

Triplet-sensitized photobleaching of crystal violet

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Abstract

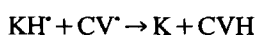
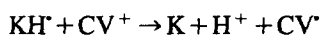
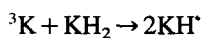
Crystal violet (CV^+) and five related triarylmethane dyes quench triplet benzophenone (3K) in acetonitrile at diffusion-controlled rates ($k_q \approx 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). The interaction with CV^+ results in bleaching of CV^+ with a quantum yield, $^K\Phi(-CV^+)$, dependent on the concentration of CV^+ with a limiting value of 0.2 at high $[CV^+]$. Benzopinacol (K_2H_2) is also formed in this reaction but its yield decreases as $[CV^+]$ increases. In contrast, although both triplet anthracene (3An) and triplet naphthalene (3Nap) are also efficiently quenched by CV^+ at diffusion-controlled rates, there is only very inefficient fading, $^{An}\Phi(-CV^+) = 1.1 \times 10^{-5}$. These results are interpreted in terms of a mechanism in which energy transfer to form triplet crystal violet, $^3CV^+$, is the only major channel in the case of anthracene and naphthalene, i.e. $^3CV^+$ (like $^1CV^+$) is unreactive. However, in the case of benzophenone, reduction of 3K by CV^+ with a rate constant $k_h = 1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ to form ketyl radicals (KH^\cdot) can compete (about 14%) with this energy transfer. The ketyl radicals so formed can either reduce CV^+ to form leuco crystal violet (CVH) or form benzopinacol.

Keywords: Triplet sensitization; Photobleaching; Crystal violet

1. Introduction

In fluids of normal viscosity triarylmethane dyes (D^+), such as crystal violet (CV^+), decay from the first excited singlet state (S_1) to the ground state (S_0) in a few picoseconds bypassing the triplet manifold [1] and quantum yields for direct photobleaching are very low, about 10^{-4} [2].

As we shall see below, the triplet state of crystal violet ($^3CV^+$), which can be produced by sensitization, also has little intrinsic reactivity. Indeed, stability of excited singlet and triplet states is generally a desirable feature of a dye. However, if a triplet sensitizer which can generate a reducing species by hydrogen abstraction is used then the dye may be bleached. Thus, in a previous paper [2] we showed that when benzophenone (K) is present in samples containing a hydrogen donor such as 2-propanol (AH_2) or benzhydrol (KH_2), photolysis results in triplet benzophenone (3K) which abstracts a hydrogen from AH_2 and KH_2 to form ketyl radicals AH^\cdot and KH^\cdot respectively, which then reduce the dye to the leuco form (CVH):



Ketyl radicals are good reducing agents by virtue of the reaction $R_2\dot{C}OH \rightarrow R_2C=O + H^+ + e^-$, significant thermodynamic driving force being gained from the formation of the carbonyl double bond. The leuco form CVH , the two-electron reduction product of CV^+ , can be quantitatively oxidized back to CV^+ by a suitable oxidizing agent [2].

In this paper we report on the 3K -induced fading of CV^+ in the absence of added reducing agent and show that the dye itself serves as a hydrogen source for 3K , forming KH^\cdot which also leads to bleaching of the dye.

2. Experimental details

Sample preparation, product analyses and irradiation procedures were in general the same as previously described [2,3]. The 200 W mercury–xenon arc–monochromator combination had an intensity of about 2.3 mJ s^{-1} at 366 nm. The YAG laser delivered about 6 mJ in 15 ns at 355 nm. Crystal violet chloride, CV^+ (Aldrich 95%), and ethyl violet (Aldrich) were recrystallized from water. Malachite green chloride (Aldrich) was used as received. Rosaniline (Eastman Kodak) and pararosaniline (Aldrich) were recrystallized from methanol. Naphthalene (Fischer) and benzophenone, K (Aldrich), were recrystallized from ethanol.

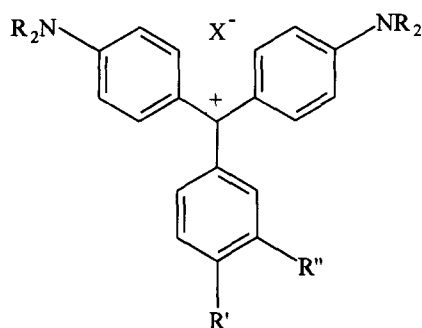


Fig. 1. Triarylmethane dyes.

