Azomethine dyes revisited. Photobleaching of azomethine dyes under photoreducing conditions

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Received (in Cambridge, UK) 27th April 1999, Accepted 20th July 1999

This paper presents the results of a study on the bleaching process of azomethine dyes (AMDs) during their irradiation in the presence of an electron donor *N*-phenylglycine (NPG). The bleaching process and singlet oxygen formation for the dyes under study occurred with very low quantum yields. Experimental results showed that the bleaching of azomethine dyes may be due to both singlet and triplet states. The prominence of the triplet state was suggested by an analysis of double reciprocal plots for bleaching quantum yields and [NPG]. Additional support for this mechanism was given by results from laser flash experiments with a cyclized form of the dye. In these experiments, a transient optical absorption was attributed to a triplet state, and this state was quenched by NPG with a rate constant of 1.2×10^7 M^{-1} s^{-1}. A similar experiment performed for a branched dye shows a broad, weak transient absorption which may also indicate a small amount of triplet-state formation. Changes in the dye structure affected the rate of photobleaching. The introduction of heavy atoms into a dye molecule only slightly increased the color-loss efficiency. The decrease or restriction of the freedom of the phenyl-group rotation did not increase the rate of the bleaching process. Significant influence of the azomethine dye structure on photobleaching rates was observed only when there was a strong electron withdrawing group in the R^2 position. The most significant increase of the bleaching rate was observed when the branching of the dye was limited, especially when the rotation of substituents around the C=N bond was prevented by structural constraints.

1. Introduction

Pyrazolone azomethine purple dyes (PAD) are commonly used in color photography as one of the color-picture forming dyes.[1] Using standard organic chemistry, one can obtain in solution PADs displaying a wide range of color, starting from orange to green.[2–6] In an earlier paper,[7] we have shown that purple PADs can photoinitiate free-radical polymerization *via* a photoinduced intermolecular electron transfer process. From the point of view of photographic technology or stereolithography, one of the most important parameters of a dye is its proclivity to be bleached by visible light.[8] Through the years, many examples of bleaching caused by UV irradiation in the presence of suitable sensitizers or in proton-donating solvents have been described in the literature.[9–13] In this paper we present the results of a study on the bleaching of azomethine dyes during the irradiation of the dyes in the presence of *N*-phenylglycine which is known to be a good electron donor.

2. Experimental

Substrates used for the preparation of dyes were purchased from Fluka, Merck or Aldrich. Ethyl acetate (EA), *N*-phenylglycine (NPG) ($E_{ox} = 0.426$ V) and 1-methylpyrrolidin-2-one (MP) were purchased from Aldrich. All dyes tested were prepared using methods described elsewhere.[3–5] The impure dyes were purified using column chromatography and finally by preparative thin layer chromatography. The purity of the dyes was checked by HPLC.[3] The final products were identified by ^{1}H NMR and mass spectroscopy.[14,15] The spectra obtained and the melting points observed[5] were evidence that the dyes were of the desired structures.

Photoreduction of azomethine dyes (AMDs) by NPG was studied spectrophotometrically in a solvent composed of 1 mL of MP and 9 mL of ethyl acetate.[16] The concentration of the dye was 3.0×10^{-5} M, and the concentration of NPG varied from 2.5×10^{-2} M to 2×10^{-1} M. Experiments were carried out in an aerated solution.[16] Samples were irradiated at 514 and 488 nm with an Omnichrome argon ion laser Model 543-500 MA with the intensity of light ranging from 200 to 450 mW cm^{-2} measured by a Coherent power meter Model Fieldmaster. The irradiation was carried out under conditions ensuring that all the incident light was absorbed. All absorption spectra were determined on a Specord M40, a Varian Cary 3E or on a Hewlett-Packard 8452A diode array spectrophotometer.

The quantum yields of singlet oxygen formation from azomethine dyes were obtained using the actinometric method described by Schaap *et al.*[17] For the quantum yield measurements the procedure was as follows: 3.45 mg of 2,3-diphenyl-1,4-dioxene † was added to a 2 mL aliquot of a $CHCl_3$ solution of the dye that was present at a concentration that ensured that all incident light was absorbed. The solution (2 mL) was irradiated with an Omnichrome argon ion laser Model 543-500MA with the intensity measured by a Coherent power meter Fieldmaster. The solution was agitated by a continuous flow of oxygen. The formation of the photooxygenated product (ethylene glycol dibenzoate ‡) was followed by GLC analysis of the solution at a temperature of 225 °C. The quantum yield of singlet oxygen formation, $\Phi(^1O_2)$, was calculated from the ratio of the rate of formation of ethylene glycol dibenzoate for the dye under study compared to the rate for polymer-based Rose bengal (RB),[18] using the known quantum yield for poly(RB)

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† IUPAC name: 5,6-dihydro-2,3-diphenyl-1,4-dioxine.
‡ IUPAC name: ethylene dibenzoate.

Table 1 Spectral characteristics of tested pyrazolone azomethine dyes measured in ethyl acetate

