

Electronic Excitation Transfer in Polymers. 3. Singlet-Singlet, Triplet-Singlet, and Triplet-Triplet Energy Transfers. Evidence for Triplet Migration among Pendant Phenyl Groups of Polystyrene

Nicholas J. Turro,* Irene E. Kochevar, Yasuhiro Noguchi, and Ming-Fea Chow

Contribution from the Chemistry Department, Columbia University,
New York, New York 10027. Received July 23, 1977

Abstract: Chemiluminescent techniques have been employed to investigate electronic energy transfer from ketone donors (acetone, acetophenone) to acceptors (e.g., 9,10-diphenylanthracene and biphenyl) in films of polystyrene and polymethyl methacrylate at 50 °C. Tetramethyl-1,2-dioxetane and 3,4-diphenyl-3,4-dimethyldioxetane were used to generate excited (singlet and triplet) acetone and (triplet) acetophenone, respectively. Analysis of quenching data in terms of the Perrin, Förster, or Dexter models all yielded critical transfer radii, R_c , in the range of 23–29 Å for singlet-singlet and for triplet-singlet energy transfer. For triplet-triplet energy transfer, the values of R_c were in the range of 11–17 Å with the exception of the acetone triplet to 1,4-dibromonaphthalene transfer in polystyrene, for which $R_c = 21$ Å. Evidence is presented which supports the postulate that triplet energy migration among the pendant phenyl groups on the polystyrene backbone may cause unexpectedly large R_c values for triplet-triplet energy transfer.

Introduction

Bimolecular electronic energy transfer

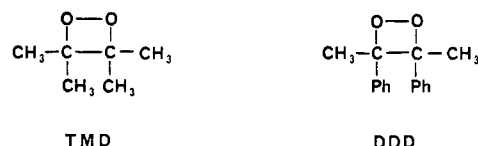


has been shown to proceed by at least three mechanisms:¹ (1) a potentially long-range mechanism by which transfer over distances is induced by dipole-dipole interactions; (2) an obligatory short-range mechanism by which transfer is induced via electron exchange interactions between the donor and acceptor molecular orbitals; (3) a radiative energy transfer, which involves sequential donor emission and reabsorption of the photon by the acceptor. Singlet-singlet (SS) energy transfers have been demonstrated to proceed by all three of these mechanisms.² Triplet-triplet (TT) energy transfer in which electronic transitions of both the donor and the acceptor are spin forbidden occurs only by the short-range electron-exchange mechanism.³ Examples of the overall spin-forbidden triplet-singlet (TS) energy transfer are known, but are relatively rare.⁴

Polymer matrices provide an opportunity to study energy transfer processes under conditions which severely restrict the translational motion of dissolved donor and acceptor molecules.⁵ In addition, polymeric media provide a means of investigating possible energy migration among chromophores attached to the polymeric backbones.⁵ Such energy migration has been demonstrated to occur on the singlet level (i.e., polyvinylanthracene⁶ and polyacenaphthalene⁷) and on the triplet level (i.e., polyvinylbenzophenone⁸ and polyvinylcarbazole⁹).

In a previous paper,¹⁰ we postulated triplet energy migration among polystyrene phenyl groups as an explanation for the apparently long-range TT energy transfer which was observed to occur between acetone and a triplet energy acceptor in polystyrene at 50 °C. However, this postulate requires relatively efficient energy transfer from acetone triplets to the pendant phenyl groups of polystyrene even though this energy transfer process is expected to be slightly endothermic ($E_T \approx 78$ kcal/mol for acetone, $E_T \approx 82$ kcal/mol for alkylbenzenes).¹¹ Furthermore, other interpretations of the observations (i.e., substantial diffusion of acetone triplet during its lifetime) are conceivable. In order to further elucidate the cause of the apparently long-range TT energy transfer process and to expand further our knowledge of the mechanism of energy transfer in polymer films we have employed chemilu-

minescence techniques in a systematic study of electronic energy transfer from excited ketones (acetone and acetophenone) to a variety of organic energy acceptors. Tetramethyl-1,2-dioxetane (TMD)¹² and 3,4-diphenyl-3,4-dimethyldioxetane



(DDD)¹³ were employed to thermally (50 °C) generate excited (singlet and triplet) acetone and excited (triplet) acetophenone, respectively. Both dioxetanes generate excited states efficiently in fluid solution ($\phi^* = 0.5$ for triplets).^{12,13} Of significance for these experiments is the fact that these two ketones differ in their triplet energies ($E_T \approx 78$ kcal/mol for acetone, $E_T \approx 72$ kcal/mol for acetophenone).¹¹

Experimental Section

Melting points are uncorrected. NMR spectra were recorded on Varian A-60 or T-60 instruments with Me₄Si as an internal standard. All values are in δ Me₄Si units.

