Photoreduction of organic dyes in ketone amine systems

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Abstract

Nucleophilic radicals, such as α-amino and ketyl radicals, produced by reaction of benzophenone triplets with amines and alcohols respectively, react efficiently by electron transfer with cationic organic dyes, such as phenosafranine, thiopyronine, methylene blue, and crystal violet. Time-resolved laser flash photolysis studies reveal a high reactivity of α-amino radicals toward these cationic dyes; in contrast, ketyl radicals are less reactive. The electron transfer rate constants for the reaction between the α-amino radical of triethanol amine and these dyes range from 2.7×10^9 M^{-1} s^{-1} (phenosafranine) to 7.5×10^9 M^{-1} s^{-1} (methylene blue). In contrast, rate constants ranging from 1.1×10^8 M^{-1} s^{-1} (phenosafranine) to 1.2×10^9 M^{-1} s^{-1} (methylene blue) were measured for the reaction of the dyes with the diphenyl ketyl radical. In dye mixtures used in conjunction with ketone–amine systems, stepwise electron transfer from an initially formed semireduced dye to a molecule of another dye occurs. For example, the primarily formed crystal violet radical reacts very rapidly ($k = 2 \times 10^9$ M^{-1} s^{-1}) with phenosafranine, thus forming the semireduced phenosafranine and regenerating crystal violet.

Keywords: Photoreduction; Organic dyes; Ketone–amine systems; Nucleophilic radicals

1. Introduction

Dyes have become important components in initiator systems for photopolymerization induced by polychromatic light [1–3]. Relevant photoinitiator compositions often contain two different initiator systems, one absorbing visible light (dye system) and the other being sensitive only to UV light. In typical dye systems, a co-initiator is needed for the formation of species capable of initiating the polymerization. Such systems, which function on the basis of the photoreduction of dyes, are well known [4]. Amines are quite appropriate as reductants because of their favorable and easily variable oxidation potentials [3].

Carbonyl groups are often used as the absorbing chromophore in UV photoinitiator systems [5,6]. In this work benzophenone (BP) was employed as a model ketone because it is one of the most frequently studied ketones. In ternary ketone–amine–dye systems many different reactions can occur upon irradiation. Reactions of excited ketones with amines [7–9] and of excited dyes with amines [3] have been studied extensively. Less frequently studied were interactions of ground state dyes with nucleophilic radicals originating from the photoinduced processes in the initiator system.

However, these "side reactions", which do not initiate polymerizations, are especially important for cross-linking of thick monomer layers. Gradual bleaching of the dye permits the polymerization to proceed gradually from the surface to the bottom of the layer. In the present work dealing with such ternary systems, the chloride salts of four cationic dyes were selected as typical components (Scheme 1): methylene blue (MB^+), thiopyronine (TP^+), phenosafranine (PS^+), and crystal violet (CV^+).

2. Experimental section

2.1. Materials

Methylene blue (MB^+Cl^-) (Aldrich), phenosafranine (PS^+Cl^-) (Fluka), and crystal violet (CV^+Cl^-) (Aldrich) were recrystallized from ethanol–water (4:1, by volume). Thiopyronine (TP^+Cl^-) (Fluka) was thrice recrystallized from ethanol. Hydrogen chloride bonded to crystalline thiopyronine ($TP^+Cl^- \cdot \frac{1}{2}HCl$) was removed by heating at 100 °C in vacuo at 0.1 Torr [10]. BP (Aldrich) was purified with the aid of neutral Al_2O_3 using n-hexane–ether (2:1, by

Scheme 1. Structures of the dyes.
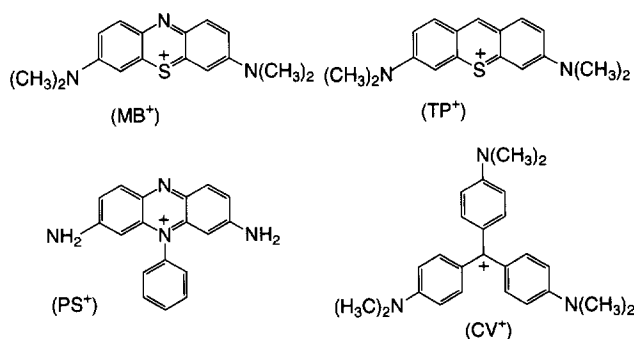
volume) as eluent. Benzhydrol (BH) (E. Merck), triethanol amine (TEOA) (Fluka), 2-propanol (Aldrich), acetonitrile (spectrophotometric grade, Aldrich), and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (Aldrich) were used as received.

2.2. Measurements

Quantum yields Φ_{-dye} of dye bleaching were determined by continuous irradiation at 365 nm in a previously described set-up [11] consisting of a high pressure mercury lamp (HBO 200, Narva, Berlin) operated in conjunction with a metal interference filter (UVIF 365, Zeiss, Jena). The absorbed dose was determined by ferrioxalate actinometry [12].

The excitation source utilized for flash photolysis studies was either a ruby laser operated in conjunction with a frequency doubler ($\lambda_{ex} = 347$ nm; flash duration, ca. 15 ns) or a frequency-doubled or tripled Nd–YAG laser ($\lambda_{ex} = 532$ nm or $\lambda_{ex} = 355$ nm respectively; flash duration, ca. 15 ns). Actinometry for $\lambda_{ex} = 347$ and 355 nm was performed using the benzophenone–naphthalene triplet system [13]. Prior to irradiation, the solutions were bubbled with argon for 20 min in order to remove oxygen. Second-order rate constants were determined by laser flash photolysis (error limit, $\pm 10\%$).

Redox potentials of the dyes were measured using cyclic voltametry (GWP 673 at 100 mV s^{-1}) using platinum electrodes with a saturated calomel electrode (SCE) as reference. Tetrabutylammonium hexafluorophosphate (Fluka) was employed as the electrolyte for 5×10^{-4} M solutions of the dye in acetonitrile. Ferrocene served as the internal standard ($E_{ox}^{P} = 0.42$ V (SCE)) [14].