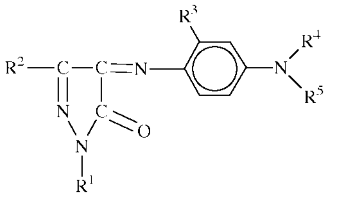
Comp.	R^1	R^2	R^3	R^4	R^5	λ_1/nm	λ_2/nm	$\varepsilon_{\lambda_1}/M^{-1}\ cm^{-1}$	$\varepsilon_{\lambda_2}/M^{-1}\ cm^{-1}$	$\varepsilon_{\lambda_2}/\varepsilon_{\lambda_1}$
I	Ph	CH_3	H	C_2H_5	C_2H_5	515	441	35000	16000	0.460
Ia	Ph	CH_3	CH_3	C_2H_5	C_2H_5	522	448	36000	16000	0.444
Ib	Ph	CH_3	H	C_2H_4OH	C_2H_5	514	439	35000	13000	0.371
Ic	Ph	CH_3	CH_3	C_2H_4OH	C_2H_5	522	440	36000	13000	0.361
Id	Ph	CH_3	CH_3	$C_2H_4NH(CH_3)SO_2$	C_2H_5	516	442	35000	14000	0.400
Ie	Ph	CH_3	H	CH_3	CH_3	508	440	34000	14000	0.411
II	Ph	NH_2	H	C_2H_5	C_2H_5	503	424	39000	9400	0.241
III	Ph	NHPh	H	C_2H_5	C_2H_5	515	427	44000	7800	0.177
IV	Ph	NHC(O)Ph	H	C_2H_5	C_2H_5	527	436	46000	7200	0.156
V	Ph	NHC(O)NHPh	H	C_2H_5	C_2H_5	532	432	53500	6200	0.116
VI	2,4,6-Ph(Cl)$_3$	CH_3	H	C_2H_5	C_2H_5	533	437	38000	9500	0.250
VII	2,4,6-Ph(Cl)$_3$	NH_2	H	C_2H_5	C_2H_5	506	416	42000	7200	0.171
VIII	2,4,6-Ph(Cl)$_3$	NHPh	H	C_2H_5	C_2H_5	520	420	48500	6300	0.130
IX	2,4,6-Ph(Cl)$_3$	NHC(O)Ph	H	C_2H_5	C_2H_5	534	434	50500	6100	0.121
X	2,4,6-Ph(Cl)$_3$	NHC(O)NHPh	H	C_2H_5	C_2H_5	537	426	55000	5900	0.107
XI	4-I-Ph	CH_3	H	C_2H_5	C_2H_5	517	429	36000	15000	0.417
XII	H	CH_3	H	C_2H_4OH	C_2H_5	507	443	25000	16000	0.640
XIII	2,4,6-Ph(Br)$_3$	CH_3	H	C_2H_5	C_2H_5	522	440	28000	8000	0.286
XIV	4-NO$_2$-Ph	CH_3	H	C_2H_4OH	C_2H_5	535	443	44000	13000	0.295
XV	2,4-Ph(NO$_2$)$_2$	$C(O)OC_2H_5$	H	C_2H_5	C_2H_5	570	456	47000	6500	0.148
XVI	2,4-Ph(NO$_2$)$_2$	$C(O)OC_2H_5$	CH_3	C_2H_5	C_2H_5	574	457	47000	6500	0.138
XVII	Ph	$C(O)OC_2H_5$	H	C_2H_5	C_2H_5	552	462	39000	14500	0.372
XVIII	Ph	$C(O)OC_2H_5$	CH_3	C_2H_5	C_2H_5	555	462	39500	15000	0.380
XIX	2,4,6-Ph(Cl)$_3$	$C(O)OC_2H_5$	H	C_2H_5	C_2H_5	554	462	40000	15000	0.375
XX	2,4,6-Ph(Cl)$_3$	$C(O)OC_2H_5$	CH_3	C_2H_5	C_2H_5	555	462	41000	15000	0.366

($\Phi(^1O_2) = 0.76$).[19] 2,3-Diphenyl-1,4-dioxene was prepared according to the method of Summerbell and Berger.[20]

The reduction potentials of the dyes were measured by cyclic voltammetry. An Electroanalytical Cypress System Model CS-1090 was used for the measurements, and an Ag–AgCl electrode served as the reference electrode. The supporting electrolyte was 0.5 M tetrabutylammonium perchlorate. The nanosecond laser flash photolysis apparatus and experimental methodology have been described in detail elsewhere.[21]

3. Results and discussion

The dyes tested were prepared by the reaction of pyrazolone with the oxidized form of *p*-phenylenediamine.[14] The structures of the dyes studied are presented below, R^1, R^2, R^3, R^4 and R^5 are listed in Table 1. The dyes were modified in two different ways in this study. The first way was by introducing substituents. These changes included introducing either a heavy atom or an electron-withdrawing group for R^1, using an electron donating or an electron accepting group for R^2 and finally modifying the part of the dye coming from the developer,[22] *e.g.* changing R^3, R^4 and R^5.



Scheme 1

For a better evaluation of the photochemistry of azomethine dyes, the second method of modification that restricts the rotational freedom of selected parts of the molecule was applied. This approach can eliminate or reduce the channels of excited-state deactivation which can cause a change in the rate of photobleaching. Several specific dyes containing the azomethine residue conjugated either with pyrazolone, pyrazolobenzimidazole, pyrazolo-1,2,4-triazole, benzoylacetanilide or quinoxalin-2-one moieties were prepared. Selected spectroscopic, photochemical and electrochemical data for these dyes are summarized in Table 2.

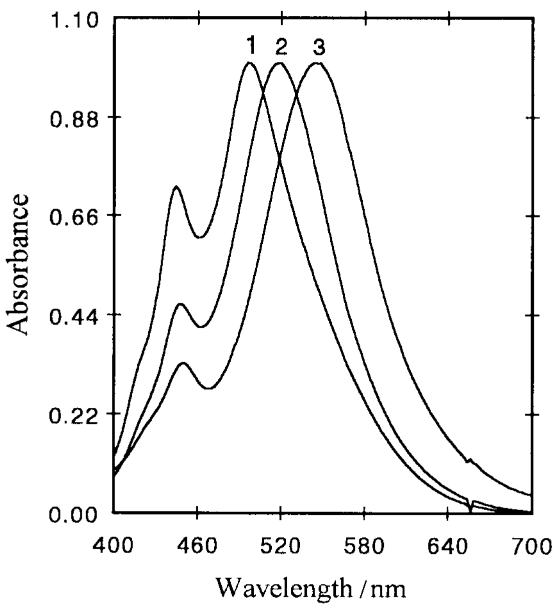
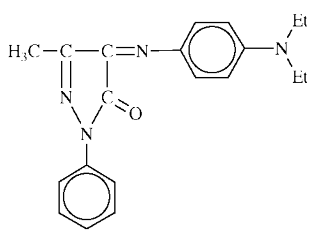


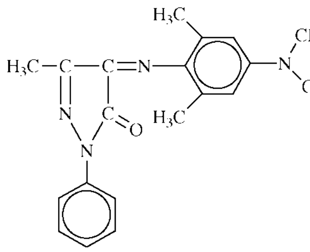
Fig. 1 The influence of the solvent polarity on the position of the absorption λ_{max} and the spectral distribution of the electronic spectra of **I**. Spectra in: (1) methylcyclohexane, (2) amyl acetate, (3) DMSO.

The electronic absorption spectra of AM dyes in the visible have characteristic double absorption bands (see Fig. 1). The half-widths of the main absorption band vary between 3000 and 4000 cm^{-1}.