Materials. Benzene (Fisher Spectroanalyzed and Matheson Coleman and Bell Spectroquality) was used as received. 1,4-Dibromonaphthalene, 9,10-diphenylanthracene, 9,10-dibromoanthracene, 9,10-diphenylethynylanthracene, naphthalene, biphenyl, and *trans*-dicyanoethylene (*t*-DCE) were obtained from commercial sources and purified by recrystallization. Emission spectra of the aromatic compounds in solution were experimentally indistinguishable from published literature spectra.¹⁴ Polystyrene, (PS, Polysciences) and polymethyl methacrylate (PMMA, Polysciences and Aldrich) were precipitated into methanol from benzene. Polymethacrylonitrile (PMAN, Polysciences) was reprecipitated from acetonitrile into methanol. For comparison, freshly distilled styrene was thermally (106 °C) polymerized in the dark. The resulting polystyrene, purified by successive dissolutions and precipitations, gave the same experimental results as the purified commercial polystyrene.

Dioxetane Preparation. (Caution! Hydroperoxides and dioxetanes are potentially explosive.)

2-Bromo-2,3-dimethyl-3-hydroperoxybutane was prepared using a modified literature procedure.¹⁵ A solution of 2,3-dimethyl-2-butene (Aldrich, 5.0 g, 59.4 mmol) in 50 mL of anhydrous ether was stirred at -40 °C (safety shield!) To this solution was added 98% hydrogen peroxide (FMC, 10.0 g, 7.0 mL, 296 mmol). 1,3-Dibromo-5,5-dimethylhydantoin (Fisher, 8.49 g, 29.7 mmol) was added in several portions over a 15-min period and the mixture was allowed to warm to room temperature over a period of 1 h. After 1 h of additional

stirring, the resulting colorless solution was washed with ice-cold water (50 mL) and saturated NaHCO_3 solution (50 mL). The dried (Na_2SO_4) organic layer was concentrated at 0 °C to give crude 2-bromo-2,3-dimethyl-3-hydroperoxybutane (11.9 g, 100%). Recrystallization at -78 °C from *n*-pentane recovered the pure product (9.0 g, 76%): NMR (CDCl_3) δ 1.45 (s, 3 H), 1.82 (s, 3 H).

Tetramethyl-1,2-dioxetane (TMD) was prepared closely following the literature procedure.^{15,16} A solution of 2-bromo-2,3-dimethyl-3-hydroperoxybutane (3.0 g, 15.2 mmol) in anhydrous ether (5 mL) was added in one portion to a slurry of silver acetate (J. T. Baker, purified, 3.5 g, 21 mmol) in ether (30 mL) which was efficiently stirred in an ice bath at 0 °C. After 2 h the precipitated silver bromide together with unreacted silver acetate were filtered off by suction and the pale yellow filtrate was washed with 10% NaOH solution (40 mL), followed with saturated NaCl solution. The dried (Na_2SO_4) ethereal layer was concentrated at 0 °C to a yellow oil. This residue was taken up in 5–7 mL of pentane, crystallized at -78 °C. The long yellow needles were filtered: 0.37 g (23.6%); NMR (CDCl_3) δ 1.57 (s); mp 72 °C (sealed tube, lit. 76–77 °C).¹⁵

2,3-Diphenyl-2,3-butanediol. Acetophenone was reduced to the pinacol, 2,3-diphenyl-2,3-butanediol, using the method of Sisido.¹⁷ The crude product after recrystallization from benzene–ligroin gave stereoisomers of the pinacol (69%). The first crop (9 g) was the pure threo isomer: mp 118–120 °C (lit. 122 °C)¹⁷; NMR (CDCl_3) δ 1.45 (s, 6.0 H), 2.60 (broad s, 1.9 H), 7.18 (s, 10.0 H). The rest of the recovered pinacol was a stereoisomeric mixture; the erythro isomer showed NMR (CDCl_3) δ 1.54 (s, 6.0 H), 2.32 (broad s, 1.8 H), 7.18 (s, 10.0 H).

