Delayed Thermal Fluorescence of Anthraquinone in Solutions[1a]

Steven A. Carlson[1b] and David M. Hercules*[1c]

Contribution from the Department of Chemistry and Laboratory for Nuclear Science,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139,
and the Department of Chemistry, University of Georgia,
Athens, Georgia 30601. *Received October 22, 1970*

Abstract: The luminescence of anthraquinone (AQ) in Freon at 25 °C consists of two sets of emission bands. The emission at longer wavelengths is phosphorescence, which has previously been observed only in frozen glasses at 77°K. The short-wavelength emission is delayed thermal fluorescence (DTF), which disappears upon cooling to 77°K. The occurrence of DTF in AQ is confirmed by plots of log (ϕ_{DTF}/ϕ_P) *vs.* $1/T$. These are linear with a slope equal to the S–T split (1400 cm^{-1}) in AQ. In addition, values of τ_{DFT} and τ_P depend on the amount of quencher present, such as oxygen, but they are equal for a given solution. This agrees with the lifetime of the AQ triplet, as measured by flash photolysis studies of T–T absorption. For AQ in Freon at 25°C, ϕ_{DTF} and ϕ_P are 0.057 ± 0.011 and 0.037 ± 0.008, respectively. A steady-state model for the AQ excited states was developed that explains the nearly 6% yield of DTF for a compound never reported to fluoresce in fluid solution ($\phi_F < 0.0005$). DTF is shown to result from thermally activated T–S crossing having a rate at least 10^2 greater than that of deactivation from the triplet. The steady-state model also shows that earlier quenching and quantum yield studies on AQ photoreduction are insufficient to assign the AQ triplet as the photoreactive state.

Anthraquinone undergoes photoreduction in deoxygenated alcohols to give the corresponding hydroquinone.[2-4] The $T_0(n,\pi^*)$ triplet state of anthraquinone has been postulated to be photoreactive on the basis of triplet-quenching experiments.[4,5] Inert hydrocarbons, having triplet levels lower than anthraquinone, quenched protoreduction, while hydrocarbons with triplet levels higher than antraquinone had no effect. The quantum yield of photoreduction measured as unity implied a unity quantum yield of the photoreactive triplet state.

Hammond and Lamola[6] measured the intersystem crossing quantum efficiency (ϕ_{isc}) of anthraquinone to be 0.87, whereas a value of unity is implied by the quantum yield of photoreduction. Although the experimental technique used to measure ϕ_{isc} has admitted drawbacks, the measurements of Lamola and Hammond for several other compounds have been confirmed by different methods.[7,8] Also, the $S_1(n,\pi^*)$–$T_0(n,\pi^*)$ triplet–singlet split in anthraquinone (1400 cm^{-1}) is smaller than for benzophenone (2200 cm^{-1}), and therefore one would expect intersystem crossing to be enhanced. Another interesting possibility is presented by this small singlet–triplet split in anthraquinone, that being the likelihood of thermal repopulation of the anthraquinone singlet from the triplet in solution at room temperature. A third aspect is also interesting. The photoreduction mechanism postulated for anthraquinone is similar to that for benzophenone.[5] Because the rates of hydrogen abstraction for benzophenone in various solvents are known, determination of the corresponding rates for anthraquinone should provide a direct comparison of the primary photoprocess in these reactions. Recently DTF has been reported for benzophenone compounds.[9,10]

The present investigation is a study of the luminescence of anthraquinone in Freon (1,1,2-trichlorotrifluoroethane). This solvent minimizes photochemical reactivity of anthraquinone and enables one to observe emission from anthraquinone in solution. The luminescence observed is composed both of phosphorescence and delayed thermal fluorescence resulting from reactivation of the anthraquinone singlet from the triplet state. The yield of DTF is substantially higher than that observed for other compounds in solution.[9-12] Stern–Volmer plots of the luminescence quenching by various alcohols and hydrocarbons gave reaction rate constants for hydrogen abstraction three to four times higher than those observed for benzophenone in the same solvents. The magnitude of the rate constant for anthraquinone indicates that the lowest triplet state is photoreactive.

Experimental Section

Chemicals. All solvents except ethanol (U.S. Industrial absolute) were Eastman spectrograde or Matheson Coleman and Bell spectroquality solvents and were used without further purification. Anthraquinone (Eastman Organic) was recrystallized four times from ethanol.