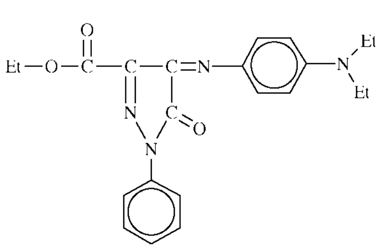
The electronic absorption spectra, *e.g.* the position of λ_{max} and the spectral distribution, characterized by the ratio of intensities of the more intense x band and the less intense y absorption band, strongly depend on the polarity of the solvent. This is due to changes in the dipole moment which a molecule undergoes upon light absorption.[23] The dyes exhibit a positive solvatochromic effect (see Fig. 2). The charge transfer (CT) transition involves ground and excited states with very different dipole moments, thus the CT absorption band should exhibit a marked solvent polarity effect. The positive solvato-



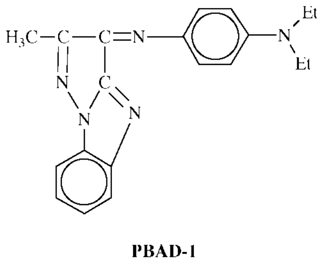
I



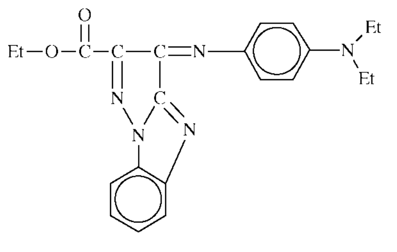
PAD-1d



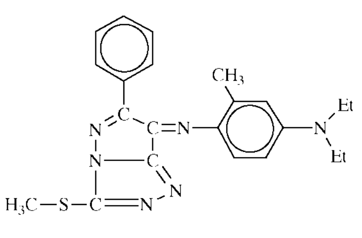
XVII



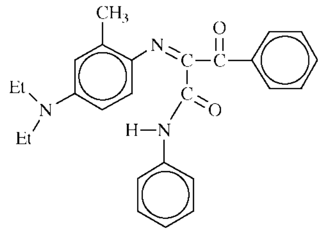
PBAD-1



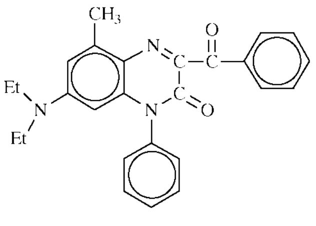
PBAD-2



PTAD



BAAD



ChAD

Table 2 Structures and basic spectroscopic photochemical and electrochemical properties of dyes tested

Comp.	λ_{max}^{ab}/ nm	$\varepsilon_{\lambda_{max}}$/M^{-1} cm^{-1}	$\Phi(^1O_2)$	λ_{max}^{fl}/nm	$\Phi_{bl} \times 10^6$	E_T[b]/kcal mol^{-1}	E_{red}/ V	$\Delta G°$/ eV
I	515	35000	5×10^{-4}	NO[a]	2.06	44	−1.020	−0.225
PAD-1d	640	12000	—	NO[a]	1.15	45	—	—
XVII	552	39000	2×10^{-4}	585	95.0	—	−0.722, −1.168	—
PBAD-1	530	38600	1×10^{-4}	585	2.25	—	−1.070	—
PBAD-2	574	39000	—	NO	98.8	—	—	—
PTAD	564	53800	—	only LE 495, 515[c]	6.34	24–28	−0.982	0.490
BAAD	433	16000	3×10^{-4}	only LE 520	15.7	41–45	−1.110	−0.120
ChAD	643	6000	0.078	only LE 520	1290	44	−1.208	−0.067

[a] NO not observed. [b] Ref. 26. [c] LE locally excited.

chromism of the tested dyes indicates that the excited state is more polar than the ground state ($\mu_g < \mu_e$).[24]

Secondly, the position and the spectral distribution of the visible part of the electronic absorption spectra are dependent on the structure of the dye (see Fig. 3a, b). When the dye structure is changed in a way that extends or reduces the π-electron systems, their electronic absorption spectra change. The changes are demonstrated by both distinct red or blue shifts and changes in the shape of the absorption spectra (see Fig. 3b).

The AM dyes listed in Table 1 either do not fluoresce or display very weak fluorescence. This is probably due to the branched and flexible structure of the AMD and the high degree of rotational freedom of each part of the molecule around bonds linking them with the pyrazolone skeleton.[25]

Visible light irradiation of AMDs in a moderately polar solvent, such as ethyl acetate, in the absence of any additives does not change their absorption spectra even after hundreds of hours of irradiation. However, after addition of an effective electron donor, *N*-phenylglycine, one sees distinct changes in the electronic absorption spectra during irradiation. This behavior is illustrated in Fig. 4.

The rate of color disappearance is dependent on light intensity (see Fig. 5) and on concentration of NPG (see Fig. 6), as well as on the dye structure. As can be seen in Table 3, the introduction of heavy atoms into a dye molecule only slightly increases the bleaching efficiency. In the case of dye **Ia** (for structure see Table 1), there is steric hindrance which may reduce the freedom of rotation of the phenyl group of the azomethine moiety. However, according to Herkstroeter,[26] the introduction of methyl groups into the *ortho* positions of the aromatic ring, attached to the azomethine nitrogen atom, accelerates the rate of azomethine group isomerization. This is possibly the reason that **Id** bleaches with a quantum yield lower than **I**. One can see an increase in bleaching efficiency when one changes the type of substituent on the pyrazolone skeleton from an electron donating (–CH_3) to an electron accepting (–C(O)OEt) group, *e.g.* **I** *vs.* **XVII** and **PBAD-1** *vs.* **PBAD-2**, Table 2. In addition, the elimination of the rotation of the phenyl residue linked to the pyrazolone skeleton (see Table 2: **I** *vs.* **PBAD-1**, and **XVII** *vs.* **PBAD-2**) does not cause any increase in photobleaching efficiency. A similar effect is observed when the pyrazolone moiety is augmented by a 1,2,4-triazole ring (see Table 2, **PTAD**). The change in the dye structure by the opening of the pyrazolone skeleton (Table 2, **BAAD**) causes a blue shift in the absorption spectra and slightly affects the bleaching efficiency. One observes a dramatic increase in the photoinitiation efficiency when the twisting motion of the C=N bond is severely hindered by structural constraints. Elimination of the motion of the C=N bond by co-planarization of the azomethine residue with other parts of the dye (see Table 2, **ChAD**) stabilizes the molecule in its excited state. An important conclusion arises from the analysis presented above: the rotation around the C=N bond is the main channel of the excited state deactivation for azomethine dyes.[25–30]