Anthracene, An (Pilot scintillation grade), and 1,2,5,6-benzanthracene (Aldrich) were used as received. Regeneration of crystal violet from bleached photolysates (see Fig. 4) using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone was carried out as previously described [2,4].

All samples (3 ml, 1 cm pathlength) for quenching constant measurements (see Table 1 and Section 3.3), CV⁺ bleaching (see Figs. 2 and 4), and K₂H₂ formation (see Fig. 3) were degassed by freeze–thaw cycles on a high vacuum line. Samples for laser transient spectroscopy of K–CV⁺ and An–CV⁺ were purged with argon for 5 min. Bleaching quantum yields for CV⁺ were determined by following the decrease in absorbance at 590 nm over the first 25% conversion. Benzopinacol quantum yields were determined by high performance liquid chromatography analysis of the products after 25% consumption of CV⁺. Quenching constants for ³K by D⁺X⁻ dyes were determined either by steady phosphorescence intensity quenching or by lifetime measurements using a weak 0.5 μs light source to excite the benzophenone

Table 1
Quenching rate constants k_q for triplet benzophenone by triarylmethane dyes in acetonitrile

Dye	k_q (M ⁻¹ s ⁻¹)
Crystal violet chloride	(1.00 ± 0.09) × 10 ¹⁰ ^a (1.00 ± 0.13) × 10 ¹⁰ ^b
Crystal violet oxalate	(0.91 ± 0.09) × 10 ¹⁰ ^a
Ethylviolet chloride	(1.04 ± 0.09) × 10 ¹⁰ ^a
Malachite green chloride	(0.98 ± 0.02) × 10 ¹⁰ ^a (1.11 ± 0.13) × 10 ¹⁰ ^b
Rosaniline chloride	(0.82 ± 0.09) × 10 ¹⁰ ^a
Pararosaniline chloride	(1.08 ± 0.09) × 10 ¹⁰ ^a

^a Determined by lifetime measurements.

^b Phosphorescence intensity quenching.

[5]. The quenching rate constant for the interaction of crystal violet with ³An was obtained by laser flash photolysis using 355 nm excitation from a YAG laser [3a] and by monitoring the decay of ³An at 418 nm in the absence and presence of CV⁺. Triplet anthracene absorption spectra were measured using an EG&G PAR OMA2 multichannel detection system with a 1 μs delay between laser excitation and detection. There is a fortuitous trough in the 405 nm region which allows detection of the build-up and decay of the “405” species. Kinetic experiments were carried out using conventional laser kinetic spectroscopy at fixed wavelengths [3a,6].

3. Results and discussion

3.1. Rate constants for interaction of triplet benzophenone with triarylmethane dyes

Triarylmethane dyes (D⁺X⁻) (Fig. 1) quench ³K at diffusion-controlled rates in acetonitrile (Table 1). Two methods were employed to determine quenching rate constants k_q . (i) Variation in the lifetime of ³K on addition of the dye D⁺ [5] was measured, employing a low intensity flash to avoid any photobleaching. The reciprocal (1/τ) of the lifetime in the presence of the dye was found to be linearly dependent on the concentration [D⁺] of the dye and k_q was then calculated by least-squares analysis from 1/τ = 1/τ₀ + k_q [D⁺], where τ₀ is the lifetime of ³K in the absence of D⁺. (ii) Steady state room temperature phosphorescence intensities I_0 and I of ³K were measured in the absence and presence respectively of varying concentrations of D⁺ [5], $I_0/I = 1 + \tau_0 k_q [D^+]$, where τ₀ was first determined by the flash method.

Table 1 shows that both methods give excellent agreement. The value of k_q for CV⁺ agrees well with that reported previously [2], but is somewhat smaller than that reported by Jockusch et al. [7]. Subsequent studies were limited to crystal violet chloride CV⁺.

3.2. Bleaching of crystal violet and the formation of benzopinacol

As stated in the introduction CV⁺ has been shown to be stable to direct photolysis for irradiation wavelengths greater than 350 nm [2]. However, irradiation at 366 nm (using a 200 W mercury–xenon arc–monochromator source) of degassed acetonitrile solutions of CV⁺ together with 1.15 × 10⁻⁴ M benzophenone resulted in rapid fading with sensitized quantum yields $^3\Phi(-CV^+)$ for CV⁺ consumption as a function of [CV⁺] shown in Fig. 2. These data as well as following results are discussed in terms of Scheme 1.