Instrumentation. Absorption spectra were recorded on a Cary Model 14 spectrophotometer. Low-temperature emission spectra were obtained using a spectrofluorometer constructed from Aminco Building Blocks in this laboratory. A GK Turner Model 210 absolute spectrofluorometer was used to record room-temperature emission spectra. Temperature regulation was provided by circulating water from a constant-temperature bath.

Luminescence lifetimes were measured using a modified TRW 31A nanosecond fluorometer system.[13] Flash photolysis studies were carried out with a unit constructed in these laboratories from Xenon Corp. components and modified as described elsewhere.[13]

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(1) (a) Taken from the Ph.D. Thesis of S. A. C., Massachusetts Institute of Technology, Sept 1969; (b) Massachusetts Institute of Technology; (c) University of Georgia.

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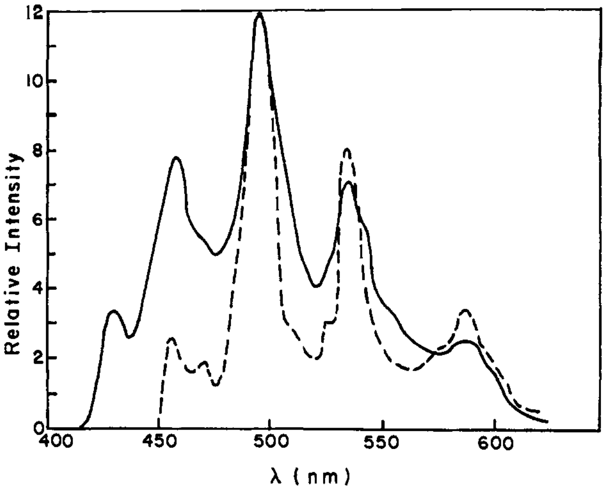

Figure 1. Luminescence spectra of anthraquinone in Freon at 77 (— — —) and 295°K (———).

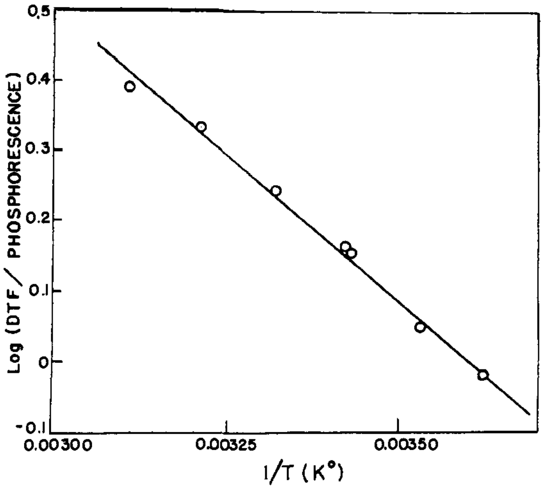

Figure 2. Variation of the delayed thermal fluorescence (DTF) of anthraquinone with temperature; 8 × 10^{-5} M AQ in Freon.

Procedures. Low-temperature emission spectra and lifetime measurements were performed on freshly prepared solutions contained in a quartz tube held in a liquid nitrogen filled dewar. Emission spectra from the Aminco instrument were corrected for photomultiplier grating response characteristics.[12] Solutions for ambient- and variable-temperature measurements were deoxgenated by bubbling with prepurified nitrogen for 30 min followed by outgassing to a residual pressure of 2 × 10^{-5} mm using six freeze–pump–thaw cycles. The cell was then sealed under vacuum.

Luminescence quantum yields were determined on the Turner Model 210 using the procedure of Turner.[14] Quinine sulfate was used as the standard.[15] When measuring the lifetime of anthraquinone luminescence at 77°K and at room temperature, the exciting radiation was passed through a Corning 7-54 filter and the emitted light through an isolation filter (Corion Instrument Corp.) with a half-band width of *ca.* 50 Å. Lifetime values were taken only from the first and second flashes, although the lifetime decreased by less than 10% after a dozen flashes.

Solutions for flash photolysis were placed in a cell similar to that described previously[16] except that the degassing bulb was replaced by a Teflon valve (Ace Glass Co.). Degassing was achieved by six freeze-pump–thaw cycles, after which the Teflon valve was closed. Solutions for flash photolysis were thermostated at 18°C by circulating water through the outer jacket of the cell. Procedures for recording absorption spectra and kinetics of flash excited intermediates have been described elsewhere.[16] Eastman Kodak 103-o spectrographic plates were used for the 300–500-nm region, 103a-F plates for the 450–650-nm region, and 1-N plates for the 620–850-nm region. All flash data were taken from the first main flash only on a given solution.

