"hot" ground state levels. Following our analyses of the trifluoro- and trichlorobenzene cations[17] we expect that these features are to be associated with transitions from the lower levels in the $j = {}^3/_2$ stack which are predicted to be very intense.[17] We defer detailed discussion of the assignments given in Table I until a future publication[18] dealing with the theory and calculation of the Jahn–Teller effect.

However, it is appropriate to point out here that the assignment of these combination bands is crucial to the understanding of the Jahn–Teller effect in this compound. We showed[17] that in the case of $C_6H_3Cl_3^+$ and $C_6H_3F_3^+$ the simple single mode model of the Jahn–Teller effect used in the earlier work on these compounds[5-7,11-13] was inadequate and gave misleading results. Not surprisingly, this appears to be the case in $C_6Cl_3F_3^+$ also and the assignments given in Table I are based on preliminary calculations using the model involving mode coupling as outlined previously.[17]

For $C_6H_3F_3^+$ and $C_6H_3Cl_3^+$, key factors in the reappraisal of their Jahn-Teller effects were the recent availability of laser excited wavelength resolved fluorescence data and the observations of vibrationally unrelaxed emission in the matrix. Similar experiments are planned for $C_6F_3Cl_3^+$ to give more information on the ground state vibrational frequencies and Jahn–Teller splittings. Such data together with the more sophisticated analysis should resolve the remaining ambiguities with respect to the Jahn–Teller distortion in this compound.

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Phosphorescence and Delayed Fluorescence of 1-Chloronaphthalene in Micellar Solutions

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Abstract: Phosphorescence, delayed monomer fluorescence, and delayed excimer fluorescence of 1-chloronaphthalene are readily observable in conventional anionic and cationic micelles. The delayed luminescences are shown to arise predominantly from triplet–triplet annihilation within a single micelle. A kinetic analysis of the data allowed evaluation of the rate constant for intramicellar triplet–triplet annihilation and the rate constant for exit of 1-chloronaphthalene from a micelle.

Introduction

The rates of exit from and entrance of aromatic compounds into micelles have been investigated recently by phosphorescence decay and by solubility measurements.[1] The rate constant for triplet energy transfer has been evaluated for aromatic arenes (donor) and rare-earth ions (acceptor). Energy transfer in these systems probably takes place at sites near the micelle–water interface.[2,3] The exit rate constants of aromatic hydrocarbons from the micelle are of the order of 10^3–10^4 s^{-1}, whereas values of 10^7–10^8 M^{-1} s^{-1} were reported for intramicellar bimolecular energy transfer processes.[4-6] Thus, in the case of aromatic hydrocarbons as phosphorescence probes, exit from the micelle followed by quenching in the aqueous phase is expected to be an important pathway for triplet deactivation. On the other hand, in the time domain of typical fluorescence decay, the arene molecules usually remain inside of the micelle and do not exit into the aqueous environment.

Relevant to the above investigations we report here the first observation of delayed fluorescence and phosphorescence of 1-chloronaphthalene (Cl-N) in conventional anionic and cationic micelles. We have investigated the time-resolved spectra of Cl-N in micellar solutions and we have observed prompt fluorescence (PF), phosphorescence (P), delayed fluorescence (DF), and delayed excimer fluorescence (DEF). Studies of the relative intensities of DF and P as a function of (1) occupancy number of Cl-N, (2) aqueous quenchers, and (3) dilution with water above the cmc lead to the conclusion that DF results predominantly from intramolecular T-T annihilation. An analysis of the triplet decay by P and triplet–triplet absorption allowed evaluation of the rate constant of triplet–triplet (T–T) annihilation in the micelles in addition to the rate constant of the competing exit of triplet Cl-N from the micelles.

Experimental Section

1. Materials. 1-Chloronaphthalene (Aldrich Chemical Co.) was purified by repeated vacuum distillation. Hexadecyltrimethylammonium bromide (HDTBr), purchased from Sigma Chemicals, was recrystallized twice from methanol after being washed with ethyl ether. Electrophoresis grade sodium dodecyl sulfate (SDS) was used as supplied from Bio-Rad Laboratories. Hexaamminecobalt(III) chloride (Alfa Products) and sodium nitrite were recrystallized twice from water. Spectrograde isooctane was passed through a silica gel column. Micellar solutions were fully degassed by repeated freeze–thaw cycles (~10^{-5} mmHg).

