

kcal/mol) the C_{2v} constrained path.

(ii) The barrier for this reaction is sensitive both to the flexibility of the basis set and to the effect of higher order excitations. The most accurate calculations predict a C_{2v} constrained barrier of 2.5 kcal/mol, implying an unconstrained barrier of ~ 1 kcal/mol. Since this barrier is very sensitive to the size of the basis set it is possible that calculations with larger basis sets will show no barrier.

As noted in the Introduction, experiments by Braun et al.¹ and Husain et al.² have shown this to be a very fast reaction at room temperature. In Braun's experiments it was shown that atomic carbon is nearly quantitatively removed from the system in a time span corresponding to about 10^3 collision with H_2 per carbon atom. Assuming a lifetime for the hot CH_2^* product of 10^{-11} – 10^{-12} s and assuming a unit collision efficiency for stabilizing the CH_2^* , Braun concluded that only one out of every 10^2 to 10^3 CH_2^* formed are stabilized. This then implies that the collision efficiency for formation of CH_2^* must be in the range 0.1–1.0. We note that, since only one of three surfaces is reactive, Braun's results imply a collision efficiency on the 3A_2 surface is excess of 0.3. This strongly suggests that there is essentially no barrier to reaction and that the steric factor on the 3A_2 surface is near unity.

Although the conclusion that there is essentially no barrier to this reaction is consistent with the trends seen in the calculations, the conclusion that the steric factor is near unity would appear, at first, to be inconsistent with a weakly avoided crossing. There are at least three ways to reconcile these theoretical and experimental results:

(i) If the reaction occurs through a weakly avoided

crossing, both the forward and reverse reactions should have small preexponential factors. This would imply that the CH_2^* lifetime might be considerably larger than the 10^{-11} to 10^{-12} s assumed in the analysis of the experimental results and that a larger fraction of the CH_2^* would therefore be stabilized. If, for example, the CH_2^* lifetime is 10^{-9} s, a reaction collision efficiency of 0.001 would be sufficient to account for the observations.

(ii) The calculations suggest the presence of a long-range minimum on the 3A_2 surface corresponding to a weakly bound complex of H_2 with $C(^3P)$. Such a minimum if deep enough to support a bound vibrational level could increase the collisional probability for crossing to the 3B_1 surface, since the vibrational motion of the complex so formed would probably span the crossing region.

(iii) The observed rate of disappearance of $C(^3P)$ in H_2 may be due to the formation of the 3A_2 complex rather than the 3B_1 ground state.

In any case it is clear that the presence of the low-lying 3A_2 state is crucial to the reaction. This state is low lying primarily due to the absence of repulsive interactions between the occupied carbon p orbitals and the H_2 orbital. In this respect H_2 is unique; no corresponding orientation of approach exists for $C(^3P) + CH_4$. Therefore it is not unreasonable that the reaction of $C(^3P)$ with CH_4 is much slower than that with H_2 , as observed.³

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Registry No. C, 7440-44-0; H_2 , 1333-74-0.

Effect of Polar Solvents on Amine Quenching for *p*-Fluorotoluene Fluorescence

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An increase in solvent polarity was found to cause a blue shift in the absorption spectrum of *p*-fluorotoluene. The Stern-Volmer constants for quenching of *p*-fluorotoluene fluorescence by primary, secondary, and tertiary aliphatic amines have been measured in 2-propanol, ethanol, and acetonitrile solvents. A strong correlation between the vertical ionization potential of the quenchers and $\log k_q$ was observed. As the vertical ionization potential increases, the quenching rate constant decreases. In acetonitrile, secondary amines were shown to have a higher quenching ability than primary and tertiary amines. This may be due to the interaction of solvent with the formed encounter complex which enhances the formation of radical anions and cations, a full discussion of which is made.

Introduction

In an earlier paper, data on the quenching of fluorotoluene isomers fluorescence by aliphatic amines in ethanol were reported.¹ Tertiary aliphatic amines were found to fluoresce when excited at a fixed wavelength of 206.2 nm² and to form a donor-acceptor complex with the singlet excited state of benzene and other aromatic compounds.^{3,4} In another study, tertiary amines were found to form exciplexes in solution,⁵ from the amine to the excited state

of naphthalene and naphthalene derivatives.