Results

Solutions of anthraquinone in EPA or Freon at 77°K exhibit a strong green phosphorescence, the spectrum of which is shown in Figure 1. The phosphorescence lifetime was 3.7 ± 0.2 msec and the 0–0 band was observed at 455 nm (21,900 cm^{-1}). When a solution of anthraquinone in Freon was allowed to return to room temperature, it still showed a weak luminescence even though it was aerated. Upon deoxygenating the intensity of the green, luminescence increased more than 30-fold. The spectrum of the room-temperature emission, also shown in Figure 1, differs from that of the low-temperature emission in that a new peak appeared at 430 nm (23,300 cm^{-1}) and the relative intensity of the 457-nm region increased.

Dozens of solutions of anthraquinone in Freon were prepared using different samples of anthraquinone, different bottles of Freon, and varying amounts of oxygen present after varying lengths of photolysis time and with different amounts of potential quenchers present such as vacuum grease and ethanol. In all cases the room-temperature luminescence included the peak at 430 nm. Although the overall intensity of the luminescence varied 100-fold depending upon the conditions of the solution, the relative intensities of the five major peaks in the spectrum remained constant. Additionally, excitation spectra were obtained by monitoring the emission peaks at 425, 485, 515, and 560 nm. All excitation spectra were identical and matched the absorption spectrum of anthraquinone in Freon. The data reported above constitute strong evidence that the new emission bands at 298°K in the anthraquinone spectrum are from an excited state of anthraquinone rather than from an impurity or some other experimental artifact.

Because the new luminescence band appeared on warming a frozen solution of anthraquinone to room temperature, a study of the intensity of the new bands relative to the total luminescence at various temperatures was carried out. It was observed that the 430-nm band increased in intensity relative to the total luminescence as the temperature of the solution was increased. This is the result to be expected for a thermally activated process such as delayed thermal fluorescence (DTF). If the new emission bands are due to DTF, a plot of the log of the ratio of thermal fluorescence intensity to total phosphorescence intensity *vs.* $1/T$ should be linear and should have a slope equal to the observed singlet–triplet split in anthraquinone. Because the delayed thermal fluorescence and phosphorescence spectra overlap, their ratio was estimated by assuming that the shapes of the phosphorescence spectra at 77°K and at room temperature were identical, determining the DTF spectrum by difference. Figure 2 shows the variation of DTF with temperature. The values range from 49% DTF at 276°K to 72% DTF at 319°K. The plot is linear, as required by DTF theory, and gives an activation energy of 1350 cm^{-1}, which is in good agreement with the measured 1400-cm^{-1} singlet–triplet split of anthraquinone.

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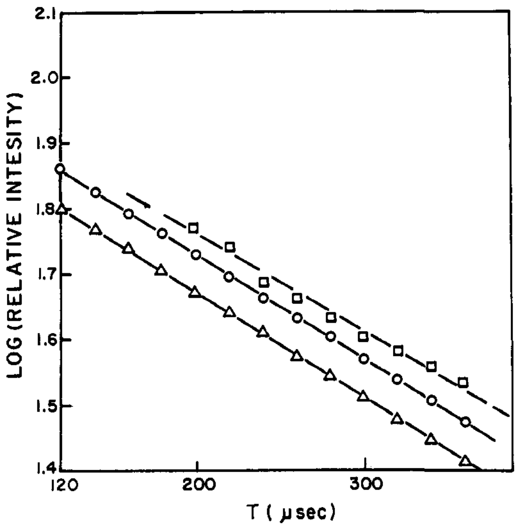

Figure 3. First-order decay plots for the delayed thermal fluorescence, △, phosphorescence, ○, and triple–triplet absorption, □, of anthraquinone in Freon.