2. Spectroscopy. a. Measurements of Phosphorescence and Delayed Fluorescence Spectra. Time-resolved spectra of phosphorescence and delayed fluorescence were measured with a high-sensitivity emission spectrophotometer (Spex Fluorolog) whose operation is based on the photon-counting method. The excitation light source used was a xenon flash lamp (EG & G, FX198U) possessing a half-width of ~3 µs, about 5000 mJ of electrical energy dissipating in each flash. The delay time after a flash excitation was determined by the output of the photomultiplier–amplifier–discriminator circuit of the spectrophotometer. The sampling time is defined as the amount of time over which data excited by a single flash are integrated. By changing the delay time and the sampling time appropriately along the phosphorescence decay curve, time-resolved spectra were obtained in time ranges from 10 µs to 1 s.

b. Measurements of Phosphorescence Decay. Phosphorescence decay was monitored by two different techniques.

(i) Photon Counting–Multichannel Digital Boxcar Technique. In this case, phosphorescence or delayed fluorescence was observed by means of a photon counting based spectrophosphorimeter which was combined with a multichannel analyzer (MCA). The emission signal at fixed observed wavelength was sent to the MCA with a scaling module (Tracor Northern, TN-1710 and 1710-26). The time resolution of the MCA was 10 µs. Decay curves of the emission were accumulated from 3 × 10^4 to 6 × 10^4 flashes. The apparatus and technique for the method of phos-

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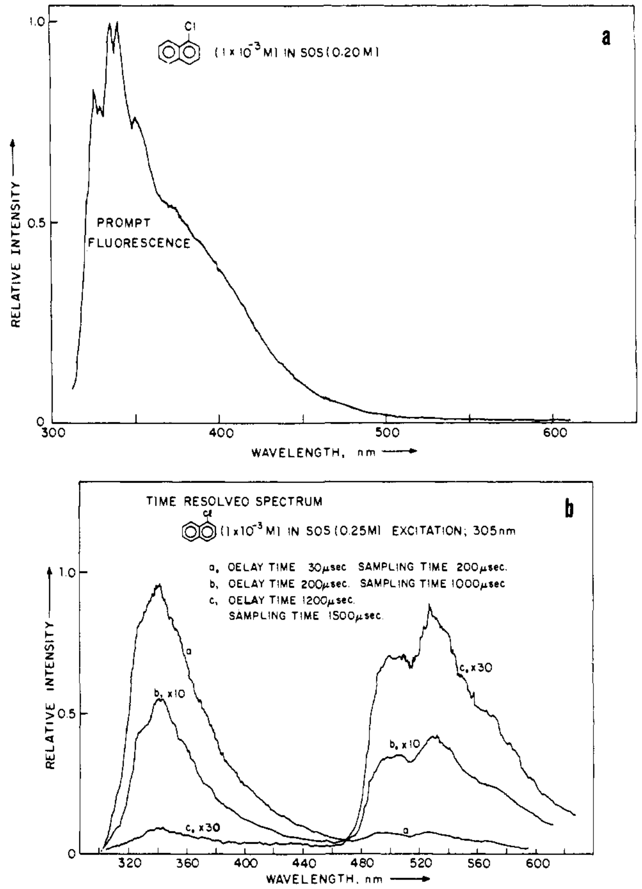

Figure 1. (a) Conventional steady state photoluminescence spectrum of a degassed aqueous solution of Cl-N with SDS. The emission around 340 nm is assigned to prompt fluorescence. (b) Time-resolved spectrum of an aqueous solution of Cl-N (1×10^{-3} M) and SDS (0.25 M) at 22 °C. The emission spectra around 340 nm and 530 nm are assigned to delayed fluorescence and phosphorescence, respectively.

phoresecence measurement have been described elsewhere.[7,8]