2,3-Diphenyl-2-butene (cis- and trans-Dimethylstilbenes). The formation and pyrolysis of the orthoformate ester derivative of 2,3-diphenyl-2,3-butanediol was based on the literature procedure.¹⁸ The stereoisomers of 2,3-diphenyl-2,3-butanediol (20.65 g, 86.2 mmol) were heated with freshly distilled triethyl orthoformate (Aldrich, 12.61 g, 85.2 mmol) with stirring at 150 °C for 38 h, during which time 3.1 mL of ethanol distilled. A catalytic amount (0.1 mL) of acetic acid was added and the resulting mixture was pyrolyzed at 170 °C. After 9 h an additional 4.0 mL of ethanol distilled. The resulting crude product (14.0 g) was fractionally recrystallized from methanol: 5.3 g of pure *trans*-dimethylstilbene, long needles, mp 100 °C (lit. 105 °C),¹⁹ and 6.1 g of the *cis*-*trans* mixture (1:9) were collected as white, granular crystals, mp 52–55 °C.

3-Bromo-2,3-diphenyl-2-hydroperoxybutane. The procedure of Umbreit and White¹³ was modified for larger scale and alternative purification steps. *trans*-Dimethylstilbene (3.24 g, 15.6 mmol) was converted to the bromohydroperoxide in tetrahydrofuran (50 mL) by stirring with 1,3-dibromo-5,5-dimethylhydantoin (Fisher, 2.50 g, 8.74 mmol) and 98% hydrogen peroxide (FMC, 5.44 g, 3.76 mL, 160 mmol) at -30 °C for 5 h. The mixture was poured into 150 mL of ice-cold water and extracted with ether. The ether layer was shaken twice with cold water, dried (Na_2SO_4), concentrated to 50 mL at 0 °C, and then cooled to -78 °C. The precipitated 2,3-dibromo-2,3-diphenylbutane (0.23 g, 64 mmol) was filtered: NMR (CDCl_3) δ 2.43 (s, 6 H), 7 (s, 10 H). The filtrate was warmed to room temperature and 1.5 g (11.9 mmol) of recrystallized anhydrous Dabco (1,4-diazabicyclo[2.2.2]octane, Eastman) in 10 mL of ether was added. The cloudy mixture was cooled in a freezer (-20 °C) overnight; the bromohydroperoxide–Dabco complex (3.62 g, 52%) crystallized as needles. The NMR spectrum (CDCl_3) showed a 1:1 complex: δ 1.95 (s, 3 H), 2.18 (s, 3 H), 2.75 (12 H), 7.05–7.20 (m, 10 H). The complex was shaken with a mixture of ether and ice water. The ether layer was shaken twice with cold water, dried over Na_2SO_4 , and concentrated to give a thermally unstable oil (required storage in a refrigerator): NMR (CDCl_3) δ 2.00 (s, 3 H), 2.22 (s, 3 H), 7.00–7.40 (m, 9.8 H).

3,4-Dimethyl-3,4-diphenyldioxetane (DDD). A solution of approximately 4.0 mmol of 3-bromo-2,3-diphenyl-2-hydroperoxybutane in 50 mL of ether was cooled in an ice bath to 0 °C. To the stirred solution was added silver acetate (J. T. Baker, purified, 0.8 g, 48 mmol). After 10 min the suspension was filtered. The yellow filtrate was washed with cold water followed with cold dilute NaHCO_3 solutions and dried over K_2CO_3 . The mixture was concentrated and applied in a small volume of hexanes to an alkaline silica gel column (30 g, Merck silica gel preneutralized with 1% NaOH solution, activated and made up in hexanes). Slow elution with 5% CH_2Cl_2 in hexanes recovered the dioxetane at room temperature in the second 100 mL of eluent; the crude yellow needles were recrystallized from

cold pentane as yellowish needles, 80 mg (8.3%). The NMR spectrum showed only one stereoisomer: (CDCl_3) δ 2.03 (s, 6 H), 7.07 (s, 10 H). Starting from a mixture of dimethylstilbene isomers (*cis*:*trans* 9:1), the threo bromohydroperoxide was obtained as a major intermediate in an analogous yield: NMR (CDCl_3) δ 1.92 (s, 3.1 H), 2.22 (s, 3.0 H), 7.1–7.6 (m, 9.8 H). This bromohydroperoxide gave a mixture of dioxetanes in a similar yield; recrystallization from cold pentane gave the same isomer as obtained from *trans*-dimethylstilbene (71%, major product). The minor isomer (29%) showed a NMR spectrum: (CDCl_3) δ 1.55 (s, 6 H), 7.45 (broad s, 10 H). The pure major isomer of the dioxetane was used throughout these experiments.

