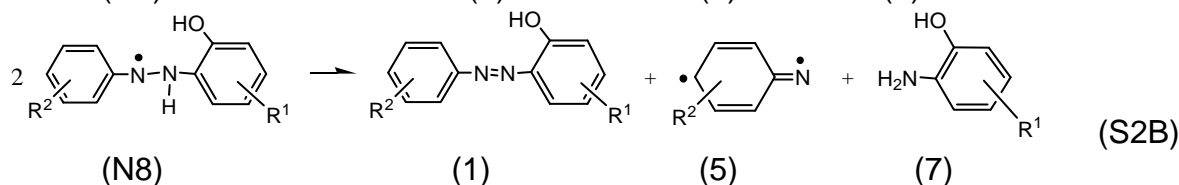
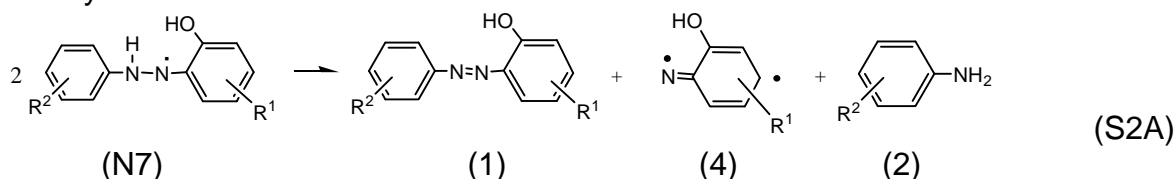
Scheme 1. Photoreduction of azo dyes via thermal disproportionation reaction between MHN radicals generated by hydrogen abstraction from substrate

1. Azo scission of azo dyes via thermal reaction of hydrazinyl radicals [3-7]

1.1 Intramolecular hydrogen abstraction by N7-hydrazinyl radical

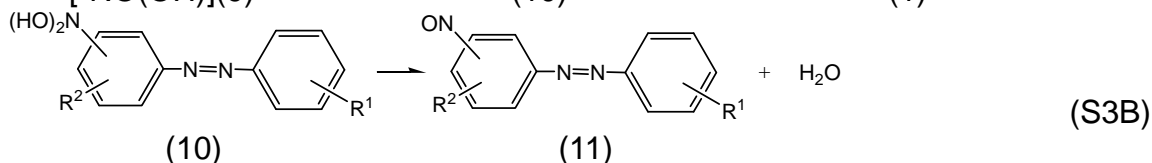
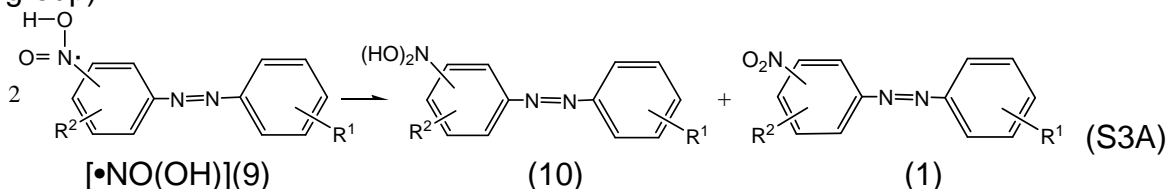