(ii) Triplet–Triplet (T–T) Absorption Measurement. The method used for the measurement of the transient triplet absorption has been described previously.[9,10] Samples were excited by a 308-nm emission pulse produced from an excimer laser (Lambda Physik, Excimer EMG 500) employing XeCl as the lasing medium. Transient absorption spectra were observed perpendicular to the direction of the excitation pulse, using a 1000-W Xe lamp as an interrogating source which was passed through a monochromator (Aminco, $^1/_4$ m) and monitored with a five-stage 1P28 photomultiplier.[10] The signal was displayed on a storage oscilloscope (Tektronix, 7623A) and the trace was photographed on 3000 ASA Polaroid film for analysis. The extinction coefficient of Cl-N at the band maximum around 420 nm has been determined to be 3.0×10^4 L M^{-1} cm^{-1}.[11-13]

Results

Figure 1a shows the conventional steady state photoluminescence of Cl-N in aqueous solutions containing 0.20 M SDS. The spectrum consists totally of prompt fluorescence. Figure 1b shows the time-resolved spectra obtained from 1×10^{-3} M Cl-N in 0.25 M SDS solution excited with a microsecond flash. The emission maximizing near 340 nm is assigned by inspection to delayed fluorescence (DF) of Cl-N and the emission maximizing near 530 nm is assigned to Cl-N phosphorescence (P). The curves a, b, and c correspond to different delay times after the exciting pulse. Thus, curve a represents the spectrum obtained after a 30-μs delay, curve b, the spectrum obtained after a 200-μs delay, and curve c, the spectrum obtained after a 1500-μs delay. The decay of the intensity of both DF and P is unimolecular and corresponds to lifetimes of ~100 and 400 μs, respectively. It is important to note that DF from Cl-N is *not* significant in homogeneous isooctane solution in the concentration region studied.

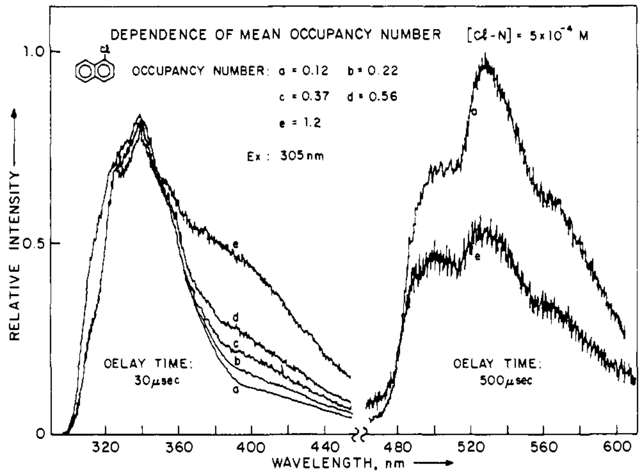

Figure 2. Dependence of mean occupancy number on the spectral intensity of DF, DEF, and phosphorescence in SDS solution at 22 °C. Mean occupancy number was varied by changing the concentration of detergent at fixed Cl-N concentration (~5×10^{-4} M). Sampling time 2000 μs.

From Figure 1b it is clear that DF dominates the emission spectrum of Cl-N at short delay times and that, as the DF intensity decreases, the phosphorescence intensity increases, relatively. At longer times only phosphorescence remains and it decays exponentially.

In order to obtain information relevant to the mechanism and triplet dynamics which lead to the behavior observed in Figure 1b, and in order to understand the basis for the striking differences in behavior in micellar compared to homogeneous solution, several types of experiments were run. The dependence of the ratio of intensities of DF to P was measured as (a) a function of ⟨Cl-N⟩, the average occupancy number of chloronaphthalene in a micelle; (b) a function of dilution with water at constant ⟨Cl-N⟩; (c) a function of the concentration of quenchers that operated selectively in the bulk aqueous phase.