Halpern and Wryzykowska⁶ have found, using photokinetic measurements, that benzene and diethylmethylamine undergo reversible energy transfer. Excitation at

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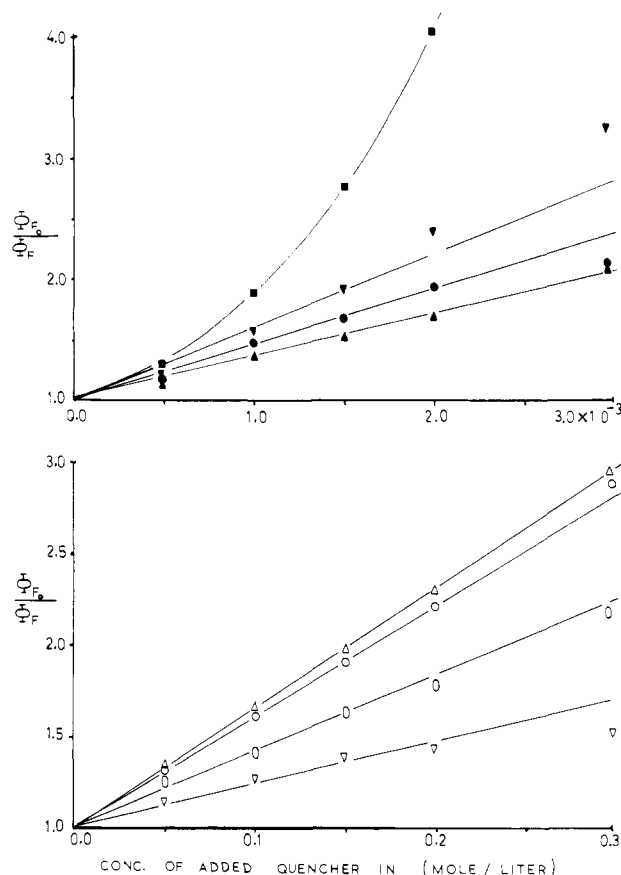


Figure 1. Stern-Volmer plots of quenching of *p*-fluorotoluene fluorescence in acetonitrile by (▽) MA, (□) EA, (○) PA, (△) BA, (●) DMA, (■) DEA, (▲) TMA, and (▼) TEA.

261 nm, which predominantly excites the aliphatic amine, leads to diffusion-controlled quenching of the amine fluorescence by benzene. Also, by using tertiary amines, Davidson and Beecroft⁷ have found that in a cyclohexane solution of benzene a little exciplex formation was observed and the main process appears to be energy transfer.

The present paper extends the fluorescence quenching studies and reports the effect of solvent polarity on the efficiency of the quenching process by primary, secondary, and tertiary aliphatic amines.

Experimental Section

Fluorescence spectra were recorded with a Farrand MKI spectrofluorometer. The description of the instrument and degassing of samples has been described elsewhere.¹ Absorption spectra for *p*-fluorotoluene in different solvents were obtained on a Pye-Unicam SP-8-100 spectrophotometer.

The *p*-fluorotoluene compound was obtained from Fluka Co. Analysis by gas-liquid partition chromatography showed less than 0.3% as impurity in the sample. No attempt was made for further purification. Aliphatic amines have been fully described elsewhere.¹

Acetonitrile and 2-propanol were obtained from BDH Co. The latter is a 70% w/w aqueous solution. Absolute ethanol was obtained from Fluka Co. as a spectroscopic grade. Gas-liquid chromatography showed these solvents to be sufficiently pure to be used without further purification, and no absorption or emission was noticed in the region of wavelength that was used for excitation of *p*-fluorotoluene.

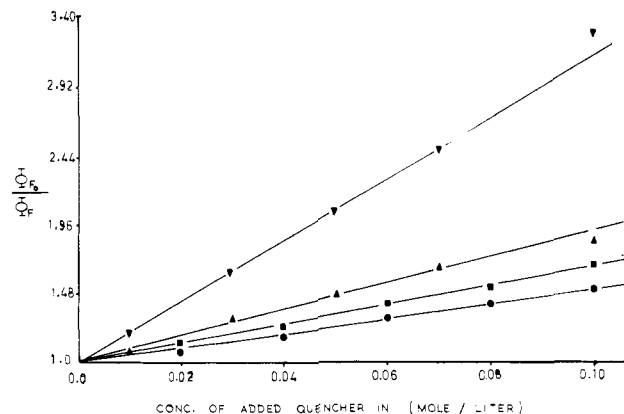


Figure 2. Stern-Volmer plots of quenching of *p*-fluorotoluene fluorescence in ethanol solvent by (●) DMA, (■) DEA, (▲) TMA, and (▼) TEA.

