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Reduction of Crystal Violet by Diphenylketyl Radicals

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Abstract: Crystal violet (CV^+) is stable to direct photolysis in acetonitrile at $\lambda_{irr} \geqslant 366$ nm even in the presence of hydrogen donors (benzhydrol and 2-propanol). However, when benzophenone (K) is present in samples containing hydrogen donor and $\lambda_{irr} \leqslant 366$ nm, sensitized photofading occurs. On the basis of chemical evidence and the concentration and intensity dependence of the sensitized quantum yields, a one-electron reduction of CV^+ by diphenylketyl (KH·) followed by hydrogen transfer to the intermediate CV· with formation of the leuco dye (CVH) is proposed. The rate constant (k_6) for the electron transfer reaction

$$CV^+ + KH\cdot \rightarrow CV\cdot + K + H^+, \qquad k_6 = 6 \pm 2 \times 10^5\ M^{-1}\ s^{-1} \tag{6}$$

has been determined by two methods both of which rely on the competition between reactions 5 and 6

$$2KH\cdot \rightarrow K_2H_2, \qquad k_5 = 1.05 \pm 0.02 \times 10^8\ M^{-1}\ s^{-1} \tag{5}$$

In the first the quantum yield of sensitized fading is determined as a function of CV^+ concentration. In the second the rates of benzpinacol formation in the absence and presence of CV^+ are followed.

Both the photophysics[1-3] and photochemistry[4-10] of triarylmethane (TAM) dyes have been widely investigated. The photophysics stems largely from the work of Forster and Hoffmann,[1] who noted that although TAM dyes (D^+) have an intense visible absorption, implying a correspondingly short singlet radiative lifetime, there was very little fluorescence in solvents of low viscosity. However, emission increased markedly as the solvent viscosity increased. It was suggested[1] that the lack of fluorescence at low viscosity was due to a very rapid nonradiative relaxation from the state initially formed on excitation ($S_{1,init}$). In high viscosity media this relaxation becomes slower, allowing fluorescence to compete. Since that time there has been considerable work in establishing the rates of the relaxation processes and the nature of the states involved.[2,3,11] In particular transient spectroscopy has demonstrated that in low viscosity fluids the lifetime of $S_{1,init}$ and the recovery of the ground state (S_0) occur on the same picosecond scale and that there is no evidence for the involvement of the triplet in the relaxation process.[2b]

Oster et al.[8] reported that TAM dyes did not undergo photofading in solutions containing mild reducing agent such as ascorbic acid except when they were bound to a high molecular weight polymer (polymethacrylic acid). In flash photolysis studies[9] they were able to detect a metastable species, presumed to be the triplet dye ($^3D^+$), only when the sample contained high molecular weight polymer. Although these data are consistent with the photophysical studies, more recent work by Allen and co-workers[4-6] is not. Using 2-propanol as solvent and for $\lambda_{irr} > 500$ nm, they reported photofading (no quantum yields given) with concomitant buildup of an intermediate which they proposed to be the triarylmethyl radical, D·. The latter was also detected by its absorption at 400 nm in flash photolysis studies of the dye in 2-propanol. The destruction of D· ($t_{1/2} \sim 50$ ms) was thought to be due to photolysis by the monitoring light which contained wavelengths <400 nm. No D· was observed in acetonitrile until benzhydrol (10^{-3} M) or benzophenone (5×10^{-8} M) was added. It was proposed[6] that following excitation and intersystem crossing to the triplet ($^3D^+$), ionization occurred and the electron so formed reduced a ground-state molecule (D^+) to D·. The much greater photostability of D^+ in acetonitrile and the lack of D· formation in that solvent were attributed to addition of the ejected electron to the cyano group making it unavailable for reduction of ground-state dye. Evidence for the involvement of $^3D^+$ was deduced from sensitization by benzophenone and oxygen quenching.[5] The role of benzhydrol was not clear except it was stated to be a hydrogen donor.

Clearly the above mechanism for photofading in solvents of low viscosity (acetonitrile, 2-propanol) is not in accord with the photophysical studies which imply very rapid and quantitative recovery of S_0 from S_1. Thus if the triplet is formed it must be a minor channel. It may also be asked why electron ejection occurs more readily from a state of low energy ($E_T = 39$ kcal/mol)[12] than from the singlet state.

Results

(a) Direct Excitation of Crystal Violet. The absorption spectrum of crystal violet chloride (CV^+Cl^-) is shown in Figure 1. Irradiation of 3.6×10^{-6} M CV^+ in the visible absorption band at 546 nm in both degassed acetonitrile and 2-propanol for 13 h led to essentially no fading, and quantum yields (Φ) of $\leqslant 10^{-7}$ are estimated. Again little if any fading occurred in both solvents when samples were irradiated for 7 h at 366 nm. This sets an upper limit to the quantum yield at this wavelength of 10^{-4}. There was also no fading in acetonitrile at $\lambda_{irr} = 313$ nm, $\Phi \leqslant 10^{-4}$. Some fading in acetonitrile was observed at 250 nm ($\Phi = 0.001$) and in 2-propanol at 313 nm ($\Phi = 0.03$).