Variation of I_{DF}/I_P as a Function of ⟨Cl-N⟩ at Fixed [Cl-N] The average occupancy number ⟨Cl-N⟩ is defined as

$$\langle \text{Cl-N} \rangle = ([\text{Cl-N}]/[\text{Det}])n$$

where [Cl-N] and [Det] are the bulk concentrations of Cl-N and detergent, respectively, and *n* is the aggregation number of the detergent. Thus, ⟨Cl-N⟩ may be varied by variation of [Cl-N], [Det], or *n*. All experiments were performed in concentration ranges of detergent for which *n* is a known quantity, and for which *n* is not subject to significant variation (in the absence of Cl-N).

In a series of experiments with [Cl-N] fixed at ~5×10^{-4} M, the concentration of SDS was varied from 0.025 to 0.25 M. From the literature value of $n = 60$,[15] we find that ⟨Cl-N⟩ varies from ~1.2 to ~0.12 for this variation of [SDS]. The experimentally observed variation of I_{DF} and I_P as a function of ⟨Cl-N⟩ is shown in Figure 2. The spectrum shown corresponds to a delay time of approximately 50 μs and sampling time of 2000 μs. Similar results were obtained in HDTBr. A new feature appears in the delayed fluorescence spectrum at the highest values of ⟨Cl-N⟩; i.e., a new band, *assigned to delayed excimer* fluorescence, is observed. From Figure 2 it is apparent that I_{DF} increases with

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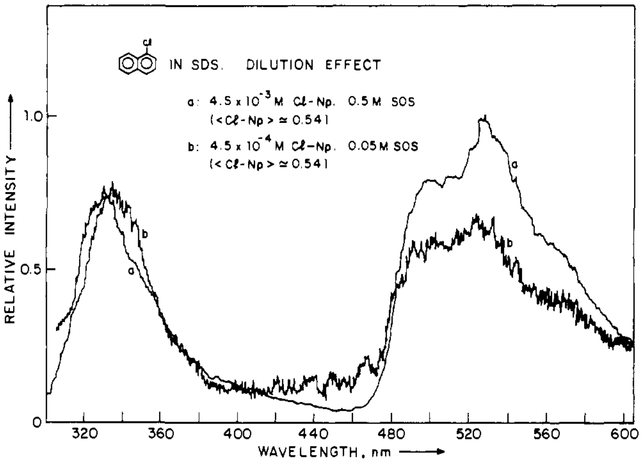


Figure 3. Dilution effect on the intensity ratio of I_{DF}/I_P. Solution of (a) was diluted 1/10 times with water (b). After a large dark noise of spectrum b was subtracted, the ratio I_{DF}/I_P gave almost the same value for both (a) and (b) spectra. Delay time and sampling time are 30 and 800 μs, respectively.

Table I. Dilution Effect of a Micellar System with Water on I_{DF}/I_P at Fixed ⟨Cl-N⟩

micelle	[Det], M	[Cl-N], M	⟨Cl-N⟩	rel I_{DF}/I_P
HDTBr	0.20	1.5×10^{-3}	0.52	3.3
	0.020	1.5×10^{-4}	0.55	2.5
SDS	0.20	1.5×10^{-3}	0.47	2.7
	0.020	1.5×10^{-4}	0.82	2.2

increasing ⟨Cl-N⟩, whereas I_P decreases with ⟨Cl-N⟩.

Variation of I_{DF}/I_P as a Function of Micelle Concentration at Fixed ⟨Cl-N⟩. Above the cmc, dilution of a micellar system with water does not significantly alter the value of ⟨Cl-N⟩; i.e., since the ratio [Cl-N]/[Det] remains constant with aqueous dilution, if n remains constant with dilution, then ⟨Cl-N⟩ also remains constant. Figure 3 shows the results of aqueous dilution on the ratio I_{DF}/I_P. Data extracted from Figure 3 are summarized in Table I. The significant qualitative result is that dilution by a factor of 10 results in a variation of I_{DF}/I_P of less than 25% for both SDS and HDTBr micellar systems.