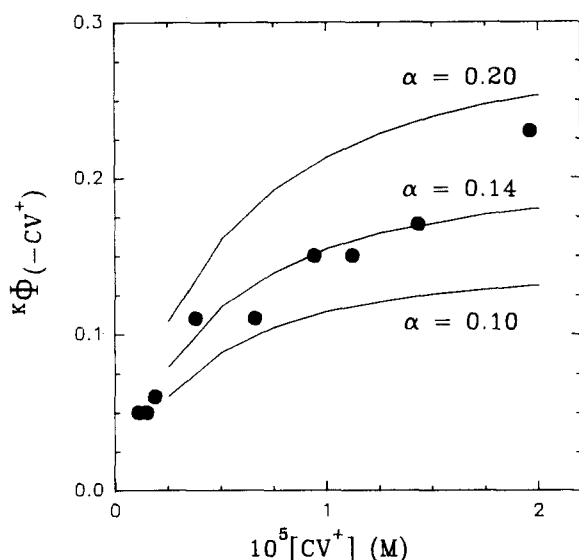
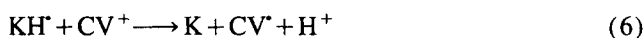
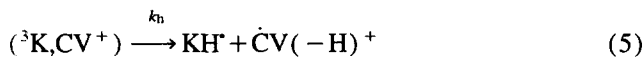
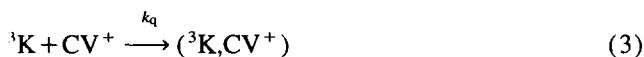


Fig. 2. Quantum yields of crystal violet consumption for the benzophenone (1.15×10^{-4} M) sensitized fading in acetonitrile. Model curves (—) are discussed in the text. Quantum yields $\kappa\Phi(-CV^+)$ based on light absorption by benzophenone, K.



Scheme 1.

In the absence of any added reducing agents or CV^+ , the decay of 3K occurs with lifetime τ_0 and is represented by the pseudo-first-order processes shown in reactions (2a) and (2b), so that $1/\tau_0 = k_d = k_{2a}[CH_3CN] + k_{2b}$. Although acetonitrile is a solvent of low reactivity, $k_{2a} = 130 \text{ M}^{-1} \text{ s}^{-1}$ [3a], reaction (2a) has to be considered as a source of KH' radicals because of the high concentration, 19 M, of the solvent.

By virtue of the presence of the amino group triarylmethane dyes form an interesting class of photoreductants. Photoreduction of aromatic ketones by amines has been extensively studied [8–13]. Often photoreduction proceeds by electron transfer from the amine to 3K to form a charge transfer complex which is followed by proton transfer to generate ketyl and aminyl radicals. Although the individual

steps may involve electron and proton transfer, the net result is H atom transfer. By analogy with such reactions we propose that CV^+ can also act as an H atom source for 3K . This is represented in Scheme 1 when the primary interaction of CV^+ with 3K , reaction (3), is followed by reaction (5). We represent the oxidized species formed by hydrogen loss from the dimethylamino group of CV^+ by the rather infelicitous nomenclature $\dot{C}V(-H)^+$ to retain consistency with our previous nomenclature and to indicate both its radical nature and that it has one H atom less than the parent CV^+ .

Reactions (6) and (7), which we have discussed previously [2], represent the reduction of ground state CV^+ by KH' to yield leuco crystal violet, CVH, while reaction (8) is the dimerization of the radicals to yield benzopinacol, K_2H_2 .

Steady state analysis for KH' yields

$$\frac{I_{abs}}{k_d + k_q[CV^+]} (k_{2a}[CH_3CN] + \alpha k_q[CV^+]) = 2k_g[KH']^2 + 2k_6[KH'][CV^+] \quad (9)$$

where $\alpha = k_h/(k_h + k_g)$. Also, the quantum yield for consumption of CV^+ is given by

$$\kappa\phi(-CV^+) = \frac{k_6[KH'][CV^+]}{I_{abs}} + \frac{\alpha k_q[CV^+]}{k_d + k_q[CV^+]} \quad (10)$$

In Eq. (9), I_{abs} , k_d , k_q are measured while k_{2a} , k_g and k_6 are known from previous work [2,3a]; thus $[KH']$ can be determined at any desired $[CV^+]$ for different trial α values. Substitution of these values into Eq. (10) generates the model curves displayed in Fig. 2. In comparing the model with the experimental data it will be seen that the best value of α is about 0.14. Thus the second-order abstraction of hydrogen by 3K from CV^+ has rate constant $[k_h/(k_h + k_g)] k_q \approx 0.14 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. This rate constant is comparable with the value of $0.27 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for the reaction of *N,N*-dimethylaniline with 3K [14]. This is not surprising since the oxidation potential for *N,N*-dimethylaniline, 0.81 V [15], is similar to that of CV^+ , 0.80 V [16].