3. Results and discussion

The photoreactions of ketones with alcohols and amines have been extensively investigated in previous studies [9,15]. Ketone triplets such as $^3BP^*$ typically react with tertiary amines, containing hydrogen in the α-position to the nitrogen, by electron transfer followed by fast proton transfer [9,16] (Eq. (1)). The resulting ketyl and amino radicals are expected to react with organic dyes. To study reactions of

diphenyl ketyl radicals separately, $^3BP^*$ was reacted with benzhydrol (BH):

(1)

(2)
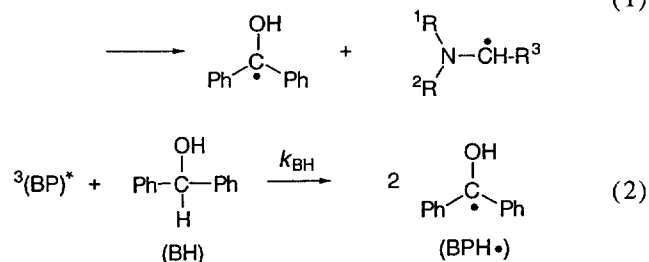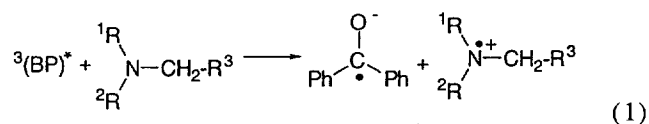
3.1. Reaction of dyes with ketyl radicals

Diphenyl ketyl radicals generated by irradiation of BP in acetonitrile solutions with laser flashes ($\lambda_{ex} = 347$ nm) in the presence of benzhydrol (Eq. (2)) possess a transient absorption in the 450–580 nm region [17–20] which decays because of dimerization with a rate constant $k_{dim} = 7.5 \times 10^8$ M^{-1} s^{-1}. This value is similar to values reported by other researchers ($k_{dim} = 10 \times 10^8$ M^{-1} s^{-1} [19] and $k_{dim} = 7 \times 10^8$ M^{-1} s^{-1} [20]).

When PS$^+$ is added to the BP–BH system the situation becomes different. Immediately after the laser flash, diphenyl ketyl radicals are detectable (Eq. (2)), but on a longer time scale the ground state absorption of PS$^+$ at 500 nm is bleached (Fig. 1(a)). Simultaneously, an absorption at 430–440 nm, assigned to the semireduced dye (PS$^•$), is formed [21] (Fig. 1(b)), indicating the reduction of PS$^+$ to PS$^•$ by the ketyl radical (Eq. (3)). It is known that PS$^•$ undergoes disproportionation by forming the leuco dye (PSH) and regenerating the dye (Eq. (4)).

(3)

(4)
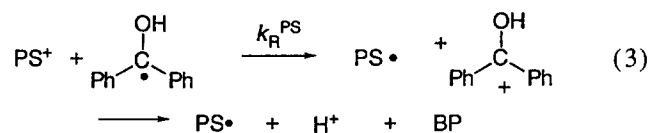
The pseudo-first-order kinetic treatment of the decay of the absorption at 500 nm yields a second-order rate constant $k_R^{PS} = 1.1 \times 10^8$ M^{-1} s^{-1} (Fig. 2). MB$^+$ exhibits a behavior similar to that of PS$^+$. The rate constant k_R^{MB} for the reaction of MB$^+$ with the diphenyl ketyl radical is 1.2×10^9 M^{-1} s^{-1} (Fig. 2). The higher value, relative to k_R^{PS}, is associated with the lower reduction potential of MB$^+$ (see Table 1). As reported previously, CV$^+$ is reduced by diphenyl ketyl radicals with a rate constant $k_R^{CV} = 2 \times 10^8$ M^{-1} s^{-1} [22].

To determine quantum yields of dye reduction, steady state irradiations of the BP–BH dye system were performed at 365 nm. With all three dyes (PS$^+$, MB$^+$, and CV$^+$) bleaching
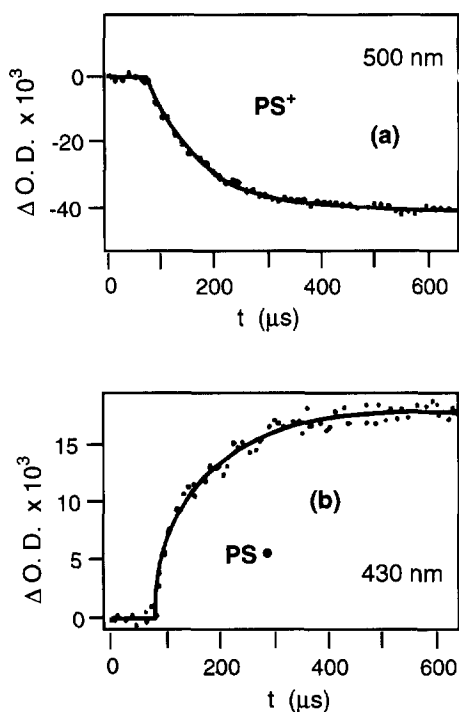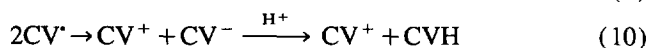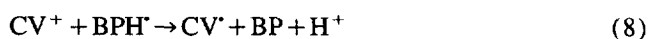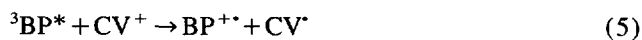
Fig. 1. Kinetic traces recorded at different wavelengths following laser flash photolysis ($\lambda_{ex} = 347$ nm; 23 °C; $D_{abs} = 6 \times 10^{-6}$ einstein l^{-1}) of an argon-saturated acetonitrile solution containing BP (1×10^{-3} M), BH (1 M), and PS$^+$ (8×10^{-5} M).