Film Preparation. Benzene solutions containing PS or PMMA and acetonitrile solutions containing PMAN (15 wt % PS or 20 wt % PMMA or PMAN), a dioxetane (usually $1\text{--}5 \times 10^{-2}$ M based on the dry polymer volume), and an acceptor were prepared by rotating aluminum foil covered vials for about 2 h at room temperature. About 0.5 g of this solution was spread on two clean microscope slides (25 × 75 mm) using a blade coater with a clearance of 0.81 ± 0.05 mm. In early experiments the films were allowed to dry at room conditions for about 1 h before being dried overnight in the dark under vacuum (0.05 mmHg). In later experiments PS and PMMA films were first dried for 2 h in a benzene vapor rich box to retard evaporation of the solvent before drying in vacuo. The latter procedure decreased intra- and interfilm emission intensity variation. The dry thickness of the films was 70 ± 2 μm .

Acetone was generated in PS films by irradiating TMD-containing films at 77 °C using a medium-pressure Hg lamp through Pyrex. Decrease in the 860-cm^{-1} dioxetane infrared absorption and appearance of a 1720-cm^{-1} acetone absorption was used to follow the progress of the photolysis.

Emission Intensity Measurements. Portions (10.5 × 18.0 mm) of the films containing a dioxetane and various concentrations of an energy acceptor were either taped to a stainless-steel block (early experiments) or sandwiched between a stainless-steel block and a thin stainless-steel strip having a hole 8 mm in diameter (later experiments). This assembly was slightly thinner than a temperature-controlled cell holder made for 1-cm square cells. The cell holder was kept at 50 °C for all experiments requiring thermal generation of the donor ketone excited state. When argon or oxygen atmospheres were required, the cell was purged with the gas at a rate of 350 mL/min. The film faced a high-sensitivity phototube (Amperex 56 AVP or EMI 9813QA) through a Jarrell-Ash 0.25-m monochromator which was generally used on zero order. Signal was usually accumulated for 10 s after reaching temperature equilibrium and five readings were averaged for each sample. Duplicate samples of each film were run. Emission intensities were generally measured within 24 h of sample preparation.

Oxygen quenching of emission was studied in films containing 0.1 M dioxetane. The luminescence spectra obtained from these films at 50 °C were recorded on a Hitachi Perkin-Elmer MPF-3L fluorescence spectrometer. Emission intensities were determined either on this instrument or with the Amperex 56 AVP or EMI 9813QA phototube.

Photoexcited emission from naphthalene in polystyrene films was observed from samples positioned 45° to the excitation and emission slits in the fluorescence spectrophotometer and backed with black cloth to decrease light scattering.

Results

Direct Chemiluminescence from Polymer Films Containing TMD. Heating of PS or PMMA films containing TMD to 50–60 °C produces a readily measured chemiluminescence (Figure 1). The emission observed from polystyrene films is assigned to acetone fluorescence based on (1) its spectral distribution which is consistent with photoexcited acetone fluorescence^{20,21} and (2) its intensity which is unaffected by purging the film with argon or oxygen gas. For example, a PS film containing TMD was degassed at 0.1 Torr for 12 h, transferred and measured in an argon atmosphere, and then remeasured in oxygen atmosphere. No significant difference was found between the emission intensities or spectra in the two atmospheres (Figure 1). The possibility that this emission is due to an impurity in the PS which accepts energy from excited acetone molecules is unlikely since PS from two different