The stability of fading in both solvents for $\lambda_{irr} \geqslant 366$ nm had its counterpart in the absence of observable transients with absorptions in the 400–550 nm region when 10^{-5} M CV^+ was excited with the output from a frequency tripled YAG laser ($\lambda_{irr} = 355$ nm). Lack of signal did not arise from poor apparatus sensitivity. Thus, 10^{-3} M benzophenone in acetonitrile gave a strong triplet absorption at 520 nm.[13,14] Also when a solution of 2×10^{-5} M

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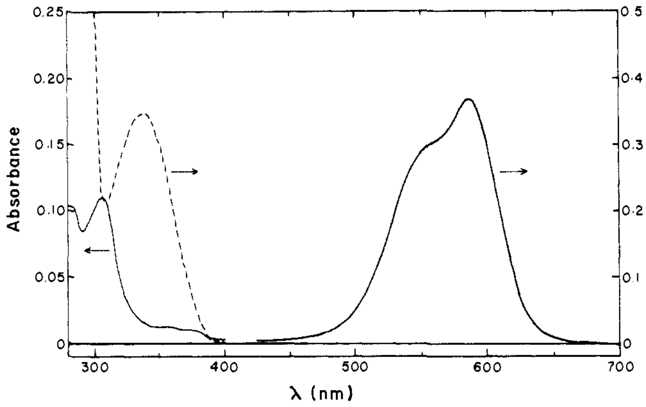

Figure 1. Absorption spectra of 2.66×10^{-3} M benzophenone (---) and 3.72×10^{-6} M crystal violet chloride (—) in acetonitrile. Path length 1.0 cm.

CV^+ and 10^{-3} M benzophenone was flashed, long lived transient(s) absorbing in the 400-nm region were observed. Such a transient has been identified[7,15] as originating from CV·, the one-electron reduction product.

(b) Photofading of Crystal Violet in the Presence of Benzhydrol. When an acetonitrile solution of 0.054 M benzhydrol (KH_2) and 3.6×10^{-6} M CV^+ was irradiated at 546 nm we could still see no fading. This implies that if low-lying $^3CV^+$ is formed on direct irradiation it is not reactive even in the presence of an efficient hydrogen donor. In contrast to irradiation at 546 nm, at 366 nm the rate of photofading increased by a factor of at least 500 with the addition of 0.054 M benzhydrol to the solution. Thus 1.9×10^{-6} M CV^+ in the presence of 0.054 M benzhydrol faded at a rate of 4×10^{-9} M s^{-1} and an apparent quantum yield of 0.05, based on light absorbed by CV^+, was calculated. However, this dramatic change was due not to reaction of an upper excited state of CV^+ with benzhydrol but to traces of benzophenone (K) in the benzhydrol, even though the latter had been recrystallized several times. Thus, Figure 2 shows the rate of photofading of CV^+ in the presence of benzhydrol as a function of added benzophenone. It can be seen that 2.7×10^{-5} M added benzophenone doubles the initial rate of disappearance of CV^+. If we assume that photolysis in the absence of added benzophenone arises from benzophenone impurity in benzhydrol, then the fractional impurity is $2.7 \times 10^{-5}/5.4 \times 10^{-2}$ (=0.05%). That this is in fact the case was confirmed by HPLC analysis which showed that benzhydrol had indeed this very low level of benzophenone impurity. Absorption spectra of concentrated benzhydrol solutions also indicated a characteristic benzophenone absorption at 350 nm. It is, therefore, clear that the photofading of CV^+ solutions containing benzhydrol is due to the presence of benzophenone. Experiments using 2-propanol confirm that the presence of a good hydrogen donor is not a sufficient condition for initiating photofading of CV^+ at $\lambda_{irr} \geq 366$ nm. For example, triplet benzophenone abstracts a hydrogen from 2-propanol with a rate constant of 2×10^6 M^{-1} s^{-1},[16,17] a reactivity ~1/3 that of benzhydrol ($k = 6 \times 10^6$ M^{-1} s^{-1} [18]). Thus we might expect 0.15 M 2-propanol to be about as effective as 0.05 M benzhydrol if hydrogen donation was the only criterion. However, as was shown in the previous section, we could observe no photofading for irradiation at 366 nm of 3.6×10^{-6} M CV^{2+} in 2-propanol (13 M) as a solvent. Nevertheless, the combination of a hydrogen donor and benzophenone allows CV^+ to be readily photoreduced and it is to this system that we now turn our attention.

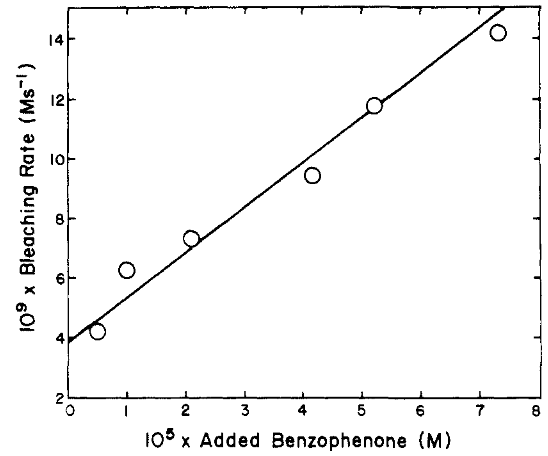

Figure 2. Rates of photofading of 1.9×10^{-6} M crystal violet and 0.054 M benzhydrol in acetonitrile as a function of added benzophenone. λ_{irr} = 366 nm.