of the ground state absorption was observed. In the case of PS$^+$ and MB$^+$ the quantum yield of bleaching is close to one; however, for CV$^+$ the situation differs in that a maximum quantum yield Φ of only 0.2 is attained and the quantum yield does not depend monotonically on the dye concentration, as in the cases of PS$^+$ and MB$^+$. The quantum yield of bleaching of CV$^+$ decreases after an initial increase at increasing concentration of BH (Fig. 3). In addition, the maximum shifts to higher concentrations of BH when the concentration of CV$^+$ is increased (Fig. 3). These results can be described by the following reactions:

$$^3BP^* + CV^+ \rightarrow BP^{+\bullet} + CV^\bullet \tag{5}$$

$$BP^{+\bullet} + CV^\bullet \rightarrow BP + CV^+ \tag{6}$$

$$BP^{+\bullet} + BH \rightarrow products \tag{7}$$

$$CV^+ + BPH^\bullet \rightarrow CV^\bullet + BP + H^+ \tag{8}$$

$$CV^\bullet + BPH^\bullet \rightarrow CVH + BP \tag{9}$$

$$2CV^\bullet \rightarrow CV^+ + CV^- \xrightarrow{\text{H}^+} CV^+ + CVH \tag{10}$$

In addition to the H abstraction from BH (Eq. (2)) by $^3BP^*$, $^3BP^*$ is oxidatively quenched by CV$^+$, a process generating CV$^\bullet$ and the benzophenone cation radical (Eq. (5)) [22]. When the highly reactive benzophenone cation radical is trapped by benzhydrol (Eq. (7)), the back electron transfer (Eq. (6)) is hindered. At rather high concentrations, BH is able to quench $^3BP^*$. This process leads to the formation of diphenyl ketyl radicals (Eq. (2)), which can reduce CV$^+$
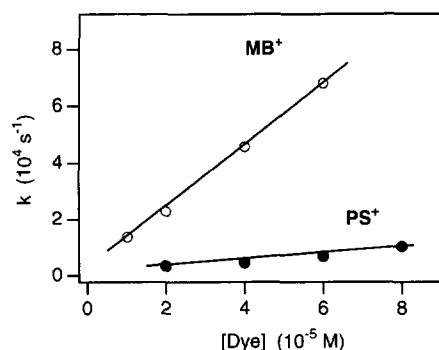

Fig. 2. Pseudo-first-order rate constant of the re-formation of PS$^+$ (500 nm) and MB$^+$ (620 nm) vs. the dye concentration (for experimental conditions see Fig. 1).

Table 1
Rate constant k_R of the reaction of α-amino and ketyl radicals with dyes in acetonitrile at 23 °C and reduction potentials $E_{red}^{1/2}$ of the dyes

	k_R ($\times 10^9$ M^{-1} s^{-1})			
	CV$^+$	PS$^+$	TP$^+$	MB$^+$
OH Ph—C—Ph	0.2 [a] 0.4 [b]	0.11		1.2
OH H$_3$C—C—CH$_3$	1.3 2.3 [c]	0.9 3.2 [c]	1.5	3.0 4.4 [c]
HO CH$_2$ H$_2$C N—CH-CH$_2$-OH H$_2$C CH$_2$ HO	5.0	2.7	3.9	7.5
$E_{red}^{1/2}$ (V) (SCE)	−0.66	−0.66	−0.64	−0.36

[a] Ref. [22].
[b] Ref. [26] (measured by pulse radiolysis).
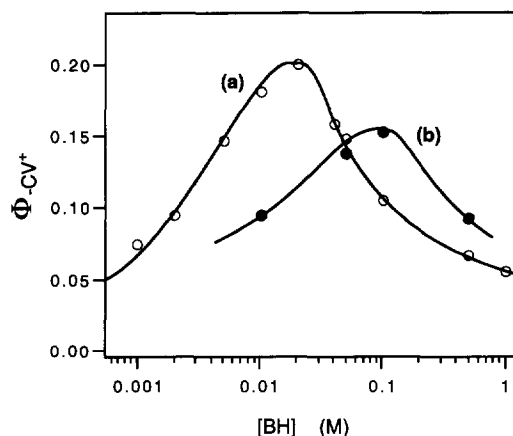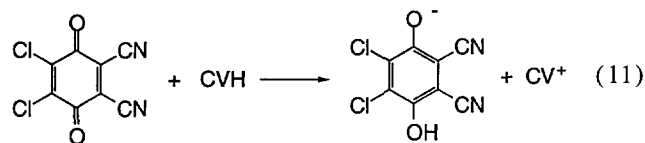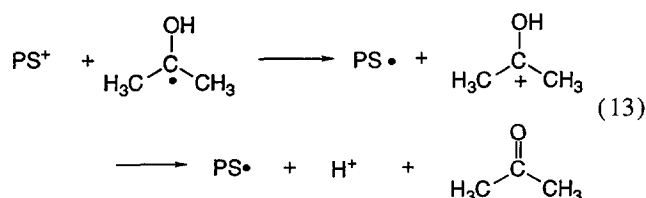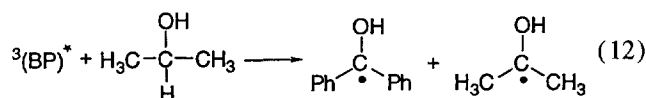[c] Ref. [27] (measured by pulse radiolysis).

Fig. 3. Quantum yield dependence of the bleaching of the absorption of CV$^+$ on the BH concentration for continuous irradiation of the system BP–BH–CV$^+$ in argon-saturated acetonitrile solution ($\lambda_{ex} = 365$ nm; 20 °C; [BP] $= 1 \times 10^{-2}$ M; [CV$^+$] $= 1 \times 10^{-5}$ M (curve a) and 1×10^{-4} M (curve b)).

(Eq. (8)). CV$^{\bullet}$ can decay by reduction with ketyl radicals (Eq. (9)) or by redox disproportionation (Eq. (10)).