Variation of I_{DF}/I_{DP} as a Function of Quencher in the Bulk Aqueous Phase at Fixed ⟨Cl-N⟩ and Fixed [Cl-N]. The long lifetime of triplet Cl-N allows triplet exit into the aqueous phase to compete with intramicellar triplet decay. We have determined that NO_2^- and Co^{3+} are excellent quenchers of Cl-N in aqueous solutions ($k_q = 5.7 \times 10^9$ and 4.3×10^9 M^{-1} s^{-1}, respectively). The common charge of the surface of SDS and NO_2^- should severely inhibit quenching of micellized Cl-N triplets relative to Cl-N triplets dissolved in the aqueous phase. Similarly, Co^{3+} should be a specific aqueous phase quencher of Cl-N in micellar HDTBr solutions.

Figure 4 shows the variation of I_{DF}/I_P ((⟨Cl-N⟩ = 0.16, [Cl-N] = 5×10^{-4} M) as a function of $[NO_2^-]$ for 0.20 M solutions of SDS. The phosphorescence intensity decreases dramatically as $[NO_2^-]$ is increased. On the other hand, I_{DF} suffers an initial drop upon addition of a low concentration of NO_2^- and then undergoes little further change upon further 100-fold increase in the concentration of NO_2^-.

Triplet–Triplet Absorption of Cl-N in Micellar Solutions. The decay characteristics of Cl-N triplets in micellar solutions were monitored by triplet–triplet (T–T) absorption. Figure 5 shows a representative decay curve for T–T absorption. The decay curves do not fit a simple first-order decay, but conform to a second-order decay at short times and a first-order decay at longer times.

Discussion

Mechanisms of Interpretation of the Data and Evaluation of Rate Constants. Before selecting a mechanism for the derivation of rate constants from our data, we consider several qualitatively distinct mechanisms. The major qualitative features of the data are (a) the variation in I_{DF} and I_P as functions of ⟨Cl-N⟩, micelle concentration [M], and quencher concentration $[Q]_w$; (b) the observation of DEF at high ⟨Cl-N⟩.

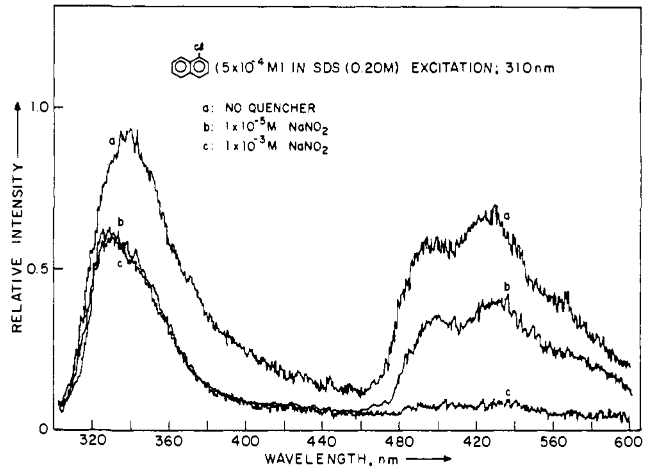


Figure 4. The effect of quencher in bulk aqueous phase on the phosphorescence and DF. Delay time and sampling time are 30 and 800 μs, respectively.