(c) Mechanism of Reduction of Crystal Violet by Diphenylketyl Radicals. The data will be discussed in terms of the following mechanism where K = Ph_2CO, KH· = $Ph_2\dot{C}OH$, KH_2 = Ph_2CHOH, K_2H_2 = $(Ph_2COH)_2$. Reaction 1 is the familiar

$$K \xrightarrow{I_{abs}} {}^3K \tag{1}$$

$$^3K \rightarrow K \qquad k_2 = 2.3 \times 10^4\ s^{-1} \tag{2}$$

$$\begin{gathered} ^3K + CV^+ \rightarrow \text{quenching and/or reaction} \\ k_3 = 1.0 \times 10^{10}\ M^{-1}\ s^{-1} \end{gathered} \tag{3}$$

$$^3K + KH_2 \rightarrow 2KH\cdot \qquad k_4 = 6.0 \times 10^6\ M^{-1}\ s^{-1} \tag{4}$$

$$2KH\cdot \rightarrow K_2H_2 \qquad k_5 = 1.05 \times 10^8\ M^{-1}\ s^{-1} \tag{5}$$

$$\begin{gathered} KH\cdot + CV^+ \rightarrow K + H^+ + CV\cdot \\ k_6 = 5.5 \times 10^5\ M^{-1}\ s^{-1} \end{gathered} \tag{6}$$

$$KH\cdot + CV\cdot \rightarrow K + CVH \tag{7}$$

formation of triplet benzophenone (^3K). Under our conditions ^3K had a lifetime in the absence of added crystal violet (CV^+) or benzhydrol (KH_2) of approximately 30×10^{-6} s[19,20] and so $k_2 = 2.3 \times 10^4$ s^{-1}. We find that crystal violet and several other triarylmethane dyes interact with ^3K at close to diffusion-controlled rates. We shall report on these studies in more detail later, but the interaction rate constant (k_3) for CV^+ with ^3K is 1.0×10^{10} M^{-1} s^{-1}. In acetonitrile, ^3K abstracts a hydrogen from KH_2 to form ketyl radicals (KH·) with a rate constant (k_4) of 6.0×10^6 M^{-1} s^{-1}.

In spite of the high value of k_3 it is still easy to adjust the concentrations of KH_2 and CV^+ so that ^3K reacts predominantly via reaction 4. Thus for $[KH_2]$ = 0.057 M and $[CV^+] = 3.8 \times 10^{-6}$ M, 90% of the triplets react by channel 4. In this regime we then have

$$I_{abs} = k_4[KH_2][^3K] \tag{8}$$

Also from the KH· steady-state condition

$$2k_4[^3K][KH_2] = 2k_5[KH\cdot]^2 + 2k_6[KH\cdot][CV^+] \tag{9}$$

The rate of consumption of crystal violet is,

$$-\frac{d[CV^+]}{dt} = k_6[CV^+][KH\cdot] \tag{10}$$

so finally,

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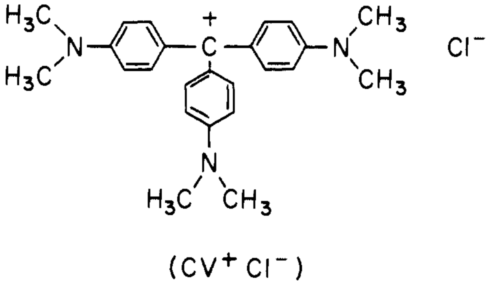
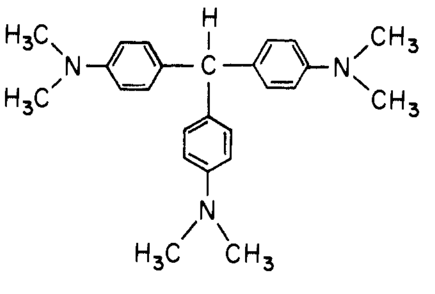
$$\frac{1}{\Phi_{\text{sens}}} = \frac{I_{\text{abs}}\,dt}{-d[\text{CV}^+]} = 1 + \frac{k_5[\text{KH}\cdot]}{k_6}\frac{1}{[\text{CV}^+]} \qquad (11)$$

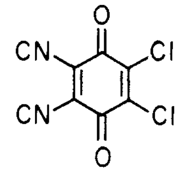
Diphenylketyl radicals (KH·) generated in reaction 4 are either "wasted" by dimerization forming benzpinacol (K_2H_2), reaction 5, or reduce CV^+, reaction 6. The combination of aromatic ketyl radicals has been considered by several authors and the rate is known to be solvent sensitive.[16,21-25] In acetonitrile we obtained $k_5 = 1.05 \times 10^8$ M^{-1} s^{-1}. The rate constant for the reduction of CV^+ by KH· is $k_6 = 5.5 \times 10^5$ M^{-1} s^{-1}; its evaluation is detailed below. The triarylmethyl radicals (CV·) so formed are then further reduced, reaction 7, to the stable leuco dye CVH.



(CV^+Cl^-)



(CVH)



(Q)

Further evidence that benzhydrol concentrations >0.05 M are sufficient to ensure the dominance of channel 4 was obtained by showing that Φ_{sens} did not change as [KH_2] was varied from 0.05 to 0.27 M. At these two extremes and for $I_0 = 1 \times 10^{-8}$ einstein/s, $[CV^+] = 1.9 \times 10^{-6}$ M, and $[K] = 5.2 \times 10^{-5}$ M we obtained $\Phi_{\text{sens}} = 0.19$ and 0.21, respectively, after allowance was made for the benzophenone impurity in benzhydrol.