Lifetime measurements were performed on the room-temperature solution emission of anthraquinone under the following conditions. The DTF emission peaks at 430 nm; the region of overlapping emission at 447, 485, and 515 nm; and the solution phosphorescence emission at 560 nm were all measured individually. The lifetime of each solution was found to be independent of the emission wavelength monitored. The lifetime of DTF matched that of phosphorescence in each of six solutions examined. By adding quenchers to some of the solutions, a range of lifetimes from 20 to 425 μsec was covered. Secondly, the intensity of the luminescence was proportional to the first power of the rate of absorption of exciting light. This could be seen in the various excitation spectra of AQ in Freon which exactly matched the absorption spectrum. As shown in Figure 3, the decays of DTF and phosphorescence were first order, with normal deoxygenation procedures yielding a lifetime 300 μsec. By very careful degassing, the luminescence lifetime could be increased to 425 μsec. The lifetime of the anthraquinone triplet state was also measured by following the decay of its triplet–triplet absorption band at 410 nm. Figure 3 also contains the first-order decay plot of the anthraquinone triplet–triplet absorption. The lifetime of 315 μsec compares favorably with the 300-μsec lifetime found for emission from solutions that had been deoxygenated according to the same procedures.

The quantum yield of luminescence (ϕ_{lum}) of anthraquinone in Freon at 25°C was found to be 0.094 ± 0.009. Since approximately 30% of the luminescence at this temperature is phosphorescence and 61% is DTF, this gives a quantum yield of phosphorescence (ϕ_{p}) of 0.037 ± 0.008 and of DTF of 0.057 ± 0.011. The increased uncertainty in the latter quantum yield reflects the uncertainty in assigning the percentage of total emission due to DTF. The luminescence lifetime measured for the same deoxygenated solution used in the quantum yield measurements was 290 μsec at 25°C.

The rate constants for hydrogen abstraction (k_{r}) by anthraquinone from various alcohols and hydrocarbons were determined by measuring the quenching effect on anthraquinone luminescence in Freon at 22.5°C. Care was taken to minimize exposure of samples even to the low light flux of the Turner 210. This was necessary to prevent significant photoreduction to 9,10-dihydroxyanthracene, which fluoresces strongly in the region of anthraquinone luminescence. Linear Stern–Volmer plots for the quenching of anthraquinone luminescence were obtained and are shown in Figure 4. The slope of each plot equals $k_{\text{r}}\tau$, where τ is the lifetime of luminescence in the absence of added quencher. The measured value of τ was 3.0×10^{-4} sec for the solutions used in these experiments, and this is the value used to calculate k_{r}, shown in Table I.

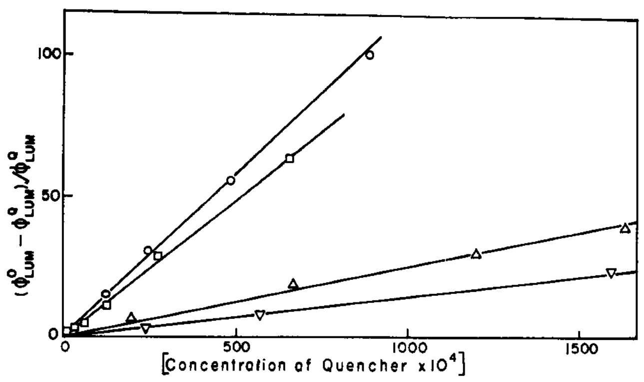

Figure 4. Stern–Volmer plots of $(\phi_{\text{lum}}{}^0 - \phi_{\text{lum}}{}^{\text{Q}})/\phi_{\text{lum}}{}^{\text{Q}}$ against quencher concentration (3×10^{-4} M AQ in Freon; 22.5°C), where $\phi_{\text{lum}}{}^0$ = luminescence without added quencher and $\phi_{\text{lum}}{}^{\text{Q}}$ = luminescence with added quencher, for quenchers: 2-propanol, ○; ethanol, □; hexane, △; and benzene, ▽.

Table I. Rate Constants for the Hydrogen Abstraction Reaction between Anthraquinone and Various Donors

Hydrogen atom donor	k_{r}, M^{-1} sec^{-1}
2-Propanol	4.0×10^6
Ethanol	3.3×10^6
Hexane	8.6×10^5
Benzene	4.8×10^5

Discussion

General Aspects. Terms such as α-phosphorescence and E-type delayed fluorescence have been used to describe fluorescence caused by thermal repopulation of a singlet state from a triplet. The trend lately[17] has been to use the more descriptive term delayed thermal fluorescence (DTF), and we will follow this convention. We will use a different approach than that employed by Parker.[12,18] This is necessary because in Parker's systems thermal repopulation of the singlet occurred for only a small percentage of the excited molecules, with the yield of DTF at least 100 times smaller than the fluorescence yield. For AQ in Freon, the yield of DTF is 600 times greater than the fluorescence yield.

