

Diffusion of Aromatic Triplets in Solution

R. D. Burkhart

Contribution from the Department of Chemistry, University of Nevada,
Reno, Nevada 89507. Received January 18, 1974

Abstract: Annihilation delayed fluorescence of anthracene and 9,10-diphenylanthracene (DPA) has been used to monitor time and space dependent triplet concentrations of these species in solution. When the excitation light is introduced as an array of illuminated strips, the intensity of delayed fluorescence is dependent upon strip dimensions at constant excitation flux and constant chopper frequency. This observed dependence is used to measure triplet diffusion coefficients. Values of 2.3×10^{-5} cm²/sec and 2.8×10^{-5} cm²/sec are obtained for DPA and anthracene, respectively, in ethanol at 25°. The results suggest that both material transfer and energy transfer contribute to the observed mobilities.

The characterization of excited states of molecules has progressed remarkably in recent years and has involved detailed analyses of electronic, vibrational, and rotational modes. A few studies have been carried out on translational properties but it is really only relatively long-lived excited states such as organic triplets where translational properties assume much importance.

Perhaps one of the most thoroughly studied systems involving migration of an electronically excited species is the triplet exciton motion in crystalline anthracene. Several different experimental methods were used in studying this system and the results have been reviewed by Birks.¹ The direct method of Ern, Avakian, and Merrifield² involving radiation through a grid of opaque and translucent regions seems to give consistently reliable results and this work has been summarized by Merrifield.³

In the present study attention was focused not upon molecular crystals but rather upon solutions of aromatic molecules. Since the crystalline phase studies showed that utilizing spatially nonhomogeneous radiation gave useful results, it was decided to try to adapt this method for solution studies. Another reason for choosing this method was that there already existed in this laboratory a background of experience on spatially nonhomogeneous irradiation involving chemically reactive systems which could be applied to photoluminescence work.

An interest in diffusion coefficients of triplets in solution stems from earlier studies on the solution phase mobility of carbon radicals^{4,5} which showed that significant radical-solvent interactions exist. This raises the question of whether or not similar interactions might be found by studying the migration of triplets. On the other hand, there is evidence showing that energy transfer between triplets of aromatic molecules and ground state singlets occurs with some facility both for chemically identical⁶⁻⁸ and for chemically different⁹ molecules.

(1) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley, New York, N. Y., 1970, p 611.

(2) V. Ern, P. Avakian, and R. E. Merrifield, *Phys. Rev.*, **148**, 862 (1966).

(3) R. E. Merrifield, *Accounts Chem. Res.*, **1**, 129 (1968).

(4) R. D. Burkhart, R. F. Boynton, and J. C. Merrill, *J. Amer. Chem. Soc.*, **93**, 5013 (1971).

(5) R. D. Burkhart and R. J. Wong, *J. Amer. Chem. Soc.*, **95**, 7203 (1973).

(6) M. Cocivera, *Chem. Phys. Lett.*, **2**, 529 (1968).

(7) J. Saltiel, D. E. Townsend, and A. Sykes, *J. Amer. Chem. Soc.*, **95**, 5968 (1973).

(8) R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **92**, 211 (1970).

(9) For example, see A. A. Lamola, *Photochem. Photobiol.*, **8**, 601 (1968).

Thus, there is the distinct possibility that a measurable component of the triplet mobility may be due to energy transfer. The direct measurement of triplet diffusion coefficients seems to be a straightforward way to investigate this possibility.

The probe used here to measure mobilities of triplets is the delayed fluorescence resulting from an annihilation reaction between two triplets. This type of delayed fluorescence has been studied extensively and is well characterized both for anthracene¹⁰ and 9,10-diphenylanthracene¹¹ which are the two subject molecules of this work. It is important to note that since the delayed fluorescence intensity is proportional to the mean square triplet concentration, then this intensity may be quite different for two solutions having the same total triplet concentration but with the triplets arranged in different spatial distributions. It is precisely the creation of a spatially intermittent concentration of triplets which one uses to measure mobilities.

It is also important to recognize that, in the experiments discussed here, the incident light intensities and absorbances of the solutions are sufficiently small that first-order processes for the removal of triplets (primarily radiationless deactivation) are much faster than the second-order delayed fluorescence process. Thus, transient triplet populations are controlled by the rate of absorption of excitation light and by the rate of first-order removal of triplets. It is clear then that although the second-order annihilation process provides the probe for gauging the spatial distribution of triplets, this process is without significance in actually affecting the magnitude of the triplet concentration.