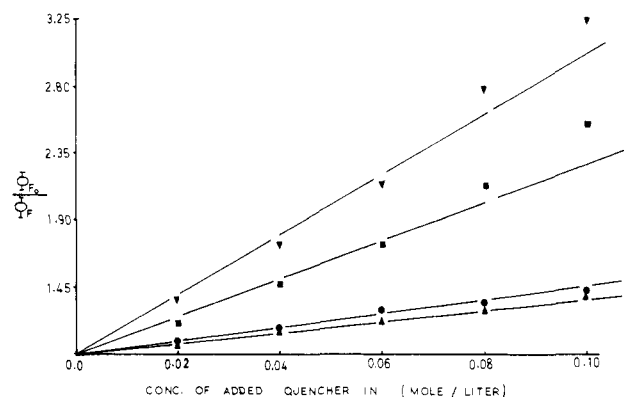


Figure 3. Stern-Volmer plots of quenching of *p*-fluorotoluene fluorescence in 2-propanol solvent by (●) DMA, (□) DEA, (▲) TMA, and (▼) TEA.

Results

The quenching of *p*-fluorotoluene fluorescence by methylamine (MA), ethylamine (EA), propylamine (PA), butylamine (BA), dimethylamine (DMA), diethylamine (DEA), trimethylamine (TMA), and triethylamine (TEA) was obtained at room temperature and at an exciting wavelength of 272.5 nm. Stern-Volmer plots for these quenching processes in acetonitrile are shown in Figure 1.

Figures 2 and 3 show the Stern-Volmer plots for quenching processes of *p*-fluorotoluene fluorescence by secondary and tertiary amines in ethanol and 2-propanol, respectively. From these slopes quenching rate constants (k_q) and quenching cross sections (δ_q^2) were calculated and are shown in Table I. A comparison of the relationship between vertical ionization potentials (IP) for the aliphatic amines (gas phase)⁸ with the corresponding quenching efficiencies in the three solvents is also shown in Table I.

Discussion

According to the Stern-Volmer plots for the fluorescence quenching of *p*-fluorotoluene by aliphatic amines in different solvents, it can be seen that the aliphatic amines are very efficient quenchers as shown in Figures 1–3. With the exception of quenching by secondary amines in acetonitrile, the efficiency of quenching decreases in the se-

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TABLE I: Quenching Parameters of *p*-Fluorotoluene in Ethanol, 2-Propanol, and Acetonitrile at an Exciting Wavelength of 272.5 nm

quencher	τ_F^a , ns	k_{sv}	$10^{-9}k_Q$, L mol ⁻¹ s ⁻¹	log k_Q	$10^{15}\delta_Q^2$, cm ² eV	IP, ^b eV
<i>p</i> -Fluorotoluene in Ethanol						
MA	8.9	0.495	0.055	7.74	0.057	8.97
EA	8.9	0.571	0.064	7.80	0.076	8.86
PA	8.9	0.654	0.073	7.86	0.095	8.78
BA	8.9	0.70	0.078	7.89	0.109	8.71
DMA	8.9	4.6	0.516	8.71	0.615	8.24
DEA	8.9	6.61	0.743	8.87	1.037	8.01
TMA	8.9	9.2	1.033	9.01	1.349	7.82
TEA	8.9	22.2	2.497	9.40	3.816	7.5
<i>p</i> -Fluorotoluene in Acetonitrile						
MA	7.1	2.095	0.295	8.47	0.305	8.97
EA	7.1	3.828	0.539	8.73	0.642	8.86
PA	7.1	6.031	0.849	8.92	1.108	8.78
BA	7.1	6.675	0.94	8.97	1.311	8.71
DMA	7.1	45.97	6.47	9.81	7.7	8.24
TMA	7.1	36.026	5.07	9.70	6.62	7.82
TEA	7.1	59.32	8.35	9.92	12.76	7.5
<i>p</i> -Fluorotoluene in 2-Propanol						
DMA	8.5	4.57	0.537	7.72	0.639	8.24
DEA	8.5	12.93	1.521	9.18	2.122	8.01
TMA	8.5	3.75	0.441	8.64	0.575	7.82
TEA	8.5	19.92	2.343	9.37	3.581	7.5