Figure 5 shows the radiative and nonradiative pathways available to a molecule in its lowest excited states. In order to show DTF, the rate of thermal repopulation of the singlet must be fast enough to compete with the

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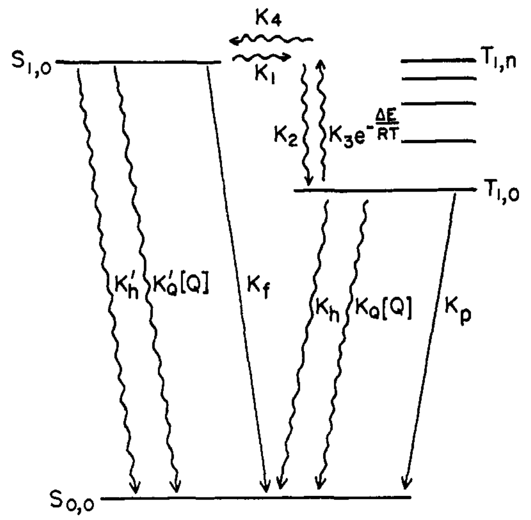

Figure 5. Model state diagram for compounds displaying delayed thermal fluorescence (DTF), where rate constants are as follows; k_h', singlet internal conversion; k_Q', singlet quenching; k_f, fluorescence; k_h, triplet internal conversion; k_Q, triplet quenching; k_p, phosphorescence; k_1, $S_{1,0}$–$T_{1,n}$ intersystem crossing; k_2, internal conversion ($T_{1,n}$–$T_{1,0}$); $k_3e^{-\Delta E/RT}$, thermal activation ($T_{1,0}$–$T_{1,n}$); and k_4, $T_{1,n}$–$S_{1,0}$ intersystem crossing.

other modes of triplet deactivation. Otherwise, all triplets will be deactivated by quenching, internal conversion, or phosphorescence, and none will pass back to the singlet. If thermal repopulation of the singlet state is much faster than the other pathways of triplet deactivation, the singlet and triplet states can be viewed as reaching thermal equilibrium before any deactivation occurs. For such a scheme, the relative concentrations of singlets [S] and triplets [T] will be equal to the rate-determining steps for their formation. Since $k_2 \gg k_1$ and $k_4 \gg k_3e^{-\Delta E/RT}$ for most molecules, [S]/[T] is approximated by $k_3e^{-\Delta E/RT}/k_1$. Thus at a given temperature for a given molecule, [S]/[T] will be constant. This is the essential characteristic of a "steady-state" system displaying DTF.

The crucial difference for compounds showing steady-state DTF is that intersystem crossing is not a deactivation pathway since the two excited states are always equilibrated. Net deactivation occurs only by quenching, internal conversion, or emission. The fast, reversible nature of intersystem crossing means that the singlet state is also deactivated whenever the triplet is deactivated, and *vice versa*.

The quantum yield for each deactivation step will be given by the rate of that step divided by the sum of the rates of all the processes.

Thus it can be seen that

$$\phi_{\mathrm{DTF}}/\phi_{\mathrm{P}} = \frac{k_f k_3 e^{-\Delta E/RT}}{k_p k_1} \tag{1}$$

Therefore, the ratio of the intensities of delayed thermal fluorescence and phosphorescence should be independent of the triplet concentration and of all triplet quenching processes. Since k_f/k_1 is the quantum yield of fluorescence (ϕ_f), for the usual case where $k_1 > (k_f + k_Q'[Q] + k_h')$, and $1/k_p$ is the natural radiative lifetime of the triplet state, $\tau_p{}^0$

$$\phi_{\mathrm{DTF}}/\phi_{\mathrm{P}} = \tau_p{}^0\phi_f k_3 e^{-\Delta E/RT} \tag{2}$$

Thus, plots of log ($\phi_{\mathrm{DTF}}/\phi_{\mathrm{P}}$) against $1/T$ should be linear and have a slope equal to the energy separation of the two excited states and an intercept equal to $\tau_p{}^0\phi_f k_3$. This is indicated by the plot for AQ in Figure 2.