The above mechanism indicates that the overall stoichiometry associated with reactions 4, 6, and 7 viz.

$$KH_2 + CV^+ \rightarrow K + H^+ + CVH \qquad (12)$$

involves a two-electron reduction of CV^+ yielding 1 mol of leuco dye CVH. The latter can be oxidized back to the original colored from by an oxidizing agent such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (Q).[26] Spectrum a in Figure 3 shows the absorption of a degassed acetonitrile solution containing 1.8×10^{-6} M CV^+, 0.054 M benzhydrol, and 1.5×10^{-4} M benzophenone. After 2 min of irradiation at 366 nm the solution is bleached, (b). The photolysis vessel is then opened and 10 μL of 2.0×10^{-3} M Q is added to the 3-mL sample. After standing for 10 min the spectrum changes to (c), indicating essentially quantitative recovery of the original dye. Exactly similar results were obtained with CV^+ and benzhydrol solution to which benzophenone had not been deliberately added but was present as a trace impurity.

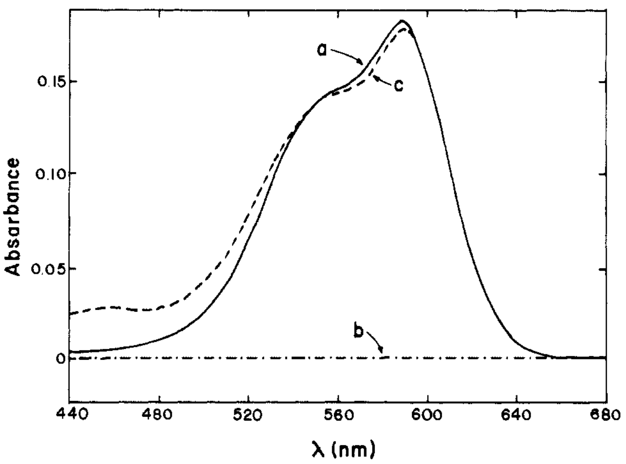


Figure 3. Fading of crystal violet and oxidation of resultant leuco dye: (a) initial solution containing 1.8×10^{-6} M crystal violet, 0.054 M benzhydrol, and 1.5×10^{-4} M benzophenone in acetonitrile (—); (b) after 2 min of irradiation at 366 nm (-··-); (c) after addition of quinone (Q) (---).

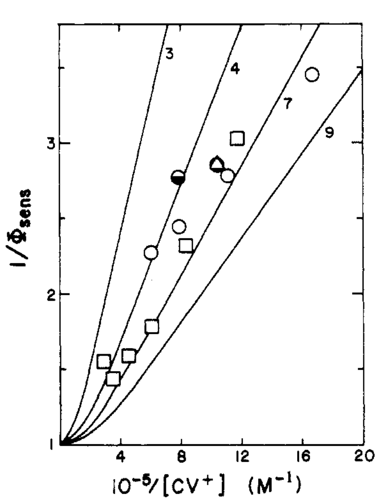


Figure 4. Quantum yields as a function of crystal violet concentration for the benzophenone-sensitized fading in the presence of benzhydrol. $[K] = 4.7 \times 10^{-4}$ M, $[KH_2] = 0.057$ M, $I_0 = 8.6 \times 10^{-10}$ einstein/s. Initial crystal violet concentrations: 3.8×10^{-6} (□), 1.9×10^{-6} (○), 1.5×10^{-6} (◒), and 1.1×10^{-6} (△) M. Full line model curves are for the values of 10^{-5} k_6 (M^{-1} s^{-1}) indicated.

(d) Rate Constant, k_6, for Interaction of Diphenylketyl Radical with CV^+. As CV^+ concentration decreases, reaction 6 competes less favorably compared to the "wastage" reaction 5 for ketyl radicals. This is shown in eq 11 by the decrease in Φ_{sens} with decreasing [CV^+]. Thus, in a given run, Φ_{sens} should decrease as CV^+ is consumed during the photolysis. Also in a series of runs the initial values of Φ_{sens} will increase with increasing initial crystal violet concentration. Both these effects are shown in Figure 4 where points of one type represent quantum yields determined in the course of a single run. The full line curves are computer generated outputs obtained by numerical integration of eq 10, [KH·] being obtained from eq 8 and 9. The various trial values

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Table I. Experimental and Model Quantum Yields as a Function of Light Flux[a]

$10^{10}I_0$ (einstein/s)	$1/\Phi_{\text{sens}}^{\text{exp}}$	$1/\Phi_{\text{sens}}^{\text{mod}}$
4.2	2.7	2.0
47.4	5.3	4.8
160	10.10	8.3

[a] $[CV^+] = 1.9 \times 10^{-6}$ M; $[KH_2] = 0.057$ M; $[K] = 5.5 \times 10^{-4}$ M.

of the only unknown, viz. k_6, are indicated for each curve. Clearly $k_6 = 5.5 \pm 1.5 \times 10^5$ M^{-1} s^{-1}. In a later paper it will be shown that channel 3 is not very efficient in photobleaching and its inclusion under the given conditions of high benzhydrol and low CV^+ concentrations results in only a very small change to the overall calculated quantum yield of sensitized photobleaching. Notice that from eq 8–11 in the region of low quantum yield, $I_{\text{abs}} \approx k_5[KH\cdot]^2$ and so $[KH\cdot]$ is constant. The slope of the $1/\Phi_{\text{sens}}$ vs. $1/[CV^+]$ curve then becomes constant at $(I_{\text{abs}}k_5)^{1/2}/k_6$. In the region of high quantum yield, where reaction 6 is important, $[KH\cdot]$ is no longer constant and decreases with increasing $[CV^+]$. This means that the slopes become less than $(I_{\text{abs}}k_5)^{1/2}/k_6$ and Φ_{sens} asymptotically approaches unity as is shown in Figure 4.