1.2 Thermal disproportionation reaction between N7- and N8-hydrazinyl radicals of azo dye and MHN radicals



2. Nitrosation of nitro group in azo dyes

2.1 Thermal disproportionation reaction between HNS radicals (Formation of nitroso group)



3. Thermal reaction between hydrazinyl and HNS radicals.

3.1 Reaction of hydrazinyl radical as hydrogen acceptor and HNS radicals as hydrogen donor (Promotion of azo scission)

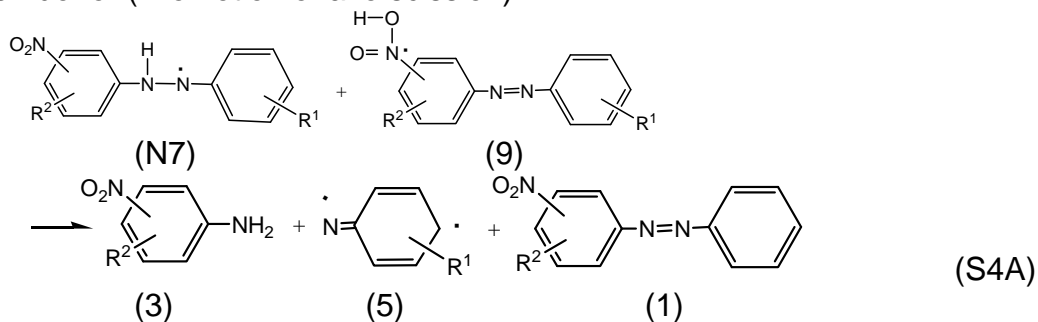


Table 1. Analyses of fading behaviors of PA fabric dyed with azo dyes exposed to a carbon arc by K/S spectra.

Dyes	λ_{\max} (nm)	Fading on PA			$\frac{K_{PA}}{K_{PET}}$	$\left(\frac{K_{PA}}{K_{PET}}\right)\left(\frac{k_i}{k_{R73}}\right)$	λ_{\max} (nm) of products detected
		LF	K_{PA}^{*1}	λ_{\max} shift			
Blue 165	629	1	7.50	blue	126	148	550
Red 167:1	525	2	0.777 ₅	blue	57.7 ₂	116.2	–
Blue 183:1	627	1	3.34 ₆	blue	72.9 ₇	76.4	450
Yellow 211	452	1	5.39	s.b. ^{*2}	47.1	48.1	–
Red 73	533	1	2.00	blue	48.1	48.1	460
Nitrophenylind	477	3	0.396 ₄	blue	12.1 ₃	44.1	430
Quinolone	430	1	4.97	red	14.4	31.4	495
Red 1	507	4	0.241 ₅	no	1.30 ₃	4.55	–
Phenylind	429	6-7	0.127 ₄	no	0.72 ₅	4.13	–
BisEtOH	500	5	0.075 ₀	no	0.28 ₃	0.78	–

*1: Initial slope of fading on PA, negative slope of $\ln(K/S)_t/(K/S)_0$ plot against the time of exposure ($\times 10^{-5} \text{ s}^{-1}$). *2: s.b. = slightly blue

Table 2. Feasibility analyses of disproportionation reaction route of N7-hydrazinyl radicals as hydrogen acceptor resulting in azo scission in terms of $\Delta_f H^0(\text{gas})$ (kcal mol⁻¹) for the corresponding reactants and products calculated by the PM5 method.

Azo scission from N7-hydrazinyl radical as hydrogen acceptor [cf. Eq. (S2A)]						
(N7)+(N8)→original dye (1)+diazo component (2)+coupling-iminyl-N7C4-biradical ^{*1} (4) + heat released (6)						
	(N7)	(N8)	(1)	(2)	(4)	(6)
Blue 165	108.8	104.6	101.2	78.6	13.4	20.2
Red 167:1	-132.3	-131.5	-162.5	6.0	-157.3	50.0
Blue 183:1	82.4	78.9	53.8	50.6	47.2	9.7
Yellow 211	20.0	18.0	14.6	8.8	23.4	-8.8
Red 73	150.3	148.1	145.2	44.8	139.1	-30.7
Nitrophenylind	128.7	130.0	125.6	0.4	140.9	-8.2
Quinolone ^{*2}	18.3	23.0	15.0	12.3	10.3	3.7
Red 1	45.4	42.9	39.7	12.3	66.8	-30.5
Phenylind	118.9	119.8	117.0	-1.0	136.9	-14.2
BisEtOH	28.4	26.4	22.5	42.8	19.4	-29.9

*1: iminyl (N7C4)-biradical of coupling component. (Nitrene N7-biradicals have the same energies.)

*2: For Quinolone, read (N11) for (N7) and (N12) for (N8), respectively.