DTF theory also imposes the requirement that the measured radiative lifetimes of DTF and phosphorescence be equal. Thus

$$\tau_{\mathrm{DTF}} = \tau_{\mathrm{P}} = \frac{1}{(k_Q'[Q] + k_h' + k_f)D_S + (k_Q[Q] + k_h + k_P)D_T} \tag{3}$$

where D_S and D_T denote the fraction of excited molecules present in the singlet and triplet states, respectively. It is necessary to include D_S and D_T since the excited molecule can be deactivated from both excited states. This adjusts for the fact that the singlet and triplet states are present at greatly different relative concentrations. The observed emission lifetime approximates the phosphorescence lifetime as if no DTF occurred since $D_T \gg D_S$ in most molecules. However, higher rate constants for singlet processes could make the D_S term significant.

DTF For AQ. The criteria for DTF outlined above are met by anthraquinone in Freon. As has been indicated, the plot of log ($\phi_{\mathrm{DTF}}/\phi_{\mathrm{P}}$) *vs.* $1/T$ is linear with a slope equal to the S–T split in AQ. The intercept value for $\tau_p{}^0\phi_f k_3$ is 1×10^3. As a corollary to this, $\phi_{\mathrm{DTF}}/\phi_{\mathrm{P}}$ is constant at a given temperature, even when the luminescence is quenched over two orders of magnitude by oxygen and/or ethanol.

Fluorescence has not been reported for AQ at room temperature or at 77 °K. Russian workers have studied the emission of AQ in the vapor phase at high temperature (>500 °K) and reported fluorescence, but no spectrum was published.[19] Other workers found vapor-phase emission to begin at 420 nm, but gave no spectrum.[20] However, it is possible to estimate the fluorescence spectrum by assuming that it will have a mirror-image relationship to the lowest energy singlet–singlet absorption band.[21] By this it can be predicted that the 0–0 band in DTF should be at *ca.* 430 nm and that the DTF spectrum should have vibrational structure. This is consistent with the DTF spectrum for AQ reported here.

Independent estimates of the rate constants of fluorescence and intersystem crossing (isc) are lacking for AQ. It is known that $\tau_p{}^0 = 1 \times 10^{-2}$ sec for AQ, and one can compute that $k_f = 10^6$ sec^{-1} on the basis of the integrated absorption spectrum. Because no fluorescence can be detected from AQ at 77 °K, ϕ_f can be estimated as less than 10^{-4}.[22] Using eq 2 and the measured value of the intercept obtained from the plot in Figure 2

$$k_3 = 10^3/\tau_p{}^0\phi_f \geqslant 10^9 \text{ sec}^{-1}$$

As indicated above for the steady-state model, $\phi_f = k_f/k_1$, and thus $k_1 \geqslant 10^{10}$ sec^{-1}. Because the uncer-

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tainty in both cases arises from the value used for ϕ_f, one may, with reasonable certainty, calculate that $k_1/k_3 = 10$.

The ratio k_1/k_3 would be expected to be unity, since it represents the ratio of rate-limiting steps for the intersystem crossing process proceeding in the different directions, *i.e.*, singlet to triplet (S → T) and triplet to singlet (T → S). However, in AQ the $S_1(n,\pi^*) \rightarrow T_0(n,\pi^*)$ isc process is formally forbidden on symmetry grounds, and thus must occur through some second-order spin–orbit mechanism. Dym, *et al.*,[23,24] have shown that intersystem crossing in benzophenone-type compounds arises from vibronic mixing of the n,π^* and π,π^* states, resulting in rapid $S_1(n,\pi^*) \rightarrow T_0(n,\pi^*)$ even though there are no $T(\pi,\pi^*)$ states interposed between the two. The value of $k_1/k_3 = 10$ is reasonable, on this basis, since the degree of mixing will be dependent on molecular geometry in the triplet and singlet states and thus could affect the rates for T → S and S → T intersystem crossing pathways.

Only a fraction of the triplets will be thermally activated to the vibrational level isoenergetic with the excited singlet state involved in the T → S isc process. This fraction will be determined by the Boltzmann factor in eq 1. This factor is particularly sensitive to the magnitude of the singlet–triplet splitting, ΔE_{ST}, as indicated by the following: for $\Delta E_{ST} = 1400$ cm^{-1}, the exponential factor is 10^{-3} at 25°C; for $\Delta E_{ST} = 2800$ cm^{-1}, the factor is 10^{-6}; for $\Delta E_{ST} = 4200$ cm^{-1}, the factor is 10^{-9}. Using these data and the values computed previously, one may compute that for AQ in Freon at 25°C, $[S]/[T] = 10^{-4}$. Using these values in eq 1, a predicted value of $\phi_{DTF}/\phi_P = 1$ is obtained, in good agreement with the measured value of 1.5.

