

EXTINCTION COEFFICIENTS AND QUANTUM YIELDS FOR TRIPLET-TRIPLET ABSORPTION USING LASER FLASH PHOTOLYSIS

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(Received March 14, 1980)

Summary

The laser flash photolysis technique was used to determine the extinction coefficients for the triplet-triplet absorption of benzophenone and naphthalene in benzene solution, and of anthracene in benzene, ethanol and cyclohexane solutions. The results obtained are compared with those of previous workers and the triplet state quantum yields for anthracene in various solvents are determined.

1. Introduction

In recent years a number of different methods have been used to determine the triplet-triplet extinction coefficients and triplet state quantum yields of many aromatic compounds. These methods have been summarized by Armand and Bensasson [1].

In the present work the peak triplet-triplet extinction coefficients and quantum yields of benzophenone, anthracene and naphthalene in solution were determined using the laser flash photolysis technique. The sample was excited with a monochromatic pulse of nitrogen laser radiation (337 nm) and the energy input to the sample was measured with respect to a standard potassium ferrioxalate actinometer [2]. The use of the calibrated laser photolysis technique leads to numerical values for the product $\epsilon_T \phi_T$ of the triplet-triplet extinction coefficient ϵ_T and the triplet quantum yield ϕ_T . Benzophenone is a convenient choice of material with which to verify the calibration of the nitrogen laser since its ϕ_T value is generally accepted to be unity [3, 4]. The value of ϵ_T for benzophenone may be used to determine the ϵ_T values for anthracene and naphthalene using the triplet energy transfer technique [5].

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2. Experimental

Solution samples were flash photolysed in a 1 cm × 1 cm × 1 cm quartz cell using nitrogen laser pulse energies of approximately 10 mJ (duration about 12 ns at full width at half-maximum) and the resulting transient absorptions were monitored using conventional kinetic spectroscopy techniques. All triplet-triplet absorption spectra were recorded using a bandpass of 2 nm. The laser output was monitored using a fast photodiode which was calibrated using a standard potassium ferrioxalate actinometer (quantum yield 1.23 at 337 nm) [2]. In order to ensure homogeneous excitation of the solution samples optical densities of less than 0.3 cm⁻¹ at 337 nm were used throughout and all samples were carefully deaerated by bubbling with oxygen-free nitrogen for at least 1 h before use.

For the triplet energy transfer process from an excited triplet donor D_T^* to a ground state acceptor A it can easily be shown that the optical densities ρ_T^D and ρ_T^A due to donor and acceptor triplets are related via the expression

$$\frac{d\rho_T^A(t)}{dt} = \frac{\epsilon_T^A}{\epsilon_T^D} \rho_T^D(t) k_1 [A] - k_3 \rho_T^A(t) \quad (1)$$

where k_1 and k_3 are the rate constants for the energy transfer process and the first order decay of A_T^* respectively. Consequently, by monitoring absorption kinetics at two wavelengths, λ_1 where only the donor triplet absorption is observed and where $\epsilon_T^D(\lambda_1)$ is known and λ_2 where the acceptor triplet build-up is observed, the value of $\epsilon_T^A(\lambda_2)$ may be obtained using expression (1).

Alternatively the ground state depletion method can be used to set a lower limit on the concentration of triplet state molecules present after photoexcitation. The decrease $\gamma_\lambda(t)$ in optical density at a wavelength λ within the ground state absorption spectrum will be given by

$$\gamma_\lambda(t) = \{\epsilon_s(\lambda) - \epsilon_T(\lambda)\} C_T(t) l \quad (2)$$

where ϵ_s is the extinction coefficient for ground state absorption, l is the optical path length and $C_T(t)$ is the time-dependent triplet state concentration. If $\epsilon_T(\lambda)$ is small in comparison with $\epsilon_s(\lambda)$ then expression (2) may be used to estimate a minimum value $C_T'(t)$ for the triplet concentration. This minimum value $C_T'(t)$ may be used, in conjunction with corresponding optical density $\rho_T(t)$ measurements in regions where $\epsilon_s = 0$, to determine an absolute upper limit $\epsilon_{Tmax}(\lambda)$ for the triplet extinction coefficient $\epsilon_T(\lambda)$.

3. Results

3.1. Benzophenone

The peak value for the ϵ_T of benzophenone in benzene solution at 533 nm was found to be 7200 M⁻¹ cm⁻¹, assuming ϕ_T to be unity [3, 4].

The shape of the benzophenone triplet absorption spectrum and the absorption maximum were in agreement with the results of Melhuish [5].