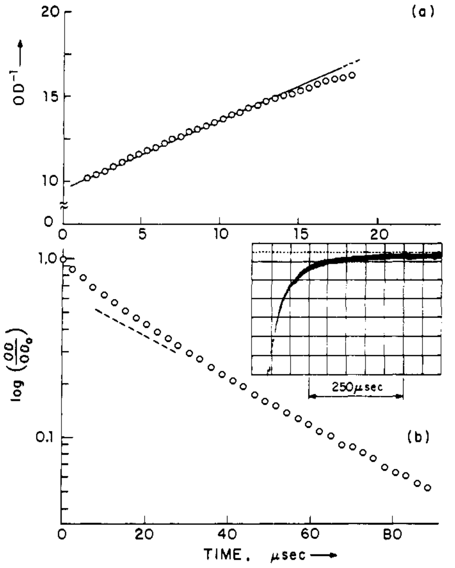


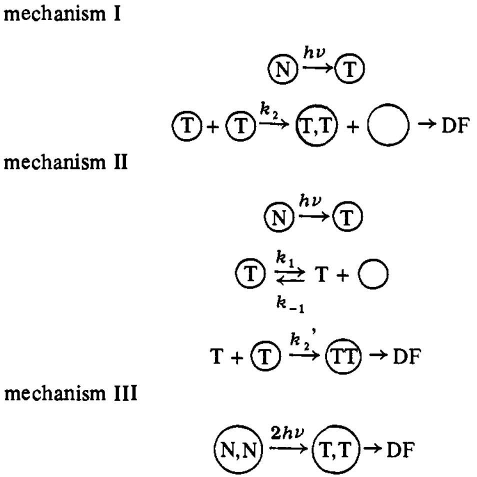
Figure 5. A decay curve of Cl-N (5×10^{-4} M) in SDS (0.20 M) with NO_2^- (1×10^{-3}) monitored by T–T absorption at 23 °C. The decay curve fit the second-order kinetics in a first time region (a) and first order in a slow time region (b).

Under the assumption that DF is due to intramicellar T–T annihilation, three distinct a priori mechanisms for production of DF may be considered for generating two triplets in one micelle. They are given in Scheme I, where circles represent micelles.

In mechanisms I and II individual naphthalenes in singly occupied micelles are excited to eventually produce micelles occupied by a single triplet, T. In mechanism III, micelles containing two (or more) naphthalenes are viewed as eventually producing a micelle containing two triplets in the same micelle. In mechanism I occupancy of two triplets in a single micelle comes about via the interaction of two single occupied micelles. In mechanism II occupancy of two triplets in the same micelle comes about via escape of a micellized triplet into the aqueous phase followed by entry of the triplet into a micelle containing a triplet molecule. These three mechanisms represent the limiting pathways by which the occupancy of two triplets in the same micelle may come about after an initial excitation pulse.

From the results discussed earlier, mechanism I (for which bimolecular interactions between micelles are rate determining) may be ruled out as the main pathway to DF since dilution in the concentration of micelles does not lead to a significant change in the value of I_{DF}/I_P.

Scheme I. Three Mechanisms for Generation of DF in Micellar Solution[a]



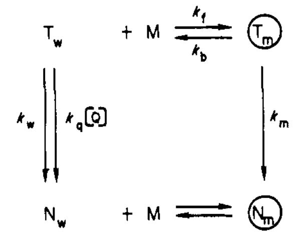
[a] N = 1-chloronaphthalene; T = 1-chloronaphthalene triplet; circle = micelle.

Mechanism II may be ruled out as the major source of DF by the observation that aqueous quenchers of Cl-N triplets fail to significantly influence the value of I_{DF} while significantly reducing I_P.

Mechanism III, however, is consistent with the results discussed above. The increase in I_{DF} relative to I_P with increasing Cl-N is simply a result of the increasing multiple occupancy expected from Poisson statistics.[4] The constancy of the value I_{DF}/I_P with decreasing micelle concentration at constant ⟨Cl-N⟩ and the specific quenching of I_P relative to I_{DF} by aqueous-phase quenchers are also consistent with mechanism III. Thus, the observation of specific quenching of I_P also suggests that the T–T annihilation process in micellar phase is faster than the exit rate of Cl-N from the micelle, and consequently is not affected significantly by aqueous-phase quencher.

In order to evaluate the rate constants for encounter of two triplets in one micelle (k_{T-T}) and for exit of Cl-N from the micelle (k_b), we may treat independently two cases of kinetics for micelles which are occupied by one and by two probes (eq 1). The treatment is appropriate if Poisson statistics hold and the intermicellar exchange of solute during the triplet lifetime is negligible.

The kinetic scheme for triplets that are partitioned between aqueous and micelle phase and for which only single occupancy is involved is given by eq 1, where T_m, T_w, N_m, and N_w denote



(1)

the triplet and the ground-state probes in aqueous and water phase, respectively. k_f, k_b, k_m, and k_w indicate rate constants for entrance into and exit from micelle and deactivation in the micelle and water phase, respectively.