Figure 6 shows a simplified state diagram for AQ in Freon at 25°C. The numerical values listed for steady-state concentrations and radiative processes were derived from the above discussion. If it is assumed that all radiationless deactivations of AQ occur from the triplet state and not from the singlet, the following realtionship holds[21]

$$\phi_P = (\tau_p/\tau_p^0)(1 - \phi_f) \qquad (4)$$

where τ_p and τ_p^0 are measured and intrinsic phosphorescence lifetimes, respectively. For anthraquinone, $\phi_f \leqslant 0.0001$, and $\tau_p = 3.7$ msec at 77°K. Therefore, $\tau_p^0 \cong 9$ msec. Since DTF is a radiative process from the singlet, ϕ_{DTF} can be substituted for ϕ_f in eq 4. On this basis ϕ_p for AQ in Freon at 25°C should be 0.030, which is in agreement with the measured ϕ_p of 0.037 ± 0.008.

The nonradiative rate constants from the singlet and triplet of AQ in Freon can now be estimated. If the singlet nonradiative processes are unimportant at 77°K and become significant at 25°C, at room temperature eq 4 must be expanded to

$$\phi_p = (\tau_p/\tau_p^0)(1 - \phi_{DTF} - \phi_Q'[Q] - \phi_h) \qquad (5)$$

This would further lower ϕ_p. Since the calculated ϕ_p of 0.030 is already at the lower limit of the measured ϕ_p, it is likely that $\phi_{DTF} \geqslant (\phi_Q[Q] + \phi_h)$. To keep the calculated ϕ_p in agreement with the measured ϕ_p, $(k_Q[Q] + k_h') > k_f = 10^6$ sec^{-1}. Since the combined quantum yield of DTF, phosphorescence, and nonradiative singlet deactivation is *ca.* 0.1, the remaining 0.9 must be the quantum yield of nonradiative triplet deactivation. Thus one may estimate $k_h \cong 10^3$ sec^{-1}.

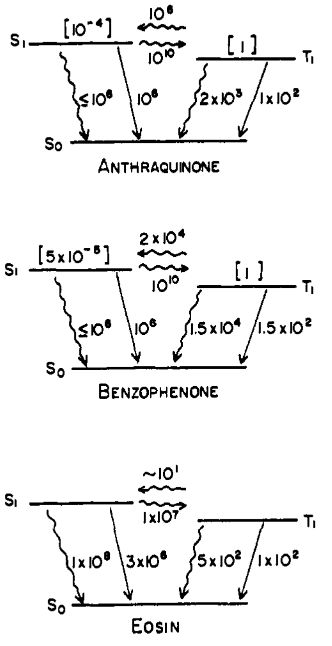

Figure 6. Simplified state diagrams for anthraquinone, benzophenone, and eosin: →, radiative deactivation processes; ⇝, nonradiative deactivation process; brackets, relative steady-state concentrations of the excited states (calculated on the basis of [T] = 1).

DTF in Other Systems. Figure 6 also shows state diagrams for eosin in ethanol[12] and benzophenone in Freon. Eosin is by far the most extensively studied DTF system. It is representative of dyes with small S–T splits such as proflavine, previously known to show DTF in fluid solution. Eosin does not obey the steady-state model developed to explain the AQ luminescence in Freon. Instead, it is a special case of DTF. In the highly fluorescent eosin, the triplet state is formed in a 2.5% yield initially. Only a small fraction (~2%) of the triplet molecules thermally repopulate the singlet; the large ϕ_f of eosin (0.72) makes observation of small $\phi_{DTF} \sim 0.0004$ very difficult. Accordingly, Parker and Hatchard employed a very sensitive spectrophosphorimeter[12] to detect the DTF of eosin, which was $^1/_{2000}$ as intense as the fluorescence. One can conclude that DTF in dyes such as eosin will be very weak (< 1%) and unimportant photochemically, since less than 1% of the initially absorbed photons manage to even once thermally repopulate the singlet from the triplet.

Molecules such as acetophenone and benzaldhyde, which have small S–T splits like AQ, could show similar DTF behavior. In addition derivatives of AQ having lowest n–π^* triplet states should show an S–T split comparable to that of AQ, since the S–T splits in an aromatic carbonyl compound and its derivatives are usually similar.[25] The key to seeing significant yields of DTF in these molecules will be the magnitude of the nonradiative processes deactivating the singlet and triplet states, and the reverse intersystem crossing transition probability. In other words, if phospho-

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rescence can be detected for these compounds in fluorocarbon solutions at room temperature, DTF should also be seen.