3.2. Anthracene

Energy transfer from the benzophenone triplet to anthracene was used to determine the extinction coefficient at 431 nm for the anthracene triplet in benzene solution. In these experiments benzophenone concentrations of 2.5×10^{-8} M were used with anthracene concentrations of 1.0×10^{-6} , 2.5×10^{-6} and 5.0×10^{-6} M to ensure sufficient donor excess. Using expression (1) an average value of 5.8 ± 0.3 was obtained for the ratio $\epsilon_T(\text{anthracene at 431 nm})/\epsilon_T(\text{benzophenone at 533 nm})$. Assuming $\epsilon_T(\text{at 533 nm}) = 7200 \text{ M}^{-1} \text{ cm}^{-1}$ for benzophenone this ratio yields a value of $42\,000 \pm 4000 \text{ M}^{-1} \text{ cm}^{-1}$ for the peak extinction coefficient (at 431 nm) of the anthracene triplet in benzene.

The triplet-triplet absorption spectra in the region 375 - 460 nm, obtained as the product $\epsilon_T\phi_T$, for anthracene in benzene, cyclohexane and ethanol solutions are shown in Fig. 1. The extinction coefficients of $48\,500 \text{ M}^{-1} \text{ cm}^{-1}$ and $52\,500 \text{ M}^{-1} \text{ cm}^{-1}$ at absorption maxima for the anthracene triplet in ethanol and cyclohexane respectively were obtained from the value determined in benzene by assuming that the oscillator strength for anthracene triplet absorption is solvent independent. Our experimentally measured $\epsilon_T\phi_T$ values used with these ϵ_T values yielded values of 0.53, 0.58 and 0.54 for the intersystem crossing ratio ϕ_T of anthracene in benzene, ethanol and cyclohexane respectively. Differences between these values are within the experimental error of the present work, *i.e.* $\phi_T = 0.55 \pm 25\%$ for anthracene in ethanol, benzene and cyclohexane. Rate constants of $0.49 \times 10^9 \text{ s}^{-1} \text{ M}^{-1}$ and $0.74 \times 10^9 \text{ s}^{-1} \text{ M}^{-1}$ were obtained for the energy transfer from benzophenone to anthracene and to naphthalene respectively.

In order to confirm our reported values ground state depletion measurements were made for anthracene in benzene, ethanol and cyclohexane solutions. As discussed in Section 2, such measurements may be used to set an upper limit on the extinction coefficients for triplet-triplet absorptions. A typical ground state depletion spectrum (given as $\gamma(t)$ values) for anthracene in benzene is shown in Fig. 2. The upper limits obtained for ϵ_T (at the absorption maxima) of the anthracene triplet in benzene, ethanol and cyclohexane solutions are given in Table 1 which also summarizes all our values.

3.3. Naphthalene

The triplet energy transfer process from benzophenone to naphthalene was used to determine a value for the peak triplet absorption coefficient of naphthalene in benzene which was found to be $11\,300 \text{ M}^{-1} \text{ cm}^{-1}$.

4. Discussion

Confirmation of the accuracy of the ferrioxalate laser energy calibration, leading to the $\epsilon_T\phi_T$ product, is seen in the close agreement between the

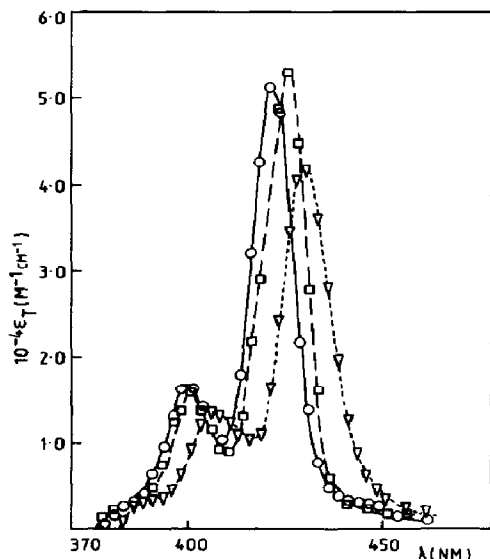


Fig. 1. Triplet-triplet absorption spectra for anthracene in ethanol (○), cyclohexane (□) and benzene (▽).

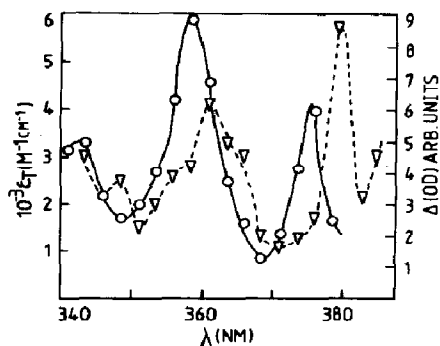


Fig. 2. Ground state depletion spectrum (○) and pure triplet state absorption spectrum (▽) of anthracene in benzene solution.