Given the interest in absolute electron transfer rate constants for ketyl radicals[27,28] we thought it would be valuable if we could develop another simple and direct technique for the evaluation of k_6 and related constants. Reaction 5 competes with reaction 6 and since k_5 is known for some solvent systems[16,21-25] and can readily be determined for others (see experimental) it is therefore natural to use this reaction as the "clock" for reaction 6. This can be done most directly by determining the fraction of the ketyl radicals generated in reaction 4 which ends up as benzpinacol. To do this we have to be able to detect very small amounts of the latter in the presence of a large excess of benzophenone and/or benzhydrol. This can be done by HPLC.

Consider the rate of pinacol formation in the photolysis of benzophenone/benzhydrol systems in the absence and presence of added crystal violet. The relevant equations are again eq 1–7 above. As before, reaction 3 can be omitted at sufficiently high benzhydrol concentration. Solving for the steady-state ketyl radical concentration in the absence and presence of CV^+ we get

$$[KH\cdot]_0 = (R_0/k_5)^{1/2} \text{ and } [KH\cdot]_{CV^+} = (R_{CV^+}/k_5)^{1/2}$$

where R_0 and R_{CV^+} are the rates of pinacaol formation in the absence and presence of crystal violet, but we also have $I_{\text{abs}} \approx k_5[KH\cdot]_0^2 \approx k_5[KH\cdot]_{CV^+}^2 + k_6[CV^+][KH\cdot]_{CV^+}$ so that finally,

$$k_6 = \frac{(R_0 - R_{CV^+})(k_5)^{1/2}}{[CV^+](R_{CV^+})^{1/2}} \tag{13}$$

When we irradiated an acetonitrile solution containing 1.9×10^{-6} M CV^+, 3.7×10^{-5} M benzophenone, and 2×10^{-2} M benzyhydrol at 366 nm we detected 0.5×10^{-6} M benzpinacol (K_2H_2) by HPLC. The same solution irradiated under similar cnditions but without CV^+ produced 2.3×10^{-6} M benzpinacol. We estimated that the average concentration of CV^+ during the run was about 1.4×10^{-6} M. Substitution of these quantities into eq 13, and again using $k_5 = 1.05 \times 10^8$ M^{-1} s^{-1}, yields $k_6 = 4 \times 10^5$ M^{-1} s^{-1}, in reasonable agreement with the previous experiments.

(e) The Effect of Light Intensity. Because of the low absorbance of benzophenone at 366 nm for the concentration range employed, we can write I_{abs} (einstein L^{-1} s^{-1}) = $2.303I_0\epsilon[K]L/V$ where I_0 (einstein s^{-1}) is the incident flux, ϵ (M^{-1} cm^{-1}) is the extinction coefficient, and [K] is the concentration (M) of benzophenone in a cell of path length L (cm). V is the volume (liters) of irradiated solution. Thus in the region of low quantum yield $1/\Phi_{\text{sens}}$ which is proportional to $I_{\text{abs}}^{1/2}$ should also be proportional to $I_0^{1/2}$. As the light intensity increases $[KH\cdot]$ increases and so the wastage reaction, being second order in $KH\cdot$, becomes relatively more important, resulting in a decrease in Φ_{sens}. Data showing this effect are given in Table I. A 40-fold increase in light intensity results in a 4-fold decrease in both the experimental and calculated values of Φ_{sens}.

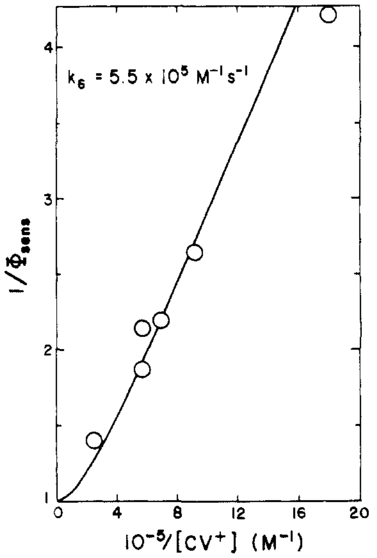

Figure 5. Quantum yields as a function of crystal violet concentration for the benzophenone-sensitized fading with 2-propanol as hydrogen donor. $[K] = 4.4 \times 10^{-4}$ M, [2-propanol] = 0.26 M, $I_0 = 8.5 \times 10^{-10}$ einstein/s. Full line model curve for $k_6 = 5.5 \times 10^5$ M^{-1} s^{-1}.