Because of the strong CV^+ absorption (see Fig. 4(a)), we could not detect the presence of KH' directly by absorption in the characteristic 525 nm region [3a] in laser flash experiments. However, good evidence for the production of these radicals is the formation of benzopinacol, K_2H_2 , reaction (8). The yields for K_2H_2 as a function of $[CV^+]$ are shown in Fig. 3. The data in Figs. 2 and 3 indicate that as $[CV^+]$ decreases the yield of K_2H_2 increases and concomitantly the bleaching yield decreases. This comes about because KH' is required for the formation of CVH (reactions (6) and (7)) and this reaction by competing for KH' reduces the yield of K_2H_2 . Using Eqs. (9) and (11),

$$\kappa\phi(K_2H_2) = \frac{k_8[KH']^2}{I_{abs}} \quad (11)$$

Fig. 3 shows model curves for the quantum yields of benzopinacol as a function of $[CV^+]$ using different values of α .

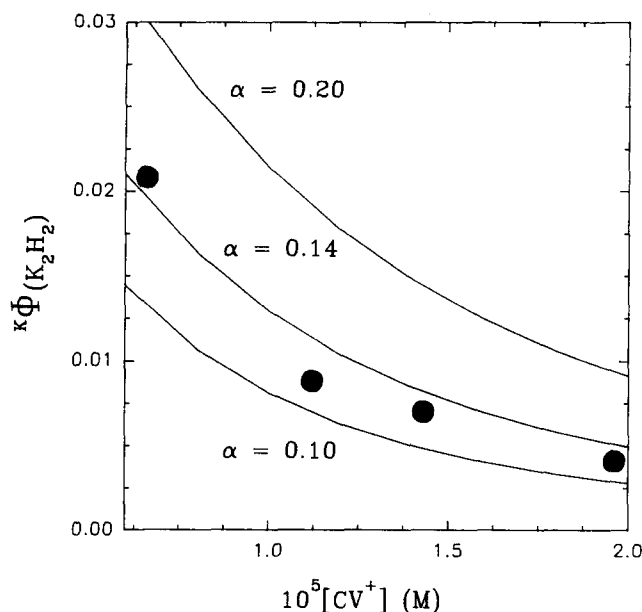


Fig. 3. Quantum yields (●) of benzopinacol formation for the benzophenone (1.15×10^{-4} M) sensitized fading of crystal violet in acetonitrile, —, model curves discussed in text.

The best value of α , 0.14, agrees nicely with the previous determination.

In a previous paper [2] we reported on the sensitized bleaching of CV^+ when all 3K was intercepted by good hydrogen donors such as isopropanol or benzhydrol (KH_2). Under these conditions, reaction (5) is unimportant and crystal violet can be reduced quantitatively to CVH by KH . This is demonstrated by the nearly complete recovery of CV^+ when a solution of $K-KH_2-CV^+$ which has been bleached by photolysis is oxidized by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (Q), Fig. 4(a). However, when no added KH_2 is present, although there is still total photobleaching, there is only partial recovery of CV^+ on oxidation, Fig. 4(b), because now some of the CV^+ has been used up in reaction (5) which does not yield CVH . In both cases regeneration of CV^+ is accompanied by the formation of another species which absorbs in the 400–600 nm region. Deconvolution of spectra 3a and 3b yielded $95\% \pm 4\%$ and $40\% \pm 7\%$ recovery of CV^+ in the cases of Figs. 4(a) and 4(b) respectively.