Experimental Section

A detailed description of the apparatus has been published elsewhere¹² so it will be discussed only in the most general terms here. A mercury arc lamp was used for excitation and the emission was observed at right angles to the excitation beam. Provision is made for the excitation beam to be filtered but in the present experiments it was not. This beam does, however, pass through glass optics and a Pyrex absorption cell before reaching the test solution so there is no excitation light below about 320 nm. The emission beam passes through a narrow pass filter with a transmission maximum at 430 nm and through a collecting lens before reaching the photomultiplier tube.

The emission and excitation beams were chopped using 1800 rpm synchronous motors rated at 1/50 hp. The phasing of emission

(10) For a recent study, see L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **91**, 6495 (1969).

(11) C. A. Parker and T. A. Joyce, *Chem. Commun.*, 744 (1967).

(12) R. D. Burkhart and J. W. Kenney III, *J. Chem. Instrum.*, in press.

and excitation pulses could be varied continuously by rotating the body of the excitation chopper motor while it is in motion. Thus, prompt and delayed emission could be measured during a single run.

The photomultiplier output was directed to a phase sensitive detector. The dc voltage from this detector, proportional to the emission signal, was measured using a potentiometer. The beam of a battery-operated tungsten lamp impinging on a silicon photo-voltaic cell located behind the excitation chopper provided a reference signal for the phase sensitive detector.

The optical system for the excitation beam was identical with that used for ordinary photographic reduction. In this case a pattern of opaque and translucent strips was placed into the beam and the image of this pattern was cast onto the test solution contained in a 1-mm absorption cell. The size of the image could be varied between one-half and one-fourth that of the original but all of the experiments described here used one-half size reduction. The sample cell was mounted in a brass cell holder with hollow walls to provide for circulation of water from a constant temperature bath. Temperatures were monitored with a thermocouple taped to the cell body.

The measurements on both anthracene and 9,10-diphenylanthracene were made in ethanolic solutions. The anthracene is 99.999% pure material purchased from James Hinton of Columbia, S. C., and the 9,10-diphenylanthracene is 99+% material purchased from Aldrich Chemical Co. The solvent ethanol was purified by the method of Leighton and coworkers¹³ and stored in a nitrogen-filled desiccator. The solutions were also stored in a nitrogen atmosphere before use.

Because of its high efficiency as a quencher of triplets oxygen must be removed by successive freeze-pump-thaw cycles using a high vacuum system. The degassed samples were sealed into short path absorption cells during a pump cycle. The cells were made of Pyrex and had a 1-mm optical path length. They are of the concentric tube variety purchased from the American Instrument Co. Samples prepared in this way showed no change in delayed fluorescence over a period of several months.

The luminescence measurements involved reading detector voltages for each of the intermittency patterns and for the system illuminated with no pattern in place. Both prompt and delayed fluorescence was measured in this way. Because larger detector amplification was needed for delayed fluorescence, stray signals from the room lights became a problem so these measurements were always made in a darkened room. Triplet lifetimes were measured from photographs of the oscilloscope display of the delayed fluorescence decay.

Results

The experimental data were interpreted using eq 1 to describe the temporal and spatial dependence of the triplet concentration. In this equation

$$dT(x,t)/dt = I(x,t) + D\nabla^2T(x,t) - T(x,t)/\tau \quad (1)$$

T is the triplet concentration, I is the net rate of triplet formation, D is the triplet diffusion coefficient, and τ is the triplet lifetime. Of course, triplets also disappear by triplet-triplet annihilation leading to delayed fluorescence but the rate of this process is negligible compared with the first-order process as will be discussed in more detail below. Ern, Avakian, and Merrifield² have solved this equation for the experimental arrangement used here in which the excitation light is introduced through a pattern of opaque and translucent strips. The solution has the form

$$\Phi_N(t) = \left\{ \exp(-2t/\tau) + \sum_{i=1}^{\infty} A_i \exp[-2(1 + l^2\pi^2/4\rho^2)t/\tau] \right\} / N(\pi/2\rho) \quad (2)$$

where $\Phi_N(t)$ is the photon flux normalized to the steady state value. The quantities A_i and N are defined by

$$A_i = 8 \sin^2(l\pi/2) / \pi^2 l^2 (1 + l^2\pi^2/4\rho^2) \quad (3)$$

(13) P. A. Leighton, R. W. Cray, and L. T. Schipp, *J. Amer. Chem. Soc.*, **53**, 3017 (1931).

and

$$N = 1 + \sum_{i=1}^{\infty} A_i \quad (4)$$

The reduced variable ρ is defined by

$$\rho = x/(D\tau)^{1/2} \quad (5)$$

where x is the distance to any point from the center of an illuminated strip as measured perpendicular to the strip. A subscript s associated with ρ is meant to indicate that particular value of ρ corresponding to the edge of a strip.