To ensure that the bleaching of CV$^+$ is caused by the reduction of the dye, the leuco crystal violet (CVH) was reoxidized by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone [23,24]. In this way it was possible to regenerate CV$^+$ with a yield of 95% (measured by UV–visible spectroscopy).

$$
\text{(structure: Cl, CN, O, benzoquinone)} + \text{CVH} \longrightarrow \text{(structure: Cl, CN, O-, OH)} + \text{CV}^+ \quad (11)
$$

It has been reported that dimethyl ketyl radicals ($E_{ox}^{1/2} = -1.3$ V (SCE) [25]) possess oxidation potential lower than that of diphenyl ketyl radicals ($E_{ox}^{1/2} \approx -0.7$ V (SCE) [18]). Thus, it is expected that the dimethyl ketyl radical will reduce the dyes more rapidly than the diphenyl ketyl radical. Dimethyl ketyl radicals were generated by irradiation of a solution of BP in 2-propanol with 347 nm laser light (Eq. (12)). In the presence of the dyes, both diphenyl ketyl radicals and dimethyl ketyl radicals are expected to reduce the cationic dyes (see Eqs. (13) and (3)):

$$
{}^3(\text{BP})^* + \text{H}_3\text{C}-\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}-\text{CH}_3 \longrightarrow \underset{\text{Ph}}{\overset{\text{OH}}{\text{C}}}_{\text{Ph}} + \underset{\text{H}_3\text{C}}{\overset{\text{OH}}{\text{C}}}_{\text{CH}_3} \quad (12)
$$

$$
\text{PS}^+ + \underset{\text{H}_3\text{C}}{\overset{\text{OH}}{\text{C}}}_{\text{CH}_3} \longrightarrow \text{PS}\bullet + \underset{\text{H}_3\text{C}}{\overset{\text{OH}}{\text{C}}}_{\text{+ CH}_3}
$$

$$
\longrightarrow \text{PS}\bullet + \text{H}^+ + \underset{\text{H}_3\text{C}}{\overset{\text{O}}{\text{C}}}_{\text{CH}_3} \quad (13)
$$

Laser flash photolysis experiments of the system BP–2-propanol–PS$^+$ show that the bleaching of the ground state absorption of the dye is due to two processes, one fast and the other slow. The slow process corresponds to the reduction of PS$^+$ by diphenyl ketyl radicals (Eq. (3)), whereas the fast process is assigned to the analogous reaction of PS$^+$ with dimethyl ketyl radicals (Eq. (13)). Identical situations were obtained with the other BP–2-propanol–dye systems. Upon separating the two processes, rate constants of the reactions of the dyes were obtained (Table 1). They are of the same magnitude as those measured by pulse radiolysis [27].

The rate constants for dimethyl ketyl radicals are significantly higher than those for diphenyl ketyl radicals, which corresponds to differences in the oxidation potentials of the ketyl radicals [18,25].

Together with the differences in the rate constants, differences in the quantum yield of dye conversion are expected. Actually, a significant difference concerning the bleaching of the ground state absorption of the dye was found. When experiments similar to those described in Fig. 3 were performed in the presence of varying amounts of 2-propanol it was found that the maximum quantum yield is higher than in the case of the BH system. Moreover, Φ_{-CV^+} increases mon-
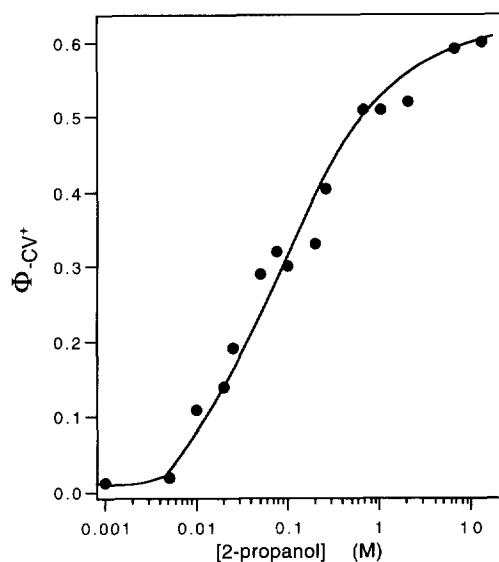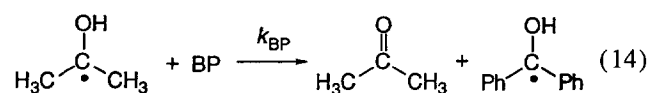

Fig. 4. Quantum yield dependence of the bleaching of the absorption of CV$^+$ on the 2-propanol concentration under continuous irradiation of the system BP–2-propanol–CV$^+$ in argon-saturated acetonitrile solution ($\lambda_{ex} = 365$ nm; 20 °C; [BP] = 1×10^{-2} M; [CV$^+$] = 1×10^{-5} M).

otonically with increasing 2-propanol concentration (Fig. 4). At low 2-propanol concentration a similar process to that described by reactions (5)–(7) is expected to cause bleaching of the CV$^+$ absorption. At higher 2-propanol concentration ^{3}BP* is quenched by the alcohol with a rate constant $k = 1.3 \times 10^6$ M^{-1} s^{-1} [7] yielding the two ketyl radicals (Eq. (12)). As dealt with above, CV$^+$ is reduced more effectively by dimethyl ketyl radicals than by diphenyl ketyl radicals. This explains why the quantum yield increases monotonically with increasing concentration (Fig. 4).