The photochemistry and photophysics of the bleaching process under photoreducing conditions are not yet clarified. According to Herkstroeter[28] the triplet energy levels in azomethines dyes are not observed directly. It is possible to locate the triplet state of azomethine dyes by applying an indirect method. Herkstroeter also showed that AMDs do not sensitize singlet oxygen formation.[29] This is probably due to very low quantum efficiencies of triplet state formation and/or very short lifetimes of the triplet states. In order to resolve this question the transient absorption spectra of intermediates for selected dyes were measured, and, in addition, an attempt to sensitize singlet oxygen, for selected dyes, was undertaken. For the photophysical study **BAAD** and **ChAD** were chosen. Flash excitation at 337 nm of an argon-purged solution of **ChAD** (Fig. 7) in the absence of any additives resulted in the appearance of transients at 460 nm and about 700 nm, separated by a negative ΔA at 645 nm corresponding to the disappearance of the ground-state of the dye. Bands at 460 and 700 nm can be ascribed to the triplet–triplet absorption of **ChAD** with the decay being a first-order process with lifetime τ = 25 μs. A similar value was also obtained for the rise-time of the negative ΔA at 645 nm. It is important to emphasize that this transient spectrum is rather intense with ΔA_{max} of the order of 0.01. Similar measurements performed for **BAAD** (Fig. 8) show only a broad, weakly absorbing transient spectrum ($\Delta A_{max} < 0.002$) indicating little possible triplet-state formation or a low extinction

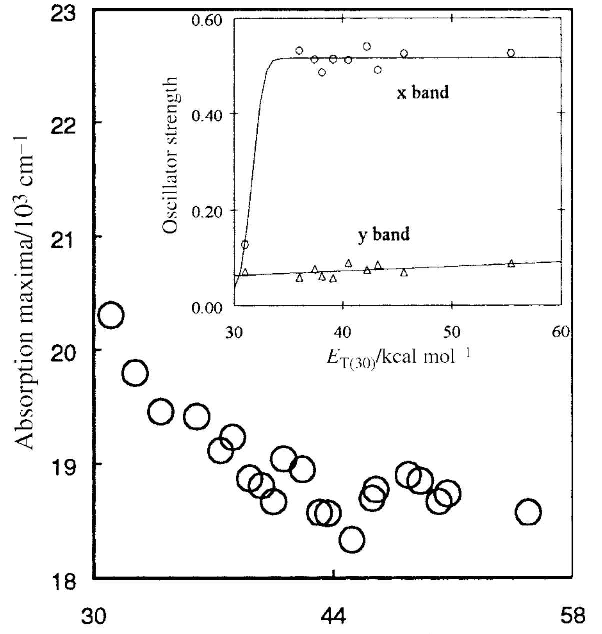


Fig. 2 Plot of observed absorption maxima versus $E_{T(30)}$ solvent polarity parameter for pyrazolone azomethine dye **VI**. Inset: Value of the oscillator strength of x and y bands for **VI** as a function of $E_{T(30)}$ solvent polarity parameter.

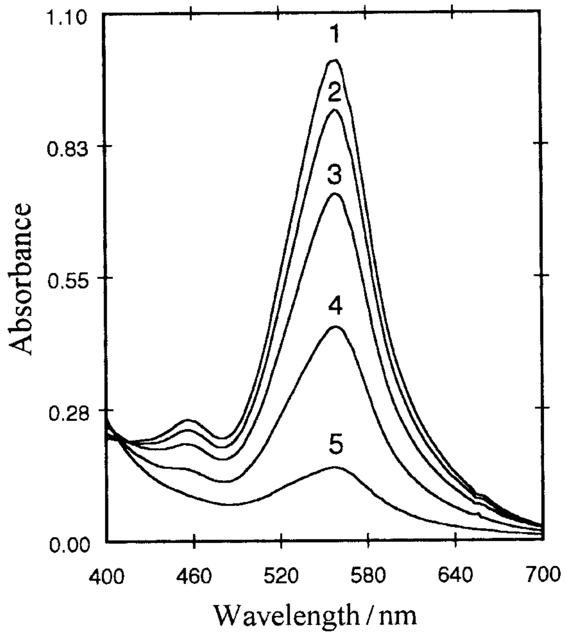


Fig. 4 The changes of the electronic absorption spectra of **XVII** in EA–MP solution during irradiation by argon-ion laser in the presence of N-phenylglycine (c = 0.1 M). Time of irradiation: (1) 0.0 min, (2) 5 min, (3) 10 min, (4) 15 min, (5) 20 min. Absorbed light intensity I_a = 300 mW cm⁻².