If we let $T(-,t)$ represent the triplet concentration at any time t using full illumination (*i.e.*, no pattern in place) then we may define

$$\gamma^2 \equiv T^2(\rho_s, \infty) / T^2(-, \infty) \quad (6)$$

as the ratio of steady state delayed fluorescence for a pattern of reduced dimensions ρ_s to that for full illumination. It is useful to define another quantity $\omega^2 \equiv T^2(\rho_s, t) / T^2(-, t)$. Since $\Phi_N(t) = T^2(\rho_s, t) / T^2(\rho_s, \infty)$, then we can say that

$$\omega^2(t) = \Phi_N(t) \gamma^2 \exp(2t/\tau) \quad (7)$$

and these values may be calculated using the time dependent and steady state solutions.

The detector response is proportional to the total photon flux during the monitor pulse. In this work the monitor pulse time was kept constant at 5.45 msec. Furthermore, there was a 0.25 msec delay between the end of an excitation pulse and the beginning of a monitor pulse. Therefore, to make the theoretical relations match the experimental arrangement $\omega^2(t)$ has to be integrated between these indicated time limits. The triplet lifetimes, τ , for 9,10-diphenylanthracene and anthracene respectively are 2.2 and 3.0 msec accounting for the small differences in integrated values of $\omega^2(t)$.

The connection between the theoretical relations and the experiment is, therefore, embodied in $\omega^2(t)$ or, more precisely, ω^2 which is the time averaged value of ω^2 . In terms of the experiment, ω^2 is the ratio of delayed fluorescence intensity with an intermittency pattern in place to that using full illumination. For the strip patterns used here for which the window to period ratio is $1/2$, it is clear that for sufficiently coarse patterns ω^2 will approach $1/2$. On the other hand, as the patterns become increasingly fine ω^2 will approach $1/4$.

The orientation of the optical system emphasized the production of a good quality image of the intermittency pattern at the test solution at the expense of a very inefficient use of the excitation light. The intensity of the excitation beam was considerably less than would normally be the case. Also, the distance over which the pattern image was in focus did not greatly exceed 1 mm and so this placed an upper limit on the optical path length of the test solution. In fact, all experiments reported here were carried out with solution thicknesses of 1 mm. Combining the effects of low incident light intensity and a short optical path length with the relatively small concentrations used ($5 \times 10^{-4} M$ for anthracene and $5.8 \times 10^{-4} M$ for 9,10-diphenylanthracene), it is apparent that the rate of light absorption is quite small and that under these conditions the transient population of triplets is never large enough to cause the rate of second-order triplet-triplet processes

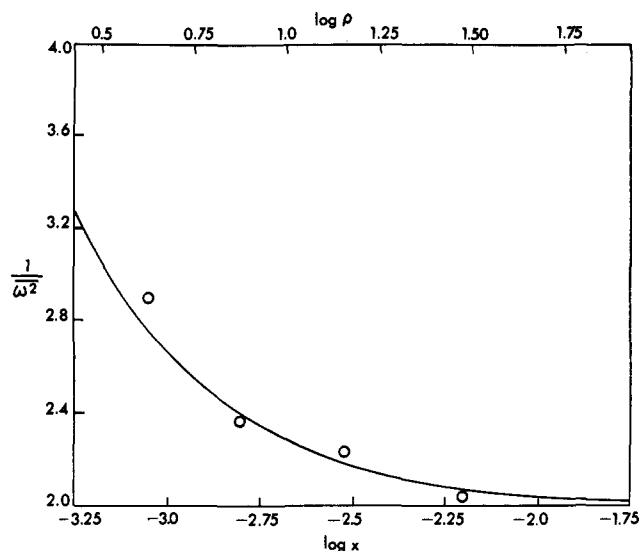


Figure 1. Experimental values of ratios of delayed fluorescence intensities of 9,10-diphenylanthracene vs. $\log x$. The solid line is a theoretical curve shifted horizontally to fit the data.

to compete effectively with first-order processes for the removal of triplets. This explains why all of our observed delayed fluorescence decay signals were strictly exponential obeying first-order kinetics. A few experiments were carried out using an altered optical system to increase the incident light intensity by a factor of three but this caused no change in the observed triplet lifetime thus confirming that first-order processes for triplet removal are dominant.