We assume that the observed transient signal arises only from the micelle phase because of extremely low concentration of the probe in aqueous phase. Under the condition of ($k_b + k_f[M] + k_q[Q]) \gg (k_m - k_w)$,[16] the kinetic equations for eq 1 give the phosphorescence decay function:

$$[T_m] = C \exp\left\{-\frac{k_m k_f[M] + k_w k_b + (k_m + k_b)k_q[Q]}{k_b + k_f[M] + k_q[Q]}t\right\} \tag{2}$$

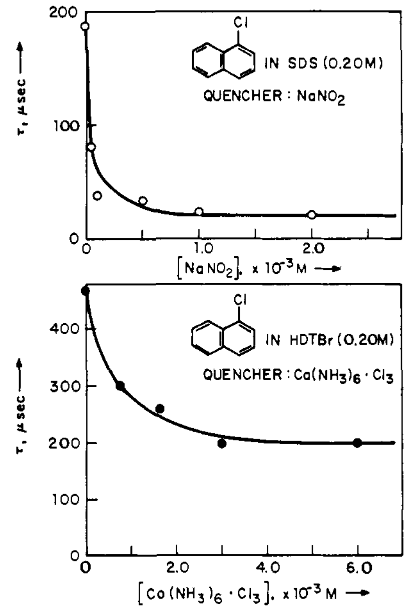


Figure 6. Dependence of quencher concentration on the first-order decay of Cl-N (5×10^{-4} M) phosphorescence at 22 °C.

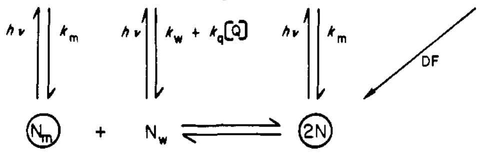
Table II. Unimolecular and Bimolecular Rate Constant of Cl-N in SDS Micelle Solution[a]

quencher ($NaNO_2$), M	unimolecular k_{obsd}, s^{-1}	bimolecular k_{T-T}, $M^{-1}\ s^{-1}$
0	5.4×10^3	2.6×10^8
5×10^{-5}	1.2×10^4	2.7×10^8
1×10^{-4}	2.6×10^4	2.8×10^8
5×10^{-4}	2.9×10^4	2.8×10^8
1×10^{-3}	4.2×10^4	2.9×10^8
2×10^{-3}	4.8×10^4	3.1×10^8

[a] [SDS] = 0.20 M; [Cl-N] = 5×10^{-4} M.

Here C represents some constant for time t.

The kinetic scheme of the micelle which is occupied by two triplets is given by eq 3. If the T–T annihilation process is much faster than the exit and entrance rates, it will not be affected by quencher in bulk aqueous phase. The time behavior for this case is separate from (2) and is given by



(3)

$$[T_m]^{-1} - [T_m^0]^{-1} = k_{T-T}t \tag{4}$$

where $[T_m^0]$ represents the concentration of triplet probe at $t = 0$. Thus the overall decay behavior of triplet Cl-N will be represented as the sum of eq 2 and 4.

Figure 6 shows the plots of the reciprocal of observed first-order rate constant (long component) k_{obsd}^{-1} as a function of quencher concentration for both SDS and HDTBr solutions, where k_{obsd}^{-1} ($=\tau_{obsd}$) is expressed as

$$\tau_{obsd} = k_{obsd}^{-1} = \frac{k_b + k_f[M] + k_q[Q]}{k_m k_f[M] + k_w k_b + (k_m + k_b)k_q[Q]} \tag{5}$$

Table II also shows the observed unimolecular and bimolecular rate constants for SDS solution. k_{obsd} initially increases, then approaches a limiting value, while k_{T-T} is constant with increasing quencher concentration, indicating that the T–T annihilation process is not affected by water-soluble quenchers. This observation is also consistent with the spectral changes shown in Figure 4.

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[16] This limitation is safely assumed for the present case: $k_m - k_w \leq {\sim}10^4\ s^{-1}$ and $k_f[M] \geq 5 \times 10^6\ s^{-1}$. More details of the method for estimation of the order are given in ref 1.

Table III. Rate Constants for Exit from and the Formation of Delayed Fluorescence in the Micelle

micelle	exit rate, s^{-1} 1-chloronaphthalene (this work)	1-bromonaphthalene (lit.)[a]	k_{T-T}, M^{-1} s^{-1}
SDS	4.3×10^4	3.3×10^4	2.8×10^8
HDTBr	1.9×10^3	4.5×10^3	0.8×10^8

[a] Reference 1.