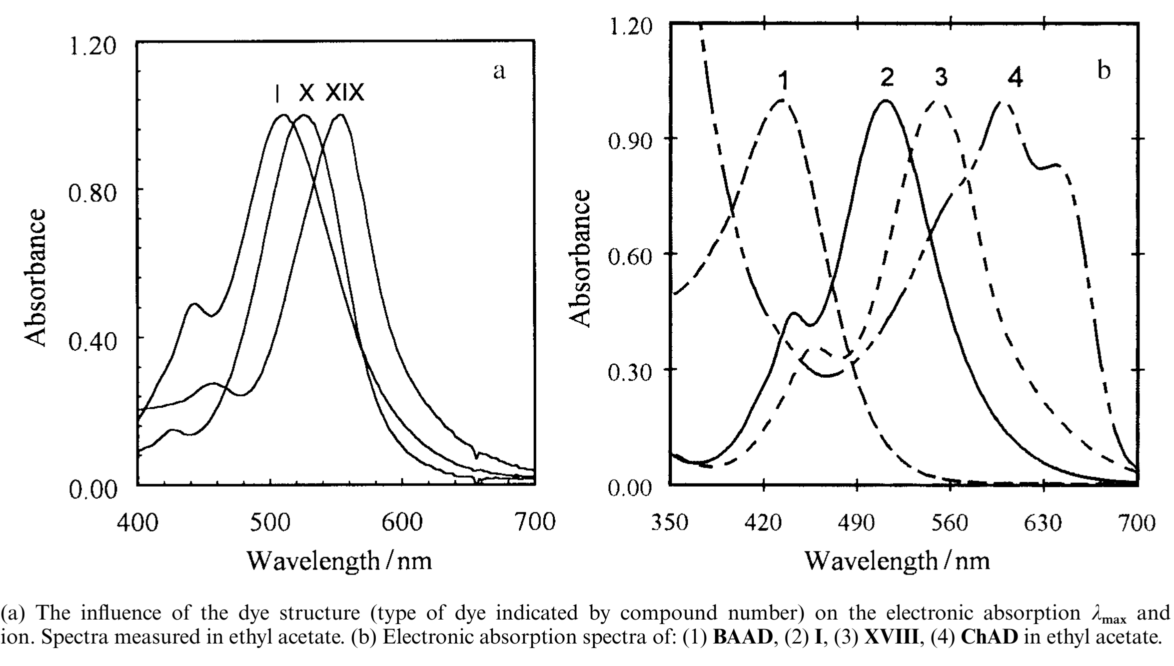


Fig. 3 (a) The influence of the dye structure (type of dye indicated by compound number) on the electronic absorption λ_{max} and spectral distribution. Spectra measured in ethyl acetate. (b) Electronic absorption spectra of: (1) **BAAD**, (2) **I**, (3) **XVIII**, (4) **ChAD** in ethyl acetate.

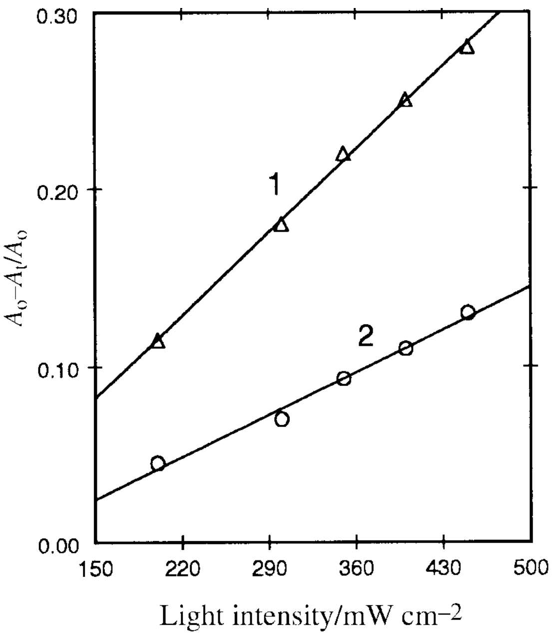


Fig. 5 The relationship between the changes of **XVII** absorbance and the absorbed light intensity. NPG concentration, $c = 0.1$ M. Time of irradiation of each sample: (1) 10 min, (2) 5 min.

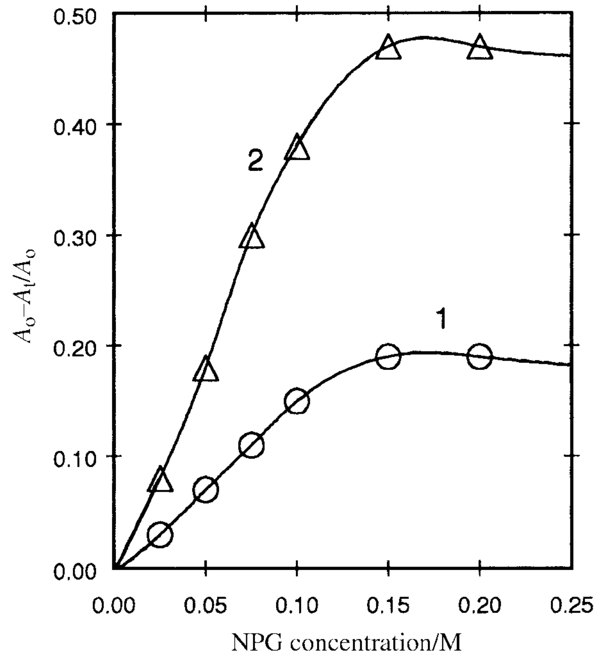


Fig. 6 The changes of the absorption of the dye as a function of the electron donor concentration. Dye: **XVII**, concentration $c = 3.0 \times 10^{-5}$ M. Time of irradiation of each sample: (1) 5 min, (2) 10 min.

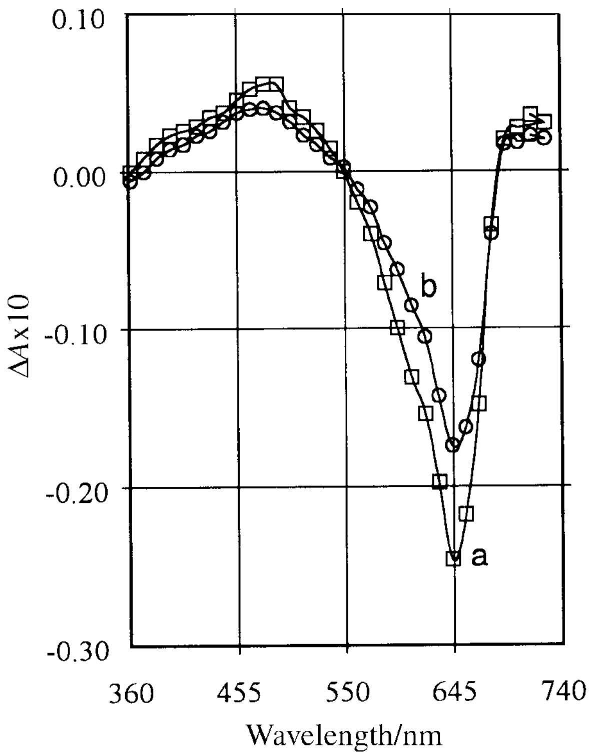


Fig. 7 Transient absorption spectra recorded for **ChAD** in MeOH solution; taken: (a) 1 µs, (b) 6 µs after flash.

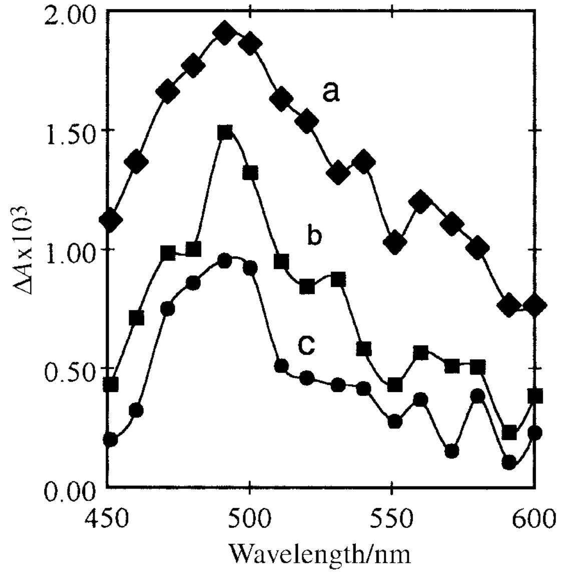


Fig. 8 Transient absorption spectra of **BAAD** in MeOH solution; taken: (a) 0.7 µs, (b) 3 µs, (c) 6 µs after flash.

coefficient. This observation suggests that for **BAAD** either the extinction coefficient of the triplet state is very small or, more likely, the quantum yield of intersytem crossing is very low.