Benzophenone has a moderate S–T split (2200 cm^{-1}) for an aromatic carbonyl compound. Figure 6 shows a DTF-type state diagram for benzophenone assuming that its value of k_3 is similar to that of AQ. Using the steady-state DTF model, one calculates ϕ_{DTF} and ϕ_P values of 0.0002 and 0.0100, respectively. DTF has recently been reported for the benzophenone[9] and 4-benzoylbenzoic acid[10] systems. The ratio of ϕ_{DTF}/ϕ_P reported for benzophenone was *ca.* 0.1, in fair agreement with the values calculated from Figure 6. It is interesting to note that ϕ_{DTF} for benzophenone is smaller than for AQ as predicted above.

Implications for Photochemistry. The discovery of DTF in anthraquinone raises questions concerning the assignment of the triplet state as being reactive in photoreduction. The evidence used by Tickle and Wilkinson to detail the AQ photoreduction mechanism was threefold: the unity yield of hydrogen abstraction, triplet quenching of the photoreduction, and the similarity of AQ to benzophenone.[5] They concluded that the AQ triplet was formed in unity yield and then readily abstracted a hydrogen from 2-propanol. However, their experimental results would be equally valid if all or part of the photoreduction occurred from the lowest AQ singlet.

A strong argument for AQ triplet-state reactivity in hydrogen abstraction is the triplet-state reactivity of benzophenone, which has been shown to thermally repopulate the singlet at a rate about 50 times less than in AQ. Thus, the possibility of hydrogen abstraction from the benzophenone singlet is much less. But it is unwise to base arguments on the similarity of benzophenone and AQ. Much of their ground-state and excited-state chemistry is different, largely because one is a nonplanar diphenyl ketone and the other is a planar quinone.

Rates of hydrogen abstraction by excited aromatic carbonyl compounds have commonly been measured by studying the effects of triplet quenching on the quantum yield of the photochemical reaction, ϕ_r.[26,27] A more direct approach was to measure the effects of hydrogen abstraction on ϕ_{lum} from which the data of Table I were obtained.

The linear Stern–Volmer plots for AQ gave values for k_r in the expected order 2-propanol > ethanol > hexane > benzene.[28] In each solvent k_r is so large that virtually all anthraquinone triplets are deactivated by hydrogen abstraction. In addition, k_r for AQ in 2-propanol and benzene is three to four times greater than k_r for benzophenone in the same solvents.[26,29,30] Because of the low quantum yield of reaction in benzene, one cannot be certain that quenching resulted only from a hydrogen abstraction reaction.

The pseudo-first-order rate constant of hydrogen abstraction for AQ in ethanol, k_r[ethanol] = 5.6×10^7 sec^{-1}, combined with the unity ϕ_r precludes photoreaction from the AQ singlet. The steady-state model for the AQ excited states shows that a process from the singlet at 25°C must have a rate constant 10^4 that of a triplet process in order to give a comparable quantum yield. Thus, if even 50% of the hydrogen abstraction were due to a singlet-state reaction, a pseudo-first-order rate constant of 5.6×10^{11} sec^{-1} would be required. This rate constant is much greater than could be derived from a diffusion-controlled process, and it is also greater than the first-order rate constant for intersystem crossing. Therefore, it seems likely that the bulk of the photochemical reaction for AQ occurs from the triplet state. However, this does not preclude a small fraction of the reaction arising from the singlet state, nor does it imply that the AQ singlet state is unreactive.

The discovery of significant DTF in AQ has significance for photochemistry in general. Generally, it has been considered that intersystem crossing was a unidirectional process. However, the steady-state model for DTF indicates that the lowest singlet and the triplet may be in thermal equilibrium if ΔE_{ST} is small. Even if $\Delta E_{ST} = 5000$ cm^{-1}, it is possible that significant singlet population may be present at room temperature. When $\Delta E_{ST} < 1500$ cm^{-1}, singlet states may account for a significant part of the photochemical reaction.

The use of triplet-state quenchers as a diagnostic criterion for triplet reactivity is not unambiguous in such systems, and particularly should be avoided in systems showing low photochemical quantum yields.

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