(f) Thermally Induced Fading of CV^+ with Diphenylketyl Radical. Neckers[21] and Weiner[22] have shown that the activation energy for the decomposition of benzpinacol to diphenyl ketyl radicals is low,

$$K_2H_2 \rightarrow 2KH\cdot \qquad E_{-5} = 33 \text{ kcal/mol} \tag{5}$$

Radicals so generated should also be able to cause the fading of the dye through reactions 4–7. This can readily be observed; an acetonitrile solution (3 mL) containing 1.8×10^{-6} M CV^+ and 8.5×10^{-6} M benzpinacol was heated for ~20 min at 100 °C and gave a colorless solution. Again addition of 12 μL of 2.0×10^{-3} M quinone Q resulted in essentially complete recovery of CV^+.

(g) 2-Propanol as Hydrogen Donor. 2-Propanol can also be used as a hydrogen donor in place of benzhydrol (KH_2). Reaction 4 is then replaced by

$$^3K + AH_2 \rightarrow KH\cdot + AH\cdot \qquad k_4' = 2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}\,{}^{16,17} \tag{4'}$$

where $AH\cdot$ represents $Me_2\dot{C}(OH)$, the dimethylketyl radical. The latter can then either react with benzophenone (eq 14) or CV^+ (eq 6′)

$$K + AH\cdot \rightarrow KH\cdot + A \tag{14}$$

$$CV^+ + AH\cdot \rightarrow CV\cdot + A + H^+ \tag{6'}$$

where A represents acetone. Because of the high 2-propanol concentrations employed (0.27 M), reaction 3 can again be neglected in comparison to (4′). The observation of a limiting quantum yield of one for the sensitized disappearance of CV^+ suggests that the reduction of CV^+ can proceed either via (6) and (7) or (6′) and (7).

If reaction 14 represents the major fate of $AH\cdot$, the steps important in the sensitized photoreduction using 2-propanol are identical with those using benzhydrol since (14) converts $AH\cdot$ to $KH\cdot$. Equation 11 then remains applicable while eq 8 and 9 are replaced by (8′) and (9′)

$$I_{\text{abs}} \approx k_4'[AH_2][^3K] \tag{8'}$$

$$2k_4'[^3K][AH_2] = 2k_5[KH\cdot]^2 + 2k_6[KH\cdot][CV^+] \tag{9'}$$

Experimental data for the variation in the sensitized yield as a function of CV^+ concentration (circles) are shown in Figure 5, together with a model curve generated by using $k_4' = 2.0 \times 10^6$

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$M^{-1}\ s^{-1}$ and $k_6 = 5.5 \times 10^5\ M^{-1}\ s^{-1}$.

Recently reported values of k_{14} are $1.8 \times 10^9\ M^{-1}\ s^{-1}$ [29a] and $2.8 \times 10^8\ M^{-1}\ s^{-1}$.[29b] Under these conditions and because [K] $\gg$ [CV^+], the rate of reaction 14 would indeed exceed that of reaction 6′. However, earlier work,[30,31a] although not giving an absolute value of k_{14}, implies that it should be $<10^7\ M^{-1}\ s^{-1}$. In this case, and if we take an upper limit for $k_6' \sim 10^9\ M^{-1}\ s^{-1}$,[31b] reaction 6′ could become a major source of AH· consumption, and the major steps following (4′) are then (14), (6′), (5), and (7) with $1/\Phi_{sens} = 1 + (k_{14}[K]/k_6')(1/[CV^+])$. The exact mechanism in the 2-propanol case will then depend upon the outcome of the reevaluation of k_{14} which is in progress.

Discussion

The data in section (a) indicate that in both the absence and presence of hydrogen donors such as 2-propanol, direct photolysis at $\lambda_{irr} \geqslant 366$ nm occurs with very low quantum yields ($\Phi < 10^{-4}$). The previously proposed intersystem crossing followed by electron ejection,[6] if it occurs, must be a minor channel. At shorter wavelengths the quantum yields do increase and these effects are being investigated.

In the presence of a hydrogen donor and benzophenone, the sensitized fading of CV^+ becomes quite rapid at $\lambda_{irr} \leqslant 366$ nm. Provided the intensity is low enough and the concentration of CV^+ high enough, so that most of the diphenylketyl radicals are trapped by CV^+, Φ_{sens} approaches unity. The high quantum yields in the sensitized reaction, as opposed to the very inefficient direct photolysis, mean that care has to be exercised in studying direct photolysis especially in H-donor solvents which may contain trace ketonic impurities. The two-electron reduction product (CVH) arising from reaction of ground-state CV^+ with ketyl radicals is formed in nearly 100% yield. By employing appropriate concentrations of KH_2 and CV^+ we minimized channel 3 for the studies reported in this paper. However, triplet benzophenone does interact efficiently with CV^+ ($k_3 = 1 \times 10^{10}\ M^{-1}\ s^{-1}$) and a fraction of these encounters leads to consumption of CV^+. Thus, at high CV^+ concentration and/or low hydrogen donor concentration a totally different photochemistry is initiated. We shall report on this system in a later paper.