3.3. Reaction of crystal violet with triplet anthracene and triplet naphthalene

Since the triplet energy E_T of CV^+ , 39 kcal mol^{-1} [17], is less than that of K , 69 kcal mol^{-1} [16], we expect efficient electronic energy transfer from 3K to yield ${}^3CV^+$. That this occurs is indicated by the diffusion-controlled values for the interaction rate constants k_q , Table 1. We believe that the “wastage” process, i.e. reaction (3) followed by reaction (4), largely represents energy transfer to form ${}^3CV^+$ followed by relaxation of the unreactive ${}^3CV^+$ back to the ground state. This was demonstrated in two ways.

(1) The triplet energy for anthracene (An), 43 kcal mol^{-1} [18], is significantly greater than that for CV^+ . Using a YAG laser to produce 3An , the quenching rate constant for CV^+ with 3An was found to be about $2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which is again close to diffusion controlled and so we again expect efficient formation of ${}^3CV^+$. However, in contrast to benzophenone, when anthracene ($1.01 \times 10^{-4} \text{ M}$) was irradiated at 366 nm in the presence of enough CV^+ ($5.88 \times 10^{-6} \text{ M}$) to intercept most of the 3An , but none of the 1An (the lifetime of excited singlet anthracene is 13.8 ns; see Ref. [19]), the yield ${}^{An}\Phi(-CV^+)$ of sensitized bleaching was very low, 1.1×10^{-5} . Similarly, when anthracene was replaced by 1,2,5,6-dibenzanthracene ($1.8 \times 10^{-4} \text{ M}$, $E_T = 52 \text{ kcal mol}^{-1}$ [18]), the sensitized quantum yield was also low, 4×10^{-5} . This indicates that the species formed on quenching is *inherently unreactive*. Also, laser flash photolysis of degassed acetonitrile solutions of both $K-CV^+$ and $An-CV^+$ resulted in rather similar kinetic spectral behaviour, i.e. bleaching of the CV^+ absorption at 590 nm with concomitant build-up of a transient which absorbed at 405 nm. It is well known that CV^+ absorbs at 405 nm and in discussing the quenching of 3K by CV^+ it has been proposed that the major channel is electron transfer, ${}^3K + CV^+ \rightarrow K^+ + CV^-$ [7]. In agreement with Jones and Goswami [20], we believe that ${}^3CV^+$ also absorbs strongly in this region. A simple explanation which encompasses the results for both the n, π^* and π, π^* sensitizers is that in both cases unreactive ${}^3CV^+$ is formed but that, in the case of 3K , the latter may also be reduced by CV^+ acting in its role as an aromatic amine.

(2) The fact that an aromatic triplet was readily quenched by CV^+ without any bleaching of the latter suggested a simple method of avoiding CV^+ bleaching in a system in which there is a potentially active sensitizer such as 3K present, namely to add a quencher which can compete with CV^+ for 3K but whose triplet will not result in CV^+ bleaching. Such a compound is naphthalene (Nap) because it does not absorb at the radiation wavelength (366 nm) and has $E_T = 61 \text{ kcal mol}^{-1}$ [18], which is less than $E_T(K)$. When naphthalene was added to $K-CV^+$ and the solution irradiated using

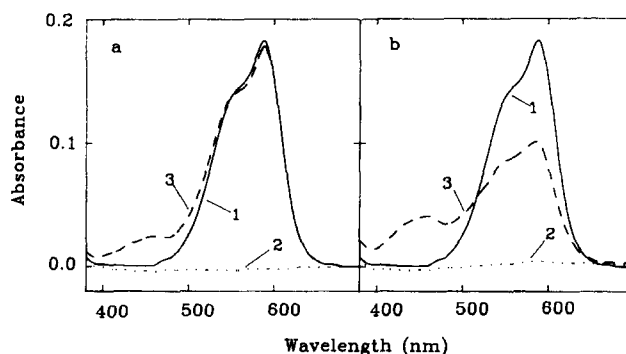


Fig. 4. Benzophenone (1.5×10^{-4} M) sensitized fading of crystal violet (1.8×10^{-6} M) and oxidation of resultant leuco dye in (a) the presence and (b) the absence of benzhydrol (5.4×10^{-2} M): spectra 1, initial spectra; spectra 2, after irradiation to complete bleaching; spectra 3, after addition of $20 \mu\text{l}$ of 2×10^{-3} M quinone (Q) to 3 ml bleached sample.