ChAD differs from **BAAD** by the presence of a bond from the amide nitrogen on the aromatic ring coming from the developer. This additional bond was introduced by first modifying the developer in a way that allowed the formation of the bond between the pyrazolone skeleton and the developer residue.[25,26] This bond prevents isomerization about the C=N bond that typically occurs in azomethine dyes. Elimination of the dye isomerization also eliminates the most effective channel of excited state deactivation (both singlet and triplet). As a result **ChAD** forms the triplet with relatively high quantum yield while **BAAD** displays a very low efficiency of triplet state formation. Coplanarization of the azomethine residue with other parts of the dye stabilizes the molecule in its excited state. This effect can be rationalized in terms of the activation energies needed for isomerization of aromatic imines, which is of the order of 20 kcal mol^{-1} or less.[25] All the dyes studied, except for **ChAD**, are without structural constraints to prevent twisting about the C=N bond. Therefore, it is apparent that the formation of the triplet state for these dyes occurs with very low quantum yield. Additional evidence indicating that the quantum yield of triplet state formation is low for the tested dyes comes from the measurement of singlet oxygen formation, which can be sensitized by dyes that form triplet states. Data obtained for selected dyes are also summarized in Table 2.

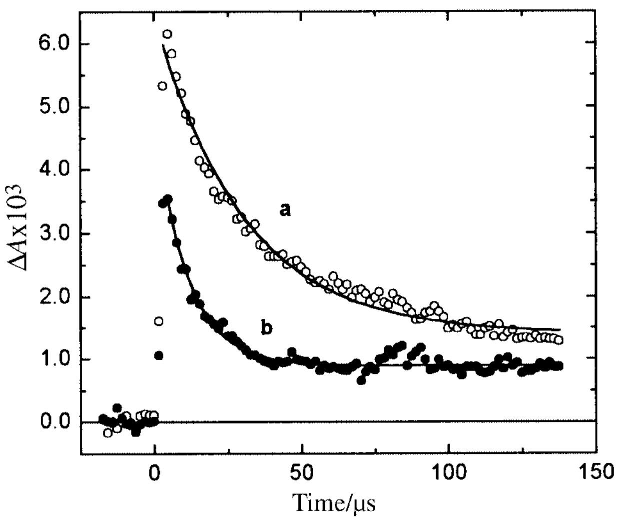


Fig. 9 Experimental kinetic traces for **ChAD** triplet decay at 460 nm (a) in the absence of any additives and (b) in the presence of NPG ($c = 3.1 \times 10^{-3}$ M).

The following kinetic scheme [eqns. (1)–(6)] for the AMDs bleaching process can account for the behavior described above.

$$\text{PAD} \xrightarrow{h\nu} \text{PAD*} \quad I_a \qquad (1)$$

$$\text{PAD*} \xrightarrow{k_{nr}} \text{PAD} \quad k_{nr}[\text{PAD*}] \qquad (2)$$

$$\text{PAD*} + \text{D} \xrightarrow{k_{el}} \text{PAD}^{-\bullet} + \text{D}^{+\bullet} \longrightarrow \text{bleaching product} \quad k_{el}[^1\text{PAD*}][\text{D}] \qquad (3)$$

$$\text{PAD*} \xrightarrow{k_{ISC}} {}^3\text{PAD*} \quad k_{ISC}[^1\text{PAD*}] \qquad (4)$$

$$^3\text{PAD*} \xrightarrow{k'_{nr}} \text{PAD} \quad k'_{nr}[^3\text{PAD*}] \qquad (5)$$

$$^3\text{PAD*} + \text{D} \xrightarrow{k'_{el}} \text{PAD}^{-\bullet} + \text{D}^{+\bullet} \longrightarrow \text{bleaching product} \quad k'_{el}[^3\text{PAD*}][\text{D}] \qquad (6)$$

The photobleaching of the AMDs may be due to either a singlet or a triplet state reaction. Fig. 9 shows experimental traces for the **ChAD** triplet decay at 460 nm (a) without additives and (b) in the presence of 3.1×10^{-3} M of *N*-phenylglycine. Based on these laser flash photolysis experiments one can conclude that the triplet state of **ChAD** is quenched by *N*-phenylglycine, which is known to be a good electron donor. Products that are formed after steady-state photolysis of **ChAD** and other AMDs in the presence of *N*-phenylglycine show that the *N*-phenylglycine photooxidation products are identical to those observed during photooxidation of *N*-phenylglycine by benzophenone. This observation suggests the occurrence of the electron transfer process.[30] The quenching rate constant, k_q, was obtained from the experimentally measured pseudo-first-order rate constant, k_{obs}, for the decay of the **ChAD** triplet using eqn. (7), where τ_T is the lifetime of the

$$k_{obs} = \tau_T^{-1} + k_q[\text{NPG}] \qquad (7)$$

ChAD triplet in the absence of *N*-phenylglycine. The calculated rate constant of **ChAD** triplet quenching is equal to 1.2×10^7 M^{-1} s^{-1}, *i.e.* is below the diffusion-controlled limit. The presence of triplet–triplet absorption (TTA) and the sensitization of singlet oxygen, coupled with the quenching of the TTA by NPG, suggest that the bleaching process of the AMDs may involve their triplet states.

Table 3 Quantum yields, k'_{NR}/k'_{bl} quotients and rate constants of the photobleaching process calculated for pyrazolone azomethine dyes (PADs) in ethyl acetate solution under photoreductive conditions. Quantum yield of the bleaching process was measured at *N*-phenylglycine concentration $c = 0.08$ M.