Ketyl radicals are well-known reducing agents by virtue of their ability to donate either a hydrogen atom or an electron.[31-38] In both cases the driving force originates from the carbonyl π-bond energy. The oxidation potential of diphenylketyl ($Ph_2\dot{C}OH \rightarrow Ph_2CO + H^+ + e^-$) is not known, but those for $H_2\dot{C}OH$, $MeH\dot{C}OH$, and $Me_2\dot{C}OH$ and the reduction potentials of the corresponding carbonyls are known.[39,40] Assuming a linear relationship between the reduction potential of the carbonyl and the oxidation potential of the ketyl together with a value for the reduction potential of benzophenone, $E_{1/2}^{red}(Ph_2CO) = -1.3$ V,[27] the oxidation potential of diphenyl ketyl, $E_{1/2}^{oxd}(Ph_2\dot{C}OH)$, was estimated to be 0.7 V.[27,41a] This may be compared with $E_{1/2}^{oxd}(Me_2\dot{C}OH) = 1.3$ V.[39] Although there is considerable uncertainty about the value for $E_{1/2}^{red}(Ph_2CO)$ and hence in the above estimate of $E_{1/2}^{oxd}(Ph_2\dot{C}OH)$, that $Ph_2\dot{C}OH$ should be a less efficient reducing agent than $Me_2\dot{C}OH$ is reasonable on other thermodynamic and experimental grounds outlined below.

From $\Delta H_f(Me_2CHOH, g) = -65.1$ kcal/mol,[42] $\Delta H_f(Me_2CO, g) = -51.9$ kcal/mol,[42] and the bond dissociation energy $D(H-C(Me_2)OH) = 91$ kcal/mol,[43] we obtain $\Delta H_f(Me_2\dot{C}OH, g) = -26.2$ kcal/mol and so $\Delta H_{15} = 340$ kcal for

$$Me_2\dot{C}OH(g) \rightarrow Me_2CO(g) + H^+(g) + e^-(g) \qquad (15)$$

$D(H-C(Ph)_2OH)$ is not known but a value of 75 kcal/mol seems reasonable in view of the benzylic resonance.[44] $\Delta H_f(Ph_2CHOH, g) = -2.3$ kcal/mol and $\Delta H_f(Ph_2CO, g) = 14.6$ kcal/mol[42] so that $\Delta H_f(Ph_2\dot{C}OH, g) = 20.6$ kcal/mol and $\Delta H_{16} = 360$ kcal for

$$Ph_2\dot{C}OH(g) \rightarrow Ph_2CO(g) + H^+(g) + e^-(g) \qquad (16)$$

Thus $(\Delta H_{15} - \Delta H_{16}) = -20$ kcal which is to be compared with $(\Delta G_{15} - \Delta G_{16}) = -23.06\ [E_{1/2}^{oxd}(Me_2\dot{C}OH) - E_{1/2}^{oxd}(Ph_2\dot{C}OH)] = -14$ kcal, obtained from the oxidation potentials of the ketyl radicals. The differences in the ΔH's and ΔG's arise mainly from the resonance stabilization of $Ph_2\dot{C}OH$ which is also manifested in the low value of $D(H-C(Ph_2)OH)$ and in the difference between the carbonyl π-bond energies of acetone and benzophenone, that is to say

$$E_\pi(Me_2CO) - E_\pi(Ph_2CO) \approx \Delta H_f(Me_2CHOH) + \\ \Delta H_f(Ph_2CO) - \Delta H_f(Ph_2CHOH) - \Delta H_f(Me_2CO) = 26 \text{ kcal}$$

From the above heats of formation, $\Delta H_{17} = -20$ kcal for,

$$Me_2\dot{C}OH(g) + Ph_2CO(g) \rightarrow Me_2CO(g) + Ph_2\dot{C}OH(g)^{41b} \qquad (17)$$

The reduction of CV^+ by diphenylketyl is analogous to the reduction of azo[33] and azomethine[34] dyes by ketyl radicals except that in the latter two hydrogen atoms are transferred to the dye while the fading of CV^+ involves an electron plus a hydrogen atom transfer to form the leuco dye. In the previous sections we outlined two methods, both employing steady-state photolysis for determining the key rate constant k_6. This offers a convenient complement to pulsed laser methods. In a typical pulse experiment the lifetime of diphenylketyl in the absence of radical quencher is 0.4 μs.[27] This means that if a quencher with a rate constant $\sim 1 \times 10^6\ M^{-1}\ s^{-1}$ is added, it has to be present in molar concentration to intercept the radicals effectively. However, in steady-state experiments, because of the much lower intensities, and hence lower ketyl radical concentrations, much smaller concentrations of quencher are effective. This can minimize many of the problems attendant with high substrate concentration. Furthermore if the quencher, such as a TAM dye, absorbs in the same region as the ketyl radical, monitoring the latter by its transient absorption may be complicated. This problem does not arise in steady-state experiments which rely on monitoring substrate absorption or product formation.

Both methods gave a value of $k_6 = 6 \pm 2 \times 10^5\ M^{-1}\ s^{-1}$. This value seems to be reasonable in view of the estimated value of

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Table II. Quantum Yields of Fading of Crystal Violet (1.9×10^{-6} M) in the Presence of Benzophenone (5.2×10^{-4} M); Effect of 2-Propanol Concentration

[2-propanol] (M)	Φ_{sens}
0.13	0.38
0.65	0.44
1.13	0.46
10.5	0.41

ΔG_6. For crystal violet we have $E_{1/2}^{red}(CV^+) = -0.81$ V (CH_3CN)[45] and -0.88 V (H_2O, pH 6.1).[46] Since ketyl radical potentials were determined in aqueous media[39] we shall use the latter value. Thus $\Delta G_6 = -23.06[E_{1/2}^{oxd}(Ph_2\dot{C}OH) + E_{1/2}^{red}(CV^+)] \approx 4$ kcal. There have been many studies[47-49] correlating the rates of electron-transfer reactions with ΔG beginning with the pioneering work of Rehm and Weller.[47] They noted that the rate constant for electron transfer started to fall off from its diffusion-controlled limit when $\Delta G° \geqslant -10$ kcal. For $\Delta G° \approx 5$ kcal, rate constants $\approx 10^6$ M^{-1} s^{-1} were obtained.