It is known that dimethyl ketyl radicals react with BP to produce diphenyl ketyl radicals (Eq. (14)). The reported rate constants k_{BP} for this reaction are at variance, ranging from 10^4 M^{-1} s^{-1} to 10^9 M^{-1} s^{-1} [16,28,29]. If $k_{BP} = 10^9$ M^{-1} s^{-1}, all dimethyl ketyl radicals are expected to react according to Eq. (14), and thus CV$^+$ would not be reduced to CV$^{\bullet}$ according to Eq. (13). In this case the shapes of the curves in Figs. 3 and 4 should be similar. However, the steady increase in the quantum yield of dye conversion with increasing 2-propanol concentration strongly indicates the involvement of the dimethyl ketyl radical in the reduction process (Eq. (13)). Therefore, our results are consistent with the low value of the rate constant: $k_{BP} = 3.5 \times 10^4$ M^{-1} s^{-1} [16].

$$
\underset{\text{H}_3\text{C}}{\overset{\text{OH}}{\text{C}}}_{\text{CH}_3} + \text{BP} \xrightarrow{k_{BP}} \underset{\text{H}_3\text{C}}{\overset{\text{O}}{\text{C}}}_{\text{CH}_3} + \underset{\text{Ph}}{\overset{\text{OH}}{\text{C}}}_{\text{Ph}} \quad (14)
$$

3.2. Reaction of dyes with α-amino radicals

α-amino radicals can be generated by irradiating solutions containing BP and amines (Eq. (1)). Acetonitrile solutions containing BP, TEOA and PS$^+$ were irradiated with 15 ns
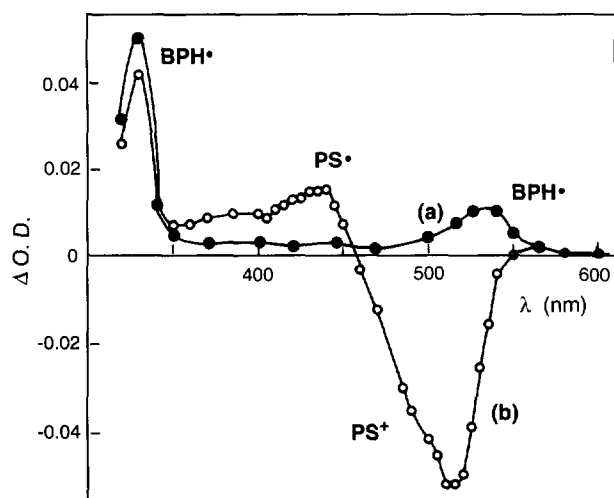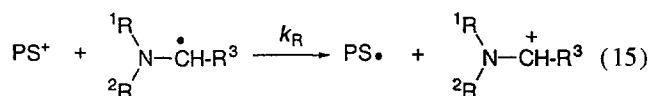
Fig. 5. Transient optical absorption spectra recorded at the end (spectrum a) and 15 μs (spectrum b) after irradiation of an argon-saturated acetonitrile solution containing BP (1×10^{-3} M), TEOA (1×10^{-2} M), and PS$^+$ (4×10^{-5} M) with a laser flash ($\lambda_{ex} = 347$ nm; 23 °C; $D_{abs} = 2.3 \times 10^{-6}$ einstein l^{-1}).

laser flashes ($\lambda_{ex} = 347$ nm). The concentration of amine was kept high enough to prevent quenching of ^{3}BP* by the dye via triplet–triplet energy transfer [22]. During the laser pulse both α-amino and diphenyl ketyl radicals were formed. The ketyl radicals were detected by their transient absorption at 330 nm and 530 nm [17,18] (Fig. 5). After the flash PS$^+$ is converted to the semireduced dye (PS$^\cdot$), which absorbs at 430 nm [21]. Meanwhile, the absorption of diphenyl ketyl radicals decreases slightly owing to a slow reaction of PS$^+$ with ketyl radicals (Eq. (3)). Thus, PS$^+$ is mainly reduced by α-amino radicals:

$$PS^+ + \overset{1R}{\underset{2R}{N}}-\overset{\cdot}{C}H\text{-}R^3 \xrightarrow{k_R} PS\cdot + \overset{1R}{\underset{2R}{N}}-\overset{+}{C}H\text{-}R^3 \quad (15)$$

The rate constants for the reaction of different dyes with α-amino radicals were obtained from plots similar to those shown in Fig. 2 and are compiled in Table 1. The rate constants decrease in the order MB$^+$ > TP$^+$ > PS$^+$, corresponding to a decrease in the reduction potentials of the dyes.

3.3. Reduction of dye mixtures by radicals

Because organic dyes typically absorb light only in a rather narrow region of the visible wavelength range, dye mixtures are employed in initiator systems to utilize polychromatic light more effectively [3]. In such mixtures a sequence of reactions occurs as will be discussed below.

3.3.1. System PS$^+$–CV$^+$–BP–TEOA

Acetonitrile solutions containing PS$^+$, CV$^+$, BP, and TEOA were continuously irradiated at 365 nm, where BP strongly absorbs the light. After intersystem crossing ^{3}BP* is produced. In order to prevent quenching of ^{3}BP* by the

dyes, a high concentration of amine (1×10^{-2} M) was employed. In this case ^{3}BP* essentially reacts with the amine to form α-amino and ketyl radicals. As discussed above, both radicals are capable of reducing the dyes. Notably, under these conditions, only PS$^+$ but not CV$^+$ is converted. The optical absorption of CV$^+$ is not bleached, as can be seen from spectra 1–3 in Fig. 6. However, after PS$^+$ is completely converted, bleaching of CV$^+$ commences and simultaneously an absorption band at 400 nm (spectra 4 and 5) corresponding to the CV$^\cdot$ is formed [26,30]. These results are rather unexpected, because the rate constants of the reaction of both dyes with α-amino and ketyl radicals are of the same magnitude (Table 1). Accordingly, both dyes should be converted at comparable rates.