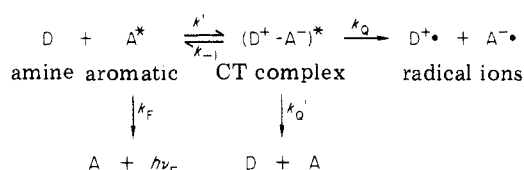
^a τ_F values were obtained by private communication:

D. Phillips and L. Botar, Chemistry Department, Southampton University, England. ^b Gas-phase vertical ionization potentials data from ref 8.

quence of tertiary amines > secondary amines > primary amines.

The quenching processes in a low-polarity medium, as in 2-propanol, may occur via the excited charge transfer complex, since the dielectric constant of the solvent is not high enough to promote radical ion formation. It will be noted for the system reported in Table I that the values of the quenching rate constant increase on changing the solvent from 2-propanol to acetonitrile. In a more polar solvent, there is the possibility that the quenching complex gives radical ions and consequently the photoreaction to regenerate the excited singlet state and the ground-state amine is suppressed.^{9,10}

It has been noticed that fluorescence quenching of some aromatic hydrocarbons by amines occurs via radical ion formation,¹¹⁻¹³ according to the following mechanism of quenching:



If the charge transfer mechanism of the fluorescence quenching is valid, then k_Q and k_Q' will depend upon the solvent polarity. It has been confirmed that additional activation energy over that required for diffusional motion

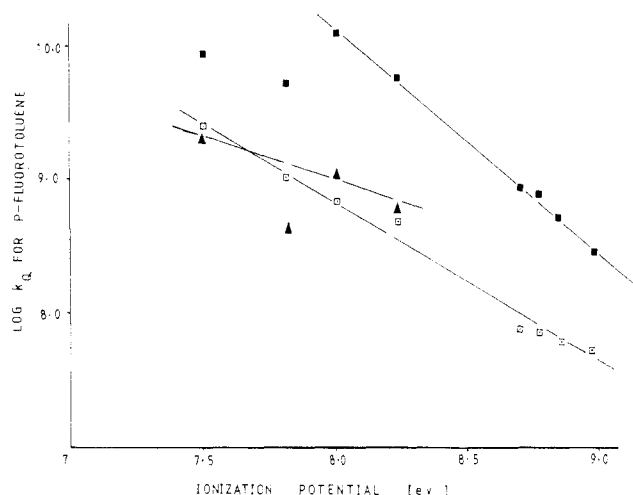


Figure 4. Variation of rate constants for quenching of *p*-fluorotoluene fluorescence with ionization potentials of quenchers in (■) acetonitrile, (□) ethanol, and (▲) 2-propanol.

is necessary for the charge transfer process.¹⁰ This indicates that not only IP values but also the solvent polarity affect the additional activation energy which decreases with increasing solvent polarity; k_Q becomes greater than k_Q' as the polarity of the solvent increases and IP decreases.

Secondary amines were shown to have a greater ability for quenching in acetonitrile than both primary and tertiary amines. This may be due to a degree of proton transfer from the amine which would increase the k_Q values. Also the possible solvation of the geometrically relaxed excited charge transfer complex with acetonitrile will increase the ionic character of the complex, and thus coordination between the $N^{\delta+}$ center of the amine with one or possibly two acetonitrile molecules would occur.

In many reports, it has been confirmed that k_Q values increase remarkably with the vertical IP of the amine.^{13,14} Weller et al.¹³ have observed a linear relationship between $\ln [k_Q/(k_{diff} - k_Q)]$ and the vertical IP of the quenchers in the quenching of acridine fluorescence by amines. Also the quenching of benzophenone triplet excited state by a number of donors gave a linear relationship between k_Q and the IP values of the donors.¹⁴ From the results obtained in this work, a linear relationship between $\log k_Q$ and the vertical ionization potential (gas phase)⁸ of the quencher has been obtained (Figure 4), and the increase in $\log k_Q$ with the vertical IP is greater in more polar solvent, which also supports a charge transfer mechanism. A similar correlation using IP (liquid phase) is not possible since no literature values for the quantity are available at the present time (there is a difference of less than 2 eV between vertical IP in the gas phase compared to that in solution).^{15,16}

The quenching rate constants of secondary and tertiary amines in acetonitrile and possibly in ethanol may be approaching diffusion-controlled values as in Figure 4. Thus, there may be possible complete transfer of the formed charge transfer complex into radical ions, and this process

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would be more favorable in a solvent of high dielectric constant.