Equation 2 shows that the limiting values at $[Q] \rightarrow \infty$ gives $k_b + k_m$ which corresponds to the constant values of k_{obsd} at high quencher concentration (Figure 6). The phosphorescence lifetime at low concentration of Cl-N (1×10^{-5} M) and high detergent concentration (0.2 M for SDS and 0.5 M HDTBr) allows evaluation of k_m. Thus, values of $k_m = 5.0 \times 10^3$ (SDS) and 2.2×10^3 s^{-1} (HDTBr) are obtained. Using these values and $k_b + k_m$, we can evaluate the exit rates. The exit rate constant and bimolecular rate constant for the T–T annihilation process are summarized in Table III in comparison with those for 1-bromonaphthalene. The T–T annihilation rate is much greater than the exit rate, leading to the observed enhancement of DF in micellar solution.

Conclusion

This study reports the first observation of delayed fluorescence of an aromatic compound in micellar solution.[17] Presumably, the combination of a modest fluorescence yield, a good intersystem crossing yield, and a long triplet lifetime is optimal for the occurrence of DF in micelles. The observation of a second-order component in triplet decay of Cl-N in micelles is consistent with T–T annihilation as a significant pathway for DF. The evaluated rate constant for T–T decay ($\sim 10^8$ M^{-1} s^{-1}) is of the order expected for "diffusion controlled" quenching in micelles such as HDTBr and SDS.[5]

Acknowledgments. The authors thank the National Institutes of Health (Grant GM25523) and the National Science Foundation (Grant NSF-CHE78-00692) for their generous support of this research.

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Negative Ion States of 1,3-Cycloalkadienes

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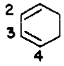
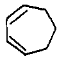
Abstract: Attachment energies for 1,3-cyclohexadiene (**1**), 1,3-cycloheptadiene (**2**), and 1,3-cyclooctadiene (**3**) as obtained from electron transmission spectra are presented. The first electron affinity was also obtained for **1** and **2**. Changes in the experimentally measured attachment energies are correlated with changes in the energies of the unoccupied molecular orbitals. The trends in the orbital energies are analyzed by INDO molecular orbital calculations in terms of $\angle C_1C_2C_3$ and the degree of twist about C_2–C_3. The data indicated the importance of through-space C_1–C_3 and C_1–C_4 interactions and reconcile the first ionization potentials of **1** and **2** with a nonplanar π system in **1** and a planar π system in **2**.

The cycloalkadienes provide an excellent opportunity to study the nature of the interaction of semilocalized π orbitals. Geometrical effects on through-space and through-bond interaction can be observed within a series of cyclodienes since the orientation of C–C double bonds relative to one another varies with ring size. The effect of each double bond on the other is reflected in the splitting of electronic states. The magnitude of the effect can be assessed from measurements of the energy required to add or remove an electron from a π orbital to create an anion or cation. We report herein measurements of energies of the negative ion states arising from electron capture into a π^* orbital of 1,3-cyclohexadiene (**1**), 1,3-cycloheptadiene (**2**), and 1,3-cyclooctadiene (**3**).



1



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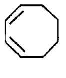

3

The series **1**–**3** provides an interesting range of orientation of the double bonds relative to one another. The conformation of cyclohexadiene (**1**) is a semichair with the diene moiety twisted approximately 18° about the C_2–C_3 bond and with $\angle C_1C_2C_3$ and $\angle C_2C_3C_4 = 120°$. It is now generally agreed that cycloheptadiene (**2**) has a C_s conformation with the carbon skeleton planar except for C_6,[2-4] although earlier work[5,6] led to suggestions that the double bonds are not coplanar. Electron-diffraction experiments[3] give $\angle C_1C_2C_3 = 129°$. The diene unit of cyclooctadiene (**3**) is highly twisted. The extent of twist is given as 42° by electron diffraction,[7] 42–65° by force-field calculations,[8-10] and 60° by vibrational spectroscopy.[4]

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