The unexpected behavior depicted in Fig. 6 could be explained by laser flash experiments. Solutions containing PS$^+$, CV$^+$, BP, and TEOA were irradiated with 15 ns flashes at 347 nm. Kinetic traces recorded at different wavelengths are shown in Fig. 7. Immediately after the laser pulse the absorption of both dyes, PS$^+$ (Fig. 7(a)) and CV$^+$ (Fig. 7(d)), is bleached as a result of the reaction of the dyes with α-amino radicals. The reduction by diphenyl ketyl radicals is negligible in this time range, because the rate constant for this reaction is much lower than that of the reaction of the α-amino radicals (Table 1). Later, the optical absorption of CV$^\cdot$ decreases (Fig. 7(c)), which gives rise to an additional conversion of PS$^+$ (Fig. 7(a)) and the re-formation of CV$^+$ (Fig. 7(d)). The kinetic trace at 405 nm (Fig. 7(c)) presents the combined changes in the absorption of both semireduced
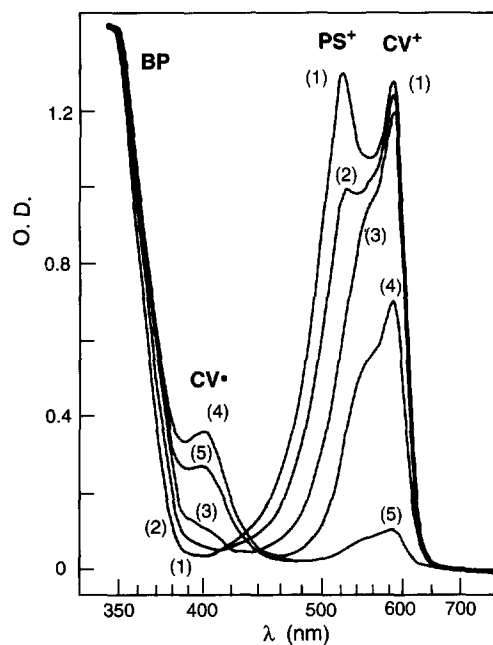

Fig. 6. Continuous irradiation of the system CV$^+$–PS$^+$–BP–TEOA in argon-saturated acetonitrile solution ($\lambda_{ex} = 365$ nm; 20 °C; [CV$^+$] $= 1 \times 10^{-5}$ M; [PS$^+$] $= 2 \times 10^{-5}$ M; [BP] $= 1 \times 10^{-2}$ M; [TEOA] $= 1 \times 10^{-2}$ M); optical absorption spectra recorded after irradiation at D_{abs} ($\times 10^{-6}$ einstein l^{-1}) $= 0$ (spectrum 1), 3.8 (spectrum 2), 7.6 (spectrum 3), 11.4 (spectrum 4), 15.2 (spectrum 5).
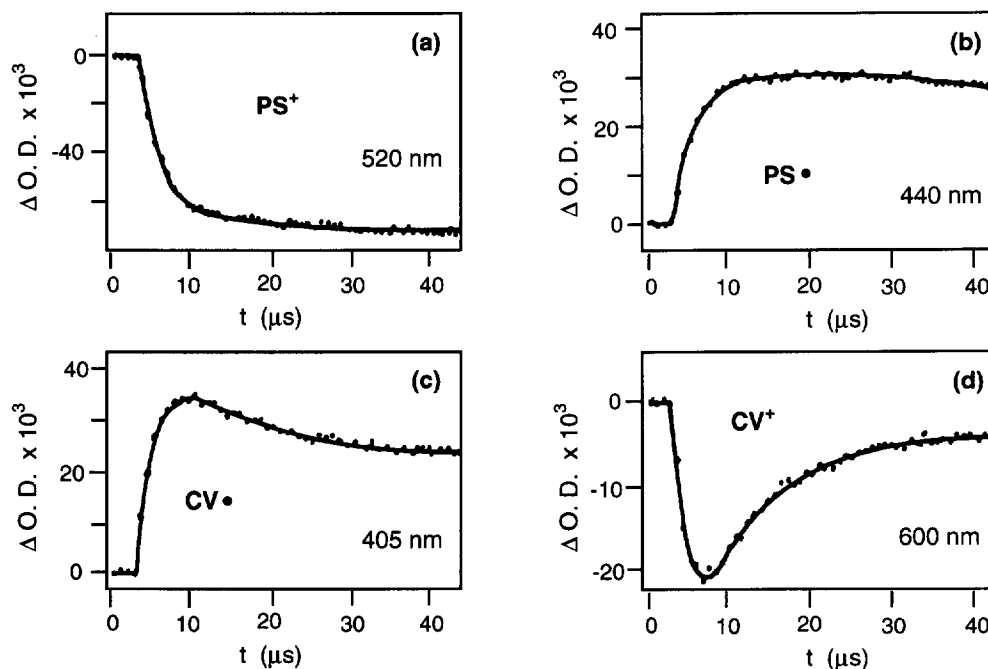
Fig. 7. Kinetic traces recorded at different wavelengths following laser flash photolysis ($\lambda_{ex} = 347$ nm; 23 °C; $D_{abs} = 2.3 \times 10^{-6}$ einstein l^{-1}) of the system CV^+–PS^+–BP–TEOA in argon-saturated acetonitrile solution ($[CV^+] = 2 \times 10^{-5}$ M; $[PS^+] = 6 \times 10^{-5}$ M; $[BP] = 1 \times 10^{-3}$ M; $[TEOA] = 1 \times 10^{-2}$ M).

dyes. In conclusion, the reformation of CV^+ is caused by the oxidation of the crystal violet radical by PS^+:

$$CV^\bullet + PS^+ \xrightarrow{k_{CV-PS}} CV^+ + PS^\bullet \qquad (16)$$

Pseudo-first-order kinetic treatment of the recovery of CV^+ at 600 nm based on experiments at various concentrations of PS^+ yields the rate constant $k_{CV-PS} = 2 \times 10^9$ M^{-1} s^{-1}. Most of the $PS^\bullet$, produced by reactions (15) and (16), undergoes disproportionation (Eq. (4)). On the basis of reaction (16) the bleaching behavior observed with continuous irradiation can be explained. Both PS^+ and CV^+ are reduced by α-amino and ketyl radicals. However, CV^+ is re-formed by the fast reaction (16), and, therefore, its conversion is not observable during continuous irradiations (Fig. 6, spectra 2 and 3) until PS^+ is completely consumed (Fig. 6, spectra 4 and 5).