In the mechanism presented in section (c) it was assumed that the CV· radicals formed in reaction 6 are removed by disproportionation with ketyl radicals (reaction 7). Similar termination steps have been proposed in other dye-fading studies.[33,34] The rate constant for reaction 7 is not known. However, both the combination and disproportionation of ketyl radicals, which like CV· are also resonance stabilized, have been studied[22,23] and $k_{comb}/k_{disp} \sim 30$. Thus in acetonitrile we expect the rate constant for $KH\cdot + KH\cdot \rightarrow K + KH_2$ to be $\sim 1/30 \times 1.05 \times 10^8 = 3.5 \times 10^6$ M^{-1} s^{-1}. It is reasonable to suppose that k_7 will have a similar value. Even if CV· were not reduced by KH·, there is evidence that CV· will disproportionate, although rather slowly ($\tau \sim 1$ s),[31b]

$$CV\cdot + CV\cdot \rightarrow CV^+ + CV^- \qquad (7a)$$

$$CV^- + H^+ \rightarrow CVH \qquad (7b)$$

If reaction 7 is replaced by reactions 7a and 7b then there is still the same overall stoichiometry, reaction 12. The set of eq 1–7b yields

$$2k_4[{}^3K][KH_2] = 2k_5[KH\cdot]^2 + k_6[KH\cdot][CV^+] \qquad (9a)$$

and

$$\frac{1}{\Phi_{sens}} = 1 + \frac{2k_5[KH\cdot]}{k_6}\frac{1}{[CV^+]} \qquad (11a)$$

in place of eq 9 and 11. Therefore changing the termination reaction 7 will at worst change the calculated value of k_6 by a factor of 2.

Experimental Section

Benzophenone, benzhydrol, crystal violet chloride, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone were purchased from Aldrich. The latter two compounds were used as received, benzophenone was recrystallized from ethanol, and benzhydrol was recrystallized (three times) from methanol–water. Acetonitrile and 2-propanol (Fisher spectro-grade) were subjected to further purification before use. Acetonitrile was first dried overnight over anhydrous potassium carbonate then refluxed over phosphorous pentoxide (5 g/L) for 2 h and distilled (bp 81 °C) 2-propanol was purified by the magnesium method (bp 82 °C). Solvents were kept over molecular sieves 4–8 mesh.

Stock solutions of the substrates in acetonitrile were prepared. Aliquots were made up to 10 mL, and 3-mL portions were transferred to photolysis cells. Typically these were rectangular 1-cm path length cells equipped with side degassing volumes and greaseless high-vacuum valves. Oxygen was removed from the samples by 3 freeze–thaw cycles with use of a high-vacuum line which was pumped down to 10^{-5} torr. The degassed samples were irradiated, with stirring, at the appropriate wavelength with use of a typical optical track consisting of a 200-W mercury-xenon arc and a Bausch and Lomb high-intensity monochromator. The rates of photobleaching were followed by observing the spectral decrease as a function of time in the 320–700 nm region with use of a Perkin-Elmer recording spectrophotometer (Model 200). The intensity of the incident light was measured with either Aberchrome-540 directly or a vacuum photodiode (Hammamutsu R275) which had been previously calibrated against Aberchrome-540.[50]

A stock solution of 2.0×10^{-3} M 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (Q) was prepared by dissolving 4.5 mg of (Q) in 10 mL of acetonitrile containing 2–3 mL of glacial acetic acid and then bubbling with nitrogen for 10 min to remove oxygen.

Quenching rate constants (k_3) for the interaction of crystal violet with triplet benzophenone were carried out as described previously.[51] The dimerization rate constant, k_5, of diphenylketyl radical was obtained by laser flash photolysis[52,53] with 347-nm excitation (ruby laser) of 10^{-3} M benzophenone and 1 M benzhydrol in acetonitrile. The rate constant was measured from the second-order radical decay monitored at 540 nm. The radical absorption coefficient was taken as 4800 M^{-1} cm^{-1}. The rate law defining k_5 is $-d[KH\cdot]/dt = 2k_5[KH\cdot]^2$, $2k_5 = 2.09 \pm 0.03 \times 10^8$ M^{-1} s^{-1}. Identical results were obtained when samples were degassed either by bubbling argon for 5 min or by freeze–thaw cycles at ca. 10^{-5} mmHg. In looking for transients produced on irradiation of CV^+ solutions (Results section (a)), 3-mL samples in 1-cm rectangular curvettes were outgassed by bubbling with argon and excited by the output of a frequency tripled YAG laser (Molectron MY32, $\lambda = 355$ nm, 10 mJ, $t_{1/2} = 15$ ns). A typical colinear arrangement[53,54] was employed for the kinetic spectroscopy.

HPLC analyses were carred out on a Waters 440 detector equipped with a wavelength extender (214 nm) to increase the sensitivity of benzpinacol detection. The order of elution with a 5-μm reverse-phase column (Waters Nova-Pak C_{18}) and 40% aqueous acetonitrile was (a) benzhydrol, (b) benzophenone, (c) benzpinacol.

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