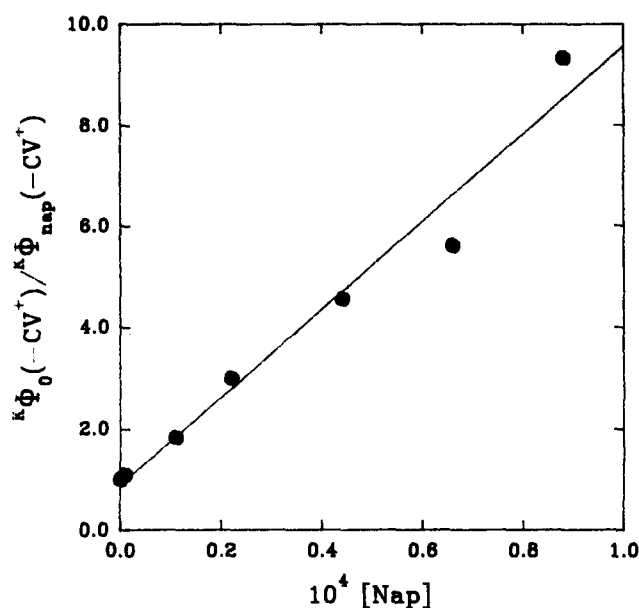


Fig. 5. Naphthalene quenching of benzophenone (5.2×10^{-5} M) sensitized fading of crystal violet (1.9×10^{-6} M) in acetonitrile.

366 nm light from the mercury–xenon arc–monochromator source, the bleaching was indeed strongly quenched as can be seen by the data in Fig. 5. We now have a competition for ^3K between CV^+ (reaction (6)) and Nap (reaction (12)):



From this we expect

$$\frac{K\phi_0(-CV^+)}{K\phi_{\text{Nap}}(-CV^+)} = 1 + \frac{k_{12}}{k_q[\text{CV}^+] + k_d} [\text{Nap}] \quad (13)$$

where $K\phi_{\text{Nap}}(-CV^+)$ and $K\phi_0(-CV^+)$ symbolize the benzophenone-sensitized quantum yield for the consumption of CV^+ in the presence and absence of naphthalene. Using $k_d = 5 \times 10^4 \text{ s}^{-1}$, $k_q = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $[\text{CV}^+] = 1.9 \times 10^{-6} \text{ M}$ and the slope $((8.7 \pm 0.7) \times 10^4 \text{ M}^{-1})$ in Fig. 5, we obtain $k_{12} = 6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, close to the expected diffusion-controlled value [21]. At the low light intensities used, the steady state concentration of ^3Nap will be quite low so that the lifetime of this species is long [18], and it will be intercepted by CV^+ to form $^3\text{CV}^+$. Thus the quenching of fading is further evidence that $^3\text{CV}^+$ is unreactive.

4. Conclusions

(1) Crystal violet (CV^+) is inherently stable to direct photolysis since both the excited singlet (S_1) and the triplet (T_1) are unreactive.

(2) In the presence of a sensitizer such as benzophenone (K) which can form ketyl radicals (KH^\cdot) in the presence of a hydrogen donor, e.g. $^3\text{K} + \text{KH}_2 \rightarrow 2\text{KH}^\cdot$, CV^+ can be reduced quantitatively to the leuco form CVH by the ketyl

radicals (KH^\cdot). In turn the leuco form can be oxidized back quantitatively to CV^+ .

(3) When no hydrogen donor is present then CV^+ reacts directly with ^3K at a diffusion-controlled rate, with $k_q = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. The major channel appears to be triplet energy transfer, but in that CV^+ is an aromatic amine it can also act as a hydrogen source. Thus KH^\cdot is again generated together with the oxidized dye radical, $\text{CV}(-\text{H})^+$. As before, the KH^\cdot radicals reduce CV^+ to CVH. However, in this case, since some of the dye is oxidized, only a fraction (about 1/2) of the photolysed CV^+ finishes up as CVH. In the limit of high $[\text{CV}^+]$ the quantum yield for sensitized bleaching can be substantial (about 0.2), depending on the ratio of hydrogen abstraction to energy transfer ($k_h/(k_h + k_g) \approx 0.14$).

(4) Although CV^+ also interacts efficiently with triplet anthracene (^3An), $k_q \approx 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, the sensitized yield for CV^+ consumption in $\text{An}-\text{CV}^+$ systems is low (1.1×10^{-5}), indicative of unreactive $^3\text{CV}^+$. The quenching of ^3K -sensitized fading of CV^+ by naphthalene is further evidence for the lack of reactivity of $^3\text{CV}^+$.

Acknowledgments

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