A comparison of data on the efficiency of fluorescence quenching of *p*-fluorotoluene in the vapor phase¹⁴ with that in solution shows that the efficiency is greater in the vapor phase. This must be due to the interfering of solvent molecules with the formed energy transfer complex which seems to slow the quenching efficiency.

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Registry No. MA, 74-89-5; EA, 75-04-7; PA, 107-10-8; BA, 109-73-9; DMA, 124-40-3; DEA, 109-89-7; TMA, 75-50-3; TEA, 121-44-8; *p*-fluorotoluene, 352-32-9.

Intracoil Triplet-Triplet Annihilation in Poly(2-vinylnaphthalene) in Benzene Solution

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The triplet state of poly(2-vinylnaphthalene) (P2VN) in benzene solution has been sensitized by the benzophenone triplet state and a naphthalenic excimer delayed fluorescence (DF) has been observed. Kinetic models have been tested against the experimental data, including the effect of the molecular weight on the time dependence of the DF. It has been concluded that a homogeneous, intracoil mechanism best fits the trend of the data. This implies that triplet migration along with the P2VN chain is occurring in the solution phase.

Introduction

Since the pioneering work of Eisinger and Shulman¹ and Cozzens and Fox,² the phenomenon of triplet energy migration along a polymer chain in low-temperature, rigid matrices has been known. One of the manifestations of triplet energy migration in polymers is the detection of delayed fluorescence, which arises from intracoil triplet-triplet (T-T) annihilation. Ushiki et al.³ have observed anthracene delayed fluorescence in fluid solution from intracoil and intercoil T-T annihilation between a pair of terminal anthracene groups on a polystyrene chain. To our knowledge, this is the only case in which delayed fluorescence has been detected that originates from intracoil T-T annihilation in fluid solution. Thus far, delayed fluorescence has not been reported for directly excited poly(2-vinylnaphthalene) (P2VN) in room temperature solutions even though it is quite prominent at low temperatures.⁴ However, this is understandable since it has been previously noted that the quantum yield from the optically excited singlet state of P2VN in room temperature solutions is very low.⁵ We have recently observed a long-lived emission peaking at ~410 nm in P2VN solutions containing efficient triplet sensitizers excited by a nitrogen laser (e.g., benzophenone and phenanthrene). Only those results for benzophenone will be discussed herein because the triplet quantum yield of nearly unity eliminates most complications due to singlet-state interactions and prompt fluorescence. The long-lived emission appears to be delayed excimer fluorescence from the polymer-bound naphthalene. A kinetic argument will be presented which analyzes these results in terms of hetero-

ogeneous and homogeneous T-T annihilation in solution.

Experimental Section

Synthesis and characterization of P2VN samples have been described elsewhere.⁶ Benzophenone was purified by several recrystallizations from ethanol. Benzene (MCB spectrograde) was washed with sulfuric acid and then aqueous sodium carbonate. The washed benzene was dried over CaCl₂ and then distilled.

The laser flash photolysis unit was the same as that used in the triplet sensitization experiments,⁶ which were carried out at the Center for Fast Kinetics Research, University of Texas at Austin. This unit incorporates a beamsplitter to divert part of the laser pulse onto a photodiode in order to measure the flash intensity. Data were used only from those laser pulses that had approximately the same intensity readings (within ±3%). The same experimental considerations that applied in the triplet sensitization experiments⁶ obtained in this experiment with the exception that the interrogation light source (150-W xenon) used for the transient absorption study was eliminated in order to record emission. The excitation intensity of the nitrogen laser was attenuated by neutral density filters (OD = 1.0) in order to diminish the T-T annihilation process between excited sensitizer molecules in the sensitizer blank solution. This was done to ensure that the energy transfer mechanism was the dominant process in the decay kinetics of the sensitizer in P2VN solutions. Time-resolved emission spectra were taken by assembling decay curves at every 5 nm. Triplet-triplet absorption was also measured in order to obtain a value for the initial concentrations and decay rates of benzophenone triplets in solution.

One other point that needs to be made is the absorption of naphthalene units at the laser wavelength ($\lambda = 337$).

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