The space intermittency data for 9,10-diphenylanthracene in ethanol at 25° are shown in Figure 1 as a graph of $(\bar{\omega}^2)^{-1}$ vs. $\log x$. Each point on this graph is an average of ten separate measurements and the solid curve is the calculated graph of $(\bar{\omega}^2)^{-1}$ vs. $\log \rho$. In order to achieve this very good fit between the theoretical curve and experimental points, the theoretical curve was shifted horizontally. The value of x corresponding to $\rho = 1$ is 2.4×10^{-4} cm and when these values of ρ and x are inserted into eq 5 along with the measured lifetime of 9,10-diphenylanthracene triplets of 2.2 msec, then the calculated diffusion coefficient is $2.3 \pm 0.6 \times 10^{-5}$ cm²/sec.

It is important to recognize that the experimental points have been normalized to yield $(\bar{\omega}^2)^{-1}$ equal to 2.0 in the limit of an infinitely coarse pattern. The actual coarse-pattern limiting values are 2.6 and 2.2 for 9,10-diphenylanthracene and anthracene, respectively. Although these values are not far from the theoretical 2.0, they are nevertheless quite reproducible. The fact that the same apparatus gives different limiting values for different chemical systems is an indication that the effect is due to chemical phenomena rather than to instrumental artifacts such as geometrical effects. This is also indicated by the fact that both vertical and horizontal orientations of the strip patterns yield diffusion coefficients which are the same within experimental error. Thus, there is a clear indication that significant numbers of triplets are formed in dark regions even with the coarsest patterns. Since they cannot diffuse to dark regions in numbers large enough to cause this observed perturbation, they must be formed there in some other way. The most reasonable mechanism for

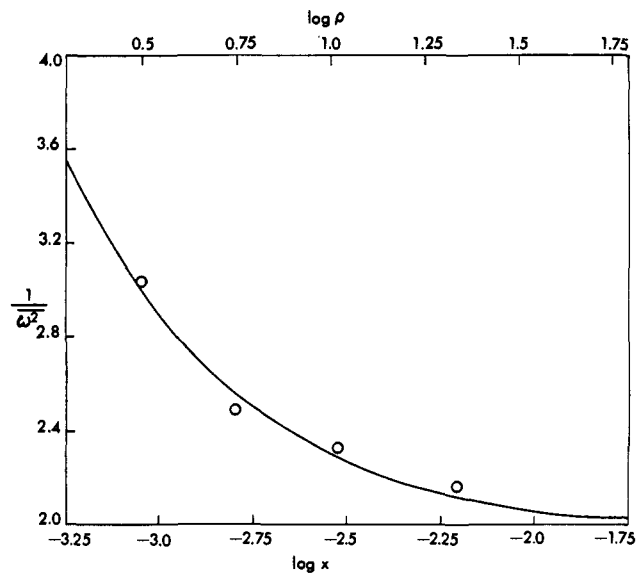


Figure 2. Experimental values of ratios of delayed fluorescence intensities of anthracene vs. $\log x$. The solid line is a theoretical curve shifted horizontally to fit the data.

this formation is that fluorescence from molecules near the edge of nonilluminated regions will be partially transmitted into these regions and reabsorbed there. This process will lead to a certain number of triplet molecules always being found in dark areas quite apart from any bulk translational motion. Since ϵ_{max} for the 0-0 transition in 9,10-diphenylanthracene is 50% larger than for anthracene,¹⁴ it is expected that the effect should be larger for the former molecule as is observed.

In Figure 2 one sees that $x = 4.6 \times 10^{-4}$ cm for $\rho = 1$ in the case of an ethanolic solution of anthracene at 25°. Combining this result with a triplet lifetime of 3.0 msec yields $D = 2.8 \pm 0.7 \times 10^{-5}$ cm²/sec for triplet anthracene.

Discussion

The most striking feature of these results is the fact that the mobility of the triplet is about twice that of the ground state molecule. In the case of anthracene an experimental value of 1.4×10^{-5} cm²/sec has been found for the diffusion coefficient of the ground state species in ethanol at 25°.¹⁵ On the basis of molecular size, 9-10-diphenylanthracene ought to have a smaller diffusion coefficient and 1×10^{-5} cm²/sec is probably a reasonable estimate. Thus, the basic question raised by these data is just why electronically excited molecules diffuse faster than their ground state counterparts.