3.3.2. System MB^+–CV^+–BP–TEOA

By continuous irradiation of acetonitrile solutions containing MB^+, CV^+, BP, and TEOA bleaching of the UV–visible spectra was observed. During irradiation MB^+ is completely converted, at first, while the concentration of CV^+ does not change (Fig. 8, spectra 1–3). The small decrease in the optical absorption at ca. 590 nm is caused by an overlay of the absorption of both dyes. At later times the CV^+ absorption is bleached (spectra 4–6). Similar laser experiments as described above were also performed in this case at 355 nm using an Nd–YAG laser. In these experiments $CV^\bullet$ was oxidized by MB^+:

$$CV^\bullet + MB^+ \xrightarrow{k_{CV-MB}} CV^+ + MB^\bullet \qquad (17)$$
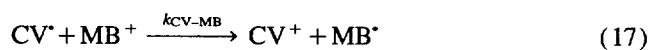
$MB^\bullet$ could be detected by its absorption at 430 nm [31]. The rate constants were measured as described in Section 3.3.1. In this case the growth of CV^+ was recorded at 550 nm because the optical absorption of MB^+ is negligible at this wavelength. The higher rate constant ($k_{CV-MB} = 3 \times 10^9$
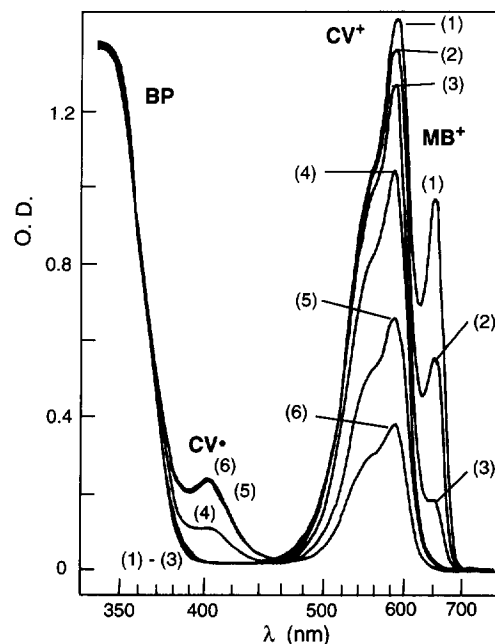

Fig. 8. Continuous irradiation of the system CV^+–MB^+–BP–TEOA in argon-saturated acetonitrile solution ($\lambda_{ex} = 365$ nm; 20 °C; $[CV^+] = 1 \times 10^{-5}$ M; $[MB^+] = 1 \times 10^{-5}$ M; $[BP] = 1 \times 10^{-2}$ M; $[TEOA] = 1 \times 10^{-2}$ M); optical absorption spectra recorded after irradiation at D_{abs} ($\times 10^{-6}$ einstein l^{-1}) = 0 (spectrum 1), 3.8 (spectrum 2), 7.6 (spectrum 3), 11.4 (spectrum 4), 15.2 (spectrum 5), 19.0 (spectrum 6).
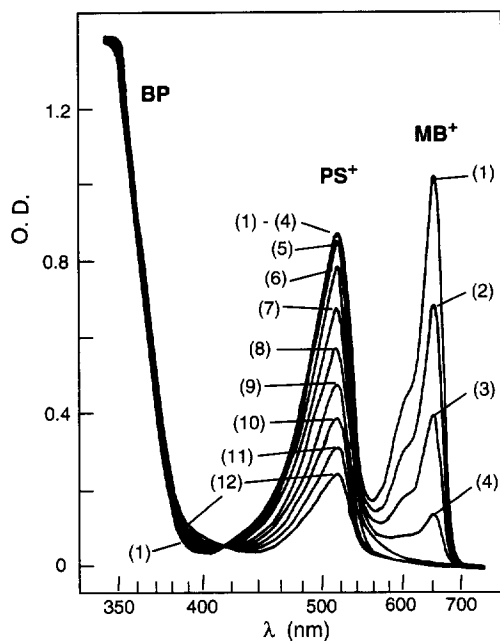
Fig. 9. Continuous irradiation of the system $MB^+-PS^+-BP-TEOA$ in argon-saturated acetonitrile solution ($\lambda_{ex}=365$ nm; 20 °C; $[MB^+]$ $=1\times10^{-5}$ M; $[PS^+]=2\times10^{-5}$ M; $[BP]=1\times10^{-2}$ M; $[TEOA]=$ 1×10^{-2} M); optical absorption spectra recorded after irradiation at doses absorbed in increments of 3.8×10^{-6} einstein l^{-1} ($D_{abs}=0$ einstein l^{-1} (spectrum 1), $D_{abs}=4.56\times10^{-5}$ einstein l^{-1} (spectrum 12)).

reaction	1	2	3	4	5	6	7
rate constant $(10^9 \text{ M}^{-1} \text{ s}^{-1})$	3.3	7.5	2.7	5.0	2.0	3.0	3.5

Scheme 2. System $^3BP^*-TEOA-MB^+-CV^+-PS^+$: the rate constant for step 1 was obtained by pseudo-first-order kinetic treatment of the phosphorescence decay of BP at 450 nm using a pulsed Nd–YAG laser at 355 nm.

M^{-1} s^{-1}) of MB^+ compared with that measured with PS^+ ($k_{CV-PS}=2\times10^9$ M^{-1} s^{-1}) can be explained by the higher reduction potential of MB^+ (Table 1).