Dye	$\Phi_{bl} \times 10^5$	$k'_{NR}/k'_{bl}/M^{-1}$	$k'_{bl}/10^{-7}$ M^{-1} s^{-1}
I	0.21	3.85	2.60
Ia	0.16	5.14	1.95
Ib	0.19	4.16	2.40
Ic	0.17	4.76	2.10
Id	0.18	4.35	2.30
Ie	0.19	4.00	2.50
II	0.13	6.25	1.60
III	0.09	9.52	1.05
IV	0.26	2.98	3.35
V	0.17	4.76	2.10
VI	0.22	3.63	2.75
VII	0.10	7.70	1.30
VIII	0.07	11.76	0.85
IX	0.21	3.85	2.60
X	0.14	5.70	1.75
XI	0.29	2.78	3.60
XII	0.17	4.65	2.15
XIII	0.32	2.53	3.95
XIV	0.40	1.94	5.15
XV	13.8	0.055	183.0
XVI	17.5	0.044	226.0
XVII	7.9	0.093	108.0
XVIII	9.5	0.085	118.0
XIX	12.2	0.058	174.0
XX	36.8	0.019	515.0

The quantum yield of the photobleaching process *via* the triplet excited state, assuming k_{NR} is the rate constant for all deactivation processes with the exception of k'_{el}, under steady-state conditions is given by eqn. (8) or in the form of eqn. (9).

$$\Phi_{bl} = \frac{k'_{bl}[\text{D}]}{(k'_{NR} + k'_{bl}[\text{D}])}\varphi_{ISC} \qquad (8)$$

$$\frac{1}{\Phi_{bl}} = \frac{1}{\varphi_{ISC}} + \frac{k'_{NR}}{\varphi_{ISC}k'_{bl}[\text{D}]} \qquad (9)$$

Fig. 10 illustrates the relationship (described by eqn. (9)) observed for several selected AMDs. The double reciprocal plots in Fig. 10 have intercepts of the order of 10^5, which according to eqn. (9) should be equal to $1/\Phi_{ISC}$. If the mechanism were pure singlet, then the intercept of the double reciprocal would be one. Numerical simulations, using the exact solution to the kinetics of eqns. (1)–(6), indicate that if there are significant contributions from the singlet mechanism, the intercept would be also one. These simulations in conjunction with the large intercepts in Fig. 10 suggest that the bleaching occurs mainly through a triplet mechanism.

Table 3 lists all the photobleaching data obtained for the dyes specified in Table 1. It is apparent from inspection of the data in Table 3 that all the studied dyes can be divided into two major groups. The first group has high dye stability under photoreductive conditions. The second group shows much higher bleaching quantum yields. Based on diffusion-controlled quenching of the dye singlet and triplet state by molecular oxygen, Herkstroeter estimated that the lifetime is less than 5×10^{-10} s for the singlet state and 10 ns for the triplet-state of pyrazolone azomethine dyes with an intramolecular heavy atom.[31] Our results for singlet oxygen formation, suggest that all the dyes tested form triplet states. More careful inspection of the data in the Table 3 shows that, taking $k'_{NR} = 10^8$ s^{-1} (based on Herkstroeter's data[28]), for the bleaching *via* a triplet state, one can easily calculate the rate constant for the bleaching process. The calculation indicates that, assuming the φ_{ISC} is equal to the quantum yield of

Table 4 The electrochemical, thermodynamic and kinetic characteristics of selected pyrazolone azomethine dyes (PADs)

Comp.	R^1	R^2	R^3	$E_{1/2}^{RED}$/V	$\Delta G_{el}^{(S)}$/ kcal mol^{-1} [a]	$\Delta G_{el}^{(T)}$/ kcal mol^{-1} [b]
I	Ph	CH_3	H	−1.020	−20.15	−10.65
Ia	Ph	CH_3	CH_3	−1.024	−19.14	−10.56
Ib	Ph	CH_3	H	—	—	—
Ic	Ph	CH_3	CH_3	−0.952	−21.72	−12.22
Id	Ph	CH_3	CH_3	−1.008	−19.97	−10.22
Ie	Ph	CH_3	H	−0.942	−22.64	−12.45
II	Ph	NH_2	H	−1.046	−20.71	−10.05
III	Ph	NHPh	H	−0.966	−21.40	−11.90
IV	Ph	NHC(O)Ph	H	−1.194	−14.99	−6.64
V	Ph	NHC(O)NHPh	H	−1.222	−13.65	−5.99
VI	$Ph(Cl)_3$	CH_3	H	−1.07	−17.2	−9.5
VII	$Ph(Cl)_3$	NH_2	H	−1.078	−19.74	−9.32
VIII	$Ph(Cl)_3$	NHPh	H	−1.004	−19.83	−11.02
IX	$Ph(Cl)_3$	NHC(O)Ph	H	−1.330	−10.93	−3.05
X	$Ph(Cl)_3$	NHC(O)NHPh	H	−1.166	−14.48	−7.29
XI	*p*-I-Ph	CH_3	H	−0.920	−22.00	−12.96
XII	H	CH_3	H	−1.144	−18.22	−7.29
XIII	$Ph(Br)_3$	CH_3	H	−0.950	−20.85	−12.27
XIV	*p*-NO_2-Ph	CH_3	H	−0.896	−20.71	−13.28
XV	$Ph(NO_2)_2$	$C(O)OC_2H_5$	H	—	—	—
XVI	$Ph(NO_2)_2$	$C(O)OC_2H_5$	CH_3	—	—	—
XVII	Ph	$C(O)OC_2H_5$	H	−1.166	−13.79	−7.29
XVIII	Ph	$C(O)OC_2H_5$	CH_3	—	—	—
XIX	$Ph(Cl)_3$	$C(O)OC_2H_5$	H	−1.212	−11.11	−6.29
XX	$Ph(Cl)_3$	$C(O)OC_2H_5$	CH_3	−1.258	−10.98	−5.16

[a] E_{oo} for singlet state is calculated as an approximate value based on electronic absorption spectrum. $E_{oo} = hc/\lambda$ where $\lambda = \lambda_{max} + 20$ nm. [b] E_{oo} for triplet state from ref. 26.