First, one should consider the experimental uncertainties in measured diffusion coefficients to see what significance ought to be attached to this disparity between excited state and ground state mobilities. The two quantities which control the overall precision are τ , the triplet lifetime, and the value of x corresponding to a given ρ (see eq 5).

Triplet lifetimes were measured by making point-by-point graphs of the logarithm of the delayed fluorescence intensity vs. time. Since the delayed fluorescence

(14) Reference 1, pp 70 and 71.

(15) E. J. Bowen and W. S. Metcalfe, *Proc. Roy. Soc., Ser. A*, **206**, 437 (1951).

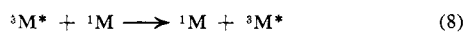
intensity is proportional to the square of the triplet concentration, then τ is twice the reciprocal of the slope of these linear graphs. Judging from limiting slopes, the relative uncertainty in τ values is $\pm 15\%$. The uncertainties in values of x depend primarily upon the placement of the theoretical curves used to fit the experimental points in Figures 1 and 2. The precision of delayed fluorescence intensities made with a given pattern is quite good, but much larger uncertainties are involved when changing from one pattern to another, so that a perfectly smooth fit to the theoretical curve is never found. Again, using limiting positions of the theoretical curve, the precision in x values is found to be about $\pm 20\%$. Thus, the overall precision in measured D values is $\pm 25\%$ and we are, therefore, left with the task of accounting for a minimum of about $7 \times 10^{-6} \text{ cm}^2/\text{sec}$ in enhanced diffusion.

There are several possibilities that should be considered to account for this enhanced diffusion. First, however, it should be mentioned that the notion of translationally hot molecules must be dismissed as a viable explanation. Calculations show that only a small fraction of an ångström could be traversed as a result of the initial photon impulse so the source of the enhanced diffusion must lie in events which occur after the absorption process has taken place.

Since the electronically excited molecule exists, for a time, in both singlet and triplet states, one should consider processes which might occur in each of these states. There seems to be no reason to believe that Brownian motion of the singlets of either DPA or anthracene could contribute significantly to this enhanced diffusion in view of their nanosecond-scale lifetimes. Presumably the Brownian motion of triplets would differ negligibly from that of the ground state molecules and so one is left with the conclusion that the enhanced diffusion is a result of energy migration and not material transfer.

As mentioned above, triplet energy transfer has been postulated before as an explanation for certain observed phenomena. For example, the nmr signals of pyrene in perdeuteriobenzene are observed to broaden when the solutions are irradiated with uv light. This was attributed to triplet energy transfer between excited and ground state pyrene molecules.⁶ The results of recent photoisomerization studies indicate that 1,3-pentadiene and 2,4-hexadiene both participate in triplet energy transfer.^{7,8}

The frequency of a triplet transfer process would depend upon the concentration of solute and upon the specific rate constant of the process



The mean-square displacement per unit time would be determined partly by this frequency and partly by the average length of each transfer event. It would also depend upon whether or not the displacements were oriented randomly in space.

Using Cocivera's specific rate constant for eq 7 of $4 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ and a solute concentration of $5 \times 10^{-4} \text{ M}$, the jump frequency would be $2 \times 10^4 \text{ sec}^{-1}$. With this frequency there is no reasonable length for a transfer event (*i.e.*, a few tens of ångströms) which can yield a random flight mean-square displacement large enough to account for the enhanced diffusion. On the other hand, a linear chain model for triplet transfer could account for the enhanced diffusion with a transfer length of about 25 Å.

Even though singlet lifetimes are much shorter than triplets, energy transfer involving singlets could account for the enhanced diffusion, again depending upon transfer length, frequency, and random flight or linear chain character of the transfer. Two types of transfer mechanisms can be envisioned here.¹⁶ First, a radiationless type of transfer



which would be relatively short range in nature and with a frequency similar to that of process 7 involving triplets. The singlet lifetimes are probably too short for this mechanism to play a significant role in enhanced diffusion. However, radiative transfer, involving fluorescence and reabsorption, could play such a role since, in the absence of quenchers, the radiative and nonradiative lifetimes will be of the same order of magnitude and transfer lengths will be on the order of the equilibrium intermolecular distances of solute molecules.

Thus, among the various possibilities, it appears that triplet-triplet transfer by a mechanism approaching linear chain character or else radiative singlet transfer offers the most attractive explanations for the observed enhanced diffusion. It is clear that further experimentation is needed to unravel the detailed nature of these processes but their importance in connection with solution photochemistry and photophysics makes continued study of definite interest.

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(16) For further details on these mechanisms, see ref 1, pp 518-576.