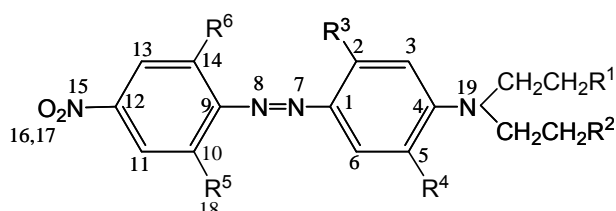


Table 3. Feasibility analyses of disproportionation reaction route of N8-hydrazinyl radicals as hydrogen acceptor resulting in azo scission in terms of $\Delta_f H^0(\text{gas})$ (kcal mol⁻¹) for the corresponding reactants and products using the PM5 method

Azo scission from N8-hydrazinyl radical as hydrogen acceptor [cf. Eq. (S2B)].						
(N8)+(N7)→original dye (1)+amino-coupling component (7)+diazo-iminyl biradical ^{*1} (5) + Heat released (6)						
	(N8)	(N7)	(1)	(7)	(5)	(6)
Blue 165	104.6	108.8	101.2	-32.5	198.5	-53.8
Red 167:1	-131.5	-132.3	-162.5	-192.5	117.7	-26.5
Blue 183:1	78.9	82.4	53.8	-30.0	168.1	-30.6
Yellow 211	18.0	20.0	14.6	-47.6	116.7	-45.7
Red 73	148.1	150.3	145.2	46.5	161.9	-55.2
Nitrophenylind	130.0	128.7	125.6	68.6	111.0	-46.5
Quinolone ^{*2}	23.0	18.3	15.0	-54.6	125.1	-44.2
Red 1	42.9	45.4	39.7	-25.0	125.1	-51.5
Phenylind	119.8	118.9	117.0	65.2	101.6	-45.1
BisEtOH	26.4	28.4	22.5	-71.8	151.2	-47.1

*1: iminyl (N8N10, N8N12 or N8C14)-biradical of diazo component. (Nitrene N8-biradicals have the same energies.)

*2: Read N11- and N12-radicals for N7- and N8-radicals, respectively.

Table 4. Analyses of fading behaviors of PA fabric dyed with azo dyes exposed to a carbon arc by K/S spectra^{*2,3}.

Dyes	Fading ratio ^{*1}	AS via disproportionation					Intramolecular AS		NS of nitro groups	
		k_{AS}^{N7} [N7][MHN]			k_{AS}^{N8} [N8][MHN]		k_{IM}^{N7}	k_{IM}^{N8}	Obs. ^{*4}	k_{NS}^{HNS}
		k_{AS}^{N7}	[N7]	[MHN]	k_{AS}^{N8}	[N8]				
Blue 165	148	(9)	large	v. L.	zero	–	(2)	zero	v. L.	v. L.
Red 167:1	116.2	(10)	large	large	v. S.	small	(5)	small	small	v. L.
Blue 183:1	76.4	(8)	v. S.	large	v. S.	small	(1)	zero	v. L.	v. L.
Yellow 211	48.1	(5)	small	large	zero	–	(4)	zero	small	v. L.
Red 73	48.1	(1)	small	large	zero	–	–	–	v. L.	v. L.
Nitrophenylind	44.1	(6)	large	large	zero	–	–	–	large	v. L.
Quinolone	31.4	(7)	large	large	zero	–	(3)	zero	large	v. L.
Red 1	4.55	(1)	v. S.	small	zero	–	–	zero	no	v. L.
Phenylind	4.13	(4)	large	small	zero	–	–	zero	no	–
BisEtOH	0.78	(1)	small	small	zero	–	–	zero	no	–

*1: Fading ratio = $(K_{PA}/K_{PET})(k_i/k_{R73})$

*2: Rate constants: small > zero (negligible). The larger the number, the higher the rates. (When the heat released (heat of reaction) is positively larger, the reaction occurs more easily. cf. Tables 2 and 3)

*3: Concentration expressed as the population ratio of total concentration: v. L. (very large) > large > small > v. S. (very small).

*4: Observation (cf. Figs. 1 and 2).