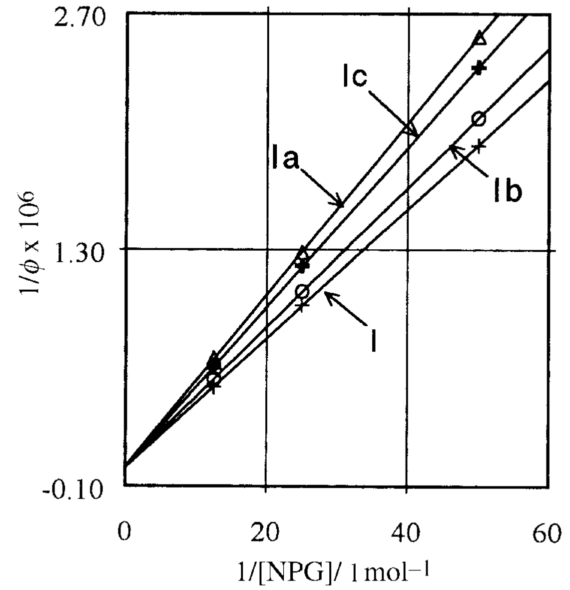


Fig. 10 The relationship between the quantum yield of the bleaching process and the electron donor concentration for high stability AMDs. $I_a = 300$ mW cm^{-2}.

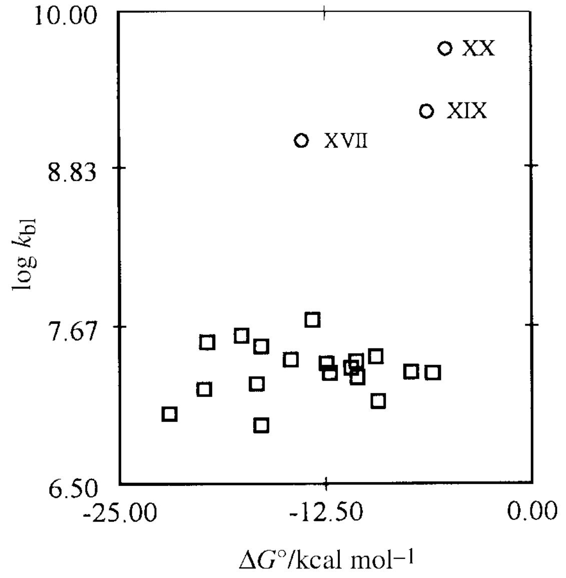


Fig. 11 The rate of the photobleaching process for selected AMDs as a function of thermodynamic driving forces, $\Delta G°$ (calculated for process through the triplet state); $I_a = 300$ mW cm^{-2}.

singlet oxygen formation ($\Phi(^1O_2)$ is about 10^{-4}), for the first group of AMDs, the rate constants of photobleaching vary between 0.8×10^7 M^{-1} s^{-1} and 10×10^7 M^{-1} s^{-1}. For the second group of the dyes, a similar treatment gives higher rate constants of photobleaching with the values ranging between 1.1×10^9 M^{-1} s^{-1} and 5.1×10^9 M^{-1} s^{-1}.

The mechanistic aspect of the photobleaching process needs clarification with regard to the first step of the reaction being a photoinduced electron transfer (PET) process.

The interaction of a donor molecule with the photoexcited acceptor may lead to either exciplex formation or radical–ion pair formation. The tendency of producing radical ions *via* PET can be predicted by using the Rehm–Weller[32] eqn. (12),

$$\Delta G_{el} = E_{ox}(D/D^{+\bullet}) - E_{red}(A^{-\bullet}/A) - Ze^2/\varepsilon a - E_{oo} \quad (12)$$

where $E_{ox}(D/D^{+\bullet})$ is the oxidation potential of the electron donor, E_{red} $(A^{-\bullet}/A)$ is the reduction potential of the electron acceptor, E_{oo} is the energy of the excited state, and $Ze^2/\varepsilon a$ is the Coulombic energy that can be neglected in the present systems.

Under thermodynamically favorable reactions ($\Delta G_{el} < 0$) the radical ions are formed as a result of the photoinduced intermolecular electron transfer process. Product formation in PET reactions is governed by secondary processes, leading either to neutral radicals or ions. Both of these species may initiate free radical polymerizations. Free radical polymerization has been observed using AMDs in the presence of *N*-phenylglycine as the electron donor.[7] This suggests that free radicals are formed during this process and that the first step of the reaction is a photoinduced intermolecular electron transfer.[33] The verification comes from electrochemical measurements and calculations of ΔG_{el}. Table 4 summarizes the reversible reduction potentials measured and the calculated ΔG_{el} values for the AMDs tested. The ΔG_{el} values are calculated for both singlet and triplet states of the dyes.

Data in Table 4 show that the intermolecular electron transfer process is thermodynamically allowed, both *via* singlet and triplet states. However, it is necessary to emphasize that the secondary processes leading to the final product formation are still not clear.[34]

One more question arises when one considers the Marcus[35] treatment of the PET reaction of AMDs bleaching. Fig. 11 illustrates the relationship between the thermodynamic driving force, $\Delta G°$, of the PET of the photoreduction process and the rate constants of the bleaching. From Fig.11 it can be seen that in the range of about 20 kcal mol^{-1} one sees a plateau indicating that the reaction is not directly controlled by the electron transfer process but is probably controlled by a combination of several factors, *e.g.* the quantum yield of intersystem crossing and the rates of processes subsequent to the photoinduced electron transfer.

We have shown earlier[7] that AMDs in the presence of *N*-phenylglycine are able to photoinitiate free radical polymerization. PET reactions of amines[20] yield amine radical cations, that after deprotonation give α-amino radicals which, usually after cross-coupling between radical pairs terminate the photoreduction. However, in very reactive solutions of polyol acrylates some of the free radicals can start a chain reaction of vinyl polymerization that competes with the color-loss process.

In summary it is important to emphasize that changes in the dye structure are translated into changes in the rate of photobleaching. The introduction of heavy atoms into a dye molecule only slightly increases the bleaching efficiency. Introduction of the CH_3 group into the R^3 position should decrease the freedom of the phenyl group rotation and as a result decrease the rate of nonradiative deactivation of the excited state and increase the rate of the bleaching process. However, after Herkstroeter,[26] the introduction of the methyl groups into the *ortho* positions of the aromatic ring, attached to the azomethine nitrogen atom, accelerates the rate of azomethine group isomerization. Significant influence of the AMD structure on photobleaching rates is observed only when the branching of the dye is limited and less distinct when a strong electron withdrawing group is substituted in the R^2 position.

Acknowledgements

This research was sponsored by the State Committee for Scientific Research (KBN), grant No. 3 TO9B 087 15, and (for G. L. H.) by the office of Basic Energy Sciences of the US Department of energy. This paper is Document No. NDRL - 4100 from the Notre Dame Radiation Laboratory.

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Paper 9/03363G