TABLE 1

Triplet state parameters for benzophenone, anthracene and naphthalene

Substance	Solvent	Peak value of $\epsilon_T \phi_T$ ($M^{-1} \text{ cm}^{-1}$)	Peak λ (nm)	ϵ_T at peak λ ($M^{-1} \text{ cm}^{-1}$)			
				Upper limit from GSDM ^a	Energy transfer ^b	Oscillator strength ^c	$\phi_T = (\epsilon_T \phi_T) / \epsilon_T$
Benzophenone	Benzene	7 200 ^d	533		7 200 ^d		1.00
Anthracene	Benzene	22 000 ^d	431	69 000	42 000 ^d	42 000	0.53
	Ethanol	28 000 ^d	421	69 500		48 500 ^d	0.58
	Cyclohexane	28 500 ^d	423	54 000		52 500 ^d	0.54
Naphthalene	Benzene	—	425		11 300 ^d		

^aGround state depletion method.

^bEnergy transfer from benzophenone.

^cApproximate values calculated assuming ϵ_T (anthracene) = $42\,000 \text{ M}^{-1} \text{ cm}^{-1}$ in benzene and that the oscillator strength is solvent independent.

^dAccurate to within $\pm 10\%$.

peak value of ϵ_T for benzene solutions of benzophenone and the work of Land [6] and Bell and Linschitz [7]. Our value of $42\,000 \text{ M}^{-1} \text{ cm}^{-1}$ for ϵ_T at maximum for anthracene in benzene is in close agreement with results published by Bensasson and Land [8]. In ethanolic solution the peak value of ϵ_T for anthracene is in excellent agreement with recent work of Tfibel and Linqvist [9] and Kobayaski *et al.* [10]. Similarly, in cyclohexane solution the average value of ϵ_T at peak is about 80% of the result reported by

Bensasson and Land [8]. However, Ledger and Salmon [11] report results for anthracene in benzene and in cyclohexane which are inconsistent with the foregoing; their results were based on the validity of the Hadley and Keller [12] treatment which requires that ϵ_T changes in a linear fashion over the region of overlap between the triplet absorption spectrum and the ground state absorption spectrum. Figure 2, showing the triplet absorption spectrum which we observed in this region, contrasts sharply with that published by Ledger and Salmon [11]. Our spectrum, which is in close agreement with the triplet spectrum in ethanolic solution of Dempster *et al.* [13] for the 340 - 380 nm region, shows that ϵ_T does not vary linearly. However, the value of $75\,000\text{ M}^{-1}\text{ cm}^{-1}$ for the anthracene triplet in ethanol reported by Dempster *et al.* differs considerably from our values. A comparison of these results is given in Table 2.

The value of ϕ_T derived from the product $\epsilon_T\phi_T$ and the extinction coefficient determined by energy transfer is somewhat less than that obtained by some other workers, as shown in Table 3. However, considerable diversity exists in published results and, as they are derived from a knowledge of ϵ_T and the product $\epsilon_T\phi_T$, it is important that both of these values should be obtained under similar experimental conditions as was the case in this work.

TABLE 2

Comparison with other recent work

Substance	Solvent	$\epsilon_{T\max}$ ($\text{M}^{-1}\text{ cm}^{-1}$)	λ_{\max} (nm)	Experi- mental method ^a	Temper- ature (K)	Reference
Benzophenone	Benzene	7 200 ^b	533			This work
		7 630	532.5	ET	290	8
		6 500	532.5	ET	290	7
Anthracene	Benzene	42 000 ^b	431			This work
		45 500	432.5	ET	290	8
		53 000 ^c	428.5	GSD-HK	290	11
		48 500 ^b	421			This work
	Ethanol	50 000 ^b	419	DF	290	9
		52 000	421	ET	290	10
		75 000	421	ET	290	13
Ethanol-methanol	90 000	-	-	113	14	
Cyclohexane	52 500 ^b	423			This work	
Naphthalene	Benzene	64 700	425	ET	290	8
		85 700 ^d	422.5	GSD-HK	290	11
		11 300 ^b	425			This work
		13 200	425	ET	290	8

^aET, energy transfer method; GSD-HK, ground state depletion method-Hadley-Keller treatment; DF, delayed fluorescence method.

^bAccurate to within $\pm 10\%$.

^c $\pm 2000\text{ M}^{-1}\text{ cm}^{-1}$.

^d $\pm 3200\text{ M}^{-1}\text{ cm}^{-1}$.

TABLE 3

Intersystem crossing ratios ϕ_T for anthracene

ϕ_T	<i>Solvent</i>	<i>Reference</i>
0.70	Ethanol	15
0.72	Liquid paraffin	16
0.58	Liquid paraffin	17
0.71	Ethanol	1
0.58	Ethanol	This work

The value of ϵ_T at maximum obtained for naphthalene in benzene solution is in good agreement with the work of Land [6].

Acknowledgment

One of the authors (K. T. V. G.) would like to acknowledge personal financial support from the Department of Education, Northern Ireland.

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