3.3.3. System $MB^+-PS^+-BP-TEOA$

Acetonitrile solutions consisting of MB^+, PS^+, BP, and TEOA were irradiated continuously at 365 nm and the optical absorption spectra shown in Fig. 9 were recorded. Also in this case a stepwise bleaching of the dye absorptions occurs, MB^+ being converted initially and PS^+ subsequently:

$$PS^\cdot + MB^+ \xrightarrow{k_{PS-MB}} PS^+ + MB^\cdot \qquad (18)$$

In this case we were not able to measure the rate constant as described in Sections 3.3.1 and 3.3.2 owing to the large number of side reactions the dye radicals undergo. Therefore, $PS^\cdot$ was produced directly by irradiation of an acetonitrile

solution consisting of PS^+, MB^+ and TEOA at 532 nm with an Nd–YAG laser beam. The reaction of $^3(PS^+)^*$ with amines is fast and results in the reduction of the dye:

$$^3(PS^+)^* + AH \xrightarrow{k} PS^\cdot + AH^{+\cdot} \qquad (19)$$
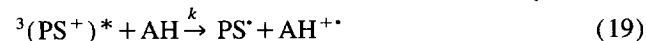
For this reaction a rate constant $k=2.8\times10^9$ M^{-1} s^{-1} was reported in the case of triethyl amine [21]. It is expected to be similar to that concerning the reduction of PS^+ with TEOA, because the oxidation potentials of these amines are similar. $PS^\cdot$ generated by the reduction of $^3(PS^+)^*$ by the amine was reoxidized by MB^+ (Eq. (18)). Kinetic traces recorded at the ground state absorption maxima of both dyes evidence the occurrence of this reaction (Fig. 10). The rate constant ($k_{PS-MB}=3.5\times10^9$ M^{-1} s^{-1}) was obtained by pseudo-first-order kinetic treatment of the growth of the PS^+ absorption at various MB^+ concentrations.

3.3.4. System $MB^+-CV^+-PS^+-BP-TEOA$

To confirm the results presented in Sections 3.3.1–3.3.3, the mutual interactions of the three systems were studied. A solution containing the three dyes, BP, and TEOA was
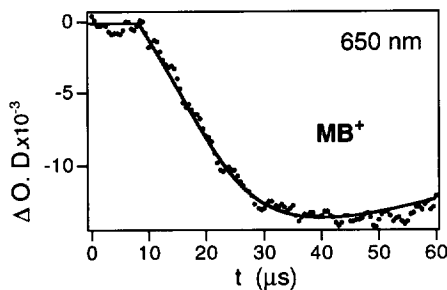

Fig. 10. Kinetic traces recorded at different wavelengths following laser flash photolysis ($\lambda_{ex}=532$ nm) of the system MB^+-PS^+-TEOA in argon–saturated acetonitrile solution ($[MB^+]=3\times10^{-5}$ M; $[PS^+]=2\times10^{-5}$ M; $[TEOA]=1\times10^{-2}$ M).
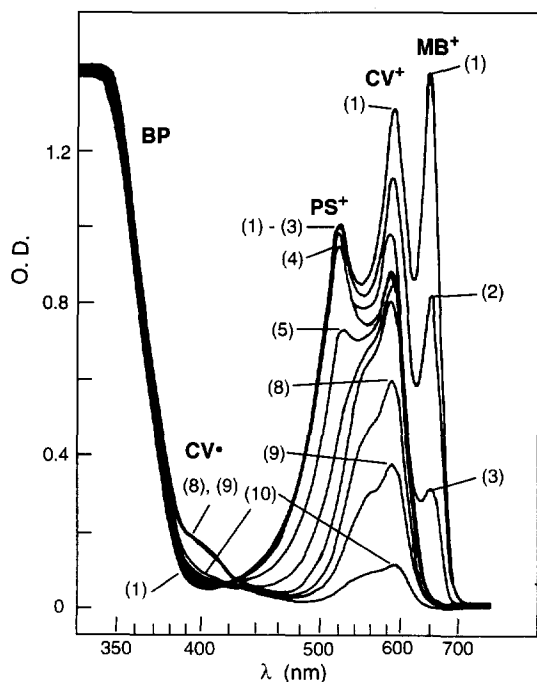
Fig. 11. Continuous irradiation of the system MB^+–CV^+–PS^+–BP–TEOA in argon-saturated acetonitrile solution ($\lambda_{ex}=365$ nm; 20 °C; $[MB^+]=1.4\times10^{-5}$ M; $[CV^+]=1\times10^{-5}$ M; $[PS^+]=2\times10^{-5}$ M; $[BP]=1\times10^{-2}$ M; $[TEOA]=1\times10^{-2}$ M); optical absorption spectra recorded after irradiation at doses absorbed in increments of 5.7×10^{-6} einstein l^{-1} ($D_{abs}=0$ einstein l^{-1} (spectrum 1), $D_{abs}=5.7\times10^{-5}$ einstein l^{-1} (spectrum 10)).

irradiated continuously at 365 nm and the optical absorption spectra shown in Fig. 11 were obtained. Spectrum 1 demonstrates the situation prior to irradiation. During the irradiation, a stepwise conversion of the dyes occurs. At first MB^+ is converted completely (spectra 2 and 3), subsequently PS^+ (spectra 4–6), and, lastly, CV^+ (spectra 7–10). The overall reaction mechanism is summarized in Scheme 2.

The observed bleaching behavior is in good agreement with the results reported in Sections 3.3.1–3.3.3. The same stepwise bleaching of the dye absorption can be initiated by the diphenyl ketyl radical. At the end of the reaction sequence the semireduced dyes undergo disproportionation analogous to reaction (4).

4. Conclusions

Organic cationic dyes are reduced effectively by nucleophilic radicals such as α-amino and ketyl radicals, the former being more reactive than the latter. The rate constants determined in the case of the heteroanthracene-type dyes (MB^+, TP^+, and PS^+) exhibit a strong dependence on their reduction potentials. The primary products are semireduced dyes which undergo subsequent disproportionation, yielding the leuco dye and the dye cation.

When mixtures of dyes are used in ketone–amine–dye systems, some additional reactions are observed. Some of the primarily formed semireduced dyes are capable of reducing other dyes very efficiently.

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