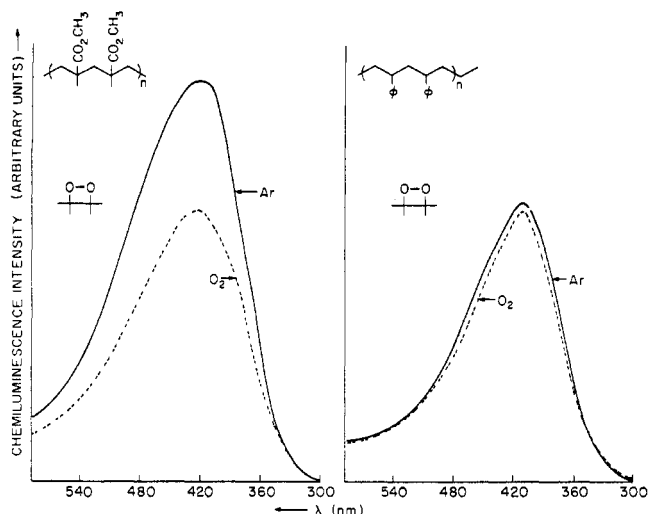


Figure 1. Chemiluminescence of TMD in polymer films. Left, polymethyl metacrylate; right, polystyrene. (—) argon atmosphere; (---) oxygen atmosphere; [TMD] = 0.1 M; temperature, 50 °C; thickness of film, 70 μ m; emission slit, 40 nm. The wide emission slits preclude accurate measurements of the emission maxima.

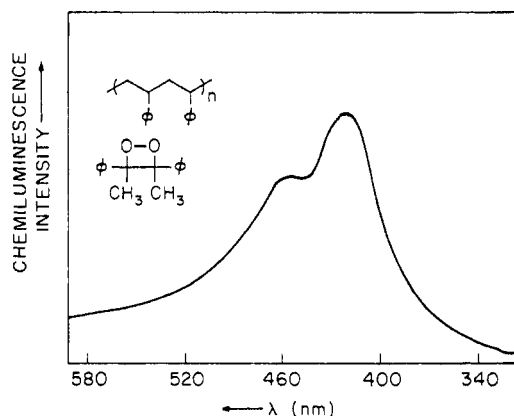


Figure 2. Chemiluminescence of DDD in polystyrene. Argon atmosphere; [DDD] = 0.1 M; temperature, 50 °C; emission slit, 28 nm.

sources (commercial and thermal polymerization) gave the same emission. In contrast, the chemiluminescence from TMD in PMMA films is quite sensitive to purging with oxygen (Figure 1). For example, an oxygen atmosphere reduces (Table I) the chemiluminescence intensity to less than half of its maximal value in an argon atmosphere. Purging with argon gas restored the intensity of the chemiluminescence to its initial value before oxygen purging. The difference in susceptibility to O_2 quenching in PS and PMMA films cannot be attributed to lower O_2 solubility in PS based on results with DDD (see below). Therefore, the emission in PS appears to be purely fluorescence (non- O_2 quenchable) and in PMMA to be fluorescence plus phosphorescence which is partially O_2 quenchable. The quenching mechanism in PS is presumably at least partially triplet-triplet energy transfer (see below).

The possibility that acetone phosphorescence is not observed in PS because of quenching of acetone triplets by the phenyl groups of PS is supported by the following calculation. In acetonitrile solution at 50 °C the triplet lifetime of acetone triplet has been determined to be $\sim 10 \mu$ s.²² To reduce the acetone phosphorescence to $1/20$ of the unquenched values (assuming a concentration of 10 M for the styryl groups) requires the rate constant of $2-4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for energy transfer from acetone triplet to the phenyl groups according to the Stern-Volmer relationship. Such a rate constant is feasible based on the <3

Table I. Effect of Oxygen on Emission from TMD- and DDD-Containing Polymer Films^a

Dioxetane	Energy acceptor	Polymer	$I_{O_2}/I_{\text{argon}}^b$
TMD		PS	1.0
TMD		PMMA	0.35
TMD	DBA ^c	PS	0.80
TMD	DBA ^d	PMMA	0.80
DDD		PS	0.30
DDD		PMMA	0.43
DDD	DBA ^e	PS	0.75

^a 50 °C, 0.1 M TMD or DDD. ^b Relative emission intensity in oxygen and argon atmosphere. ^c [DBA] = 0.0036 M. ^d [DBA] = 0.040 M. ^e [DBA] = 0.0420 M.

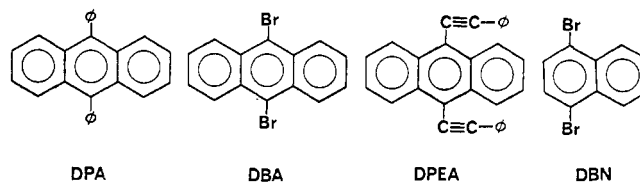
kcal/mol gap between acetone triplet and alkyl-substituted benzene triplet energy levels as calculated from

$$\Delta \ln k = -\Delta E_t/RT \quad (1)$$

Using a value of 3 kcal/mol for ΔE and $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for isoenergetic energy transfer (considering the effect of back transfer) yields $9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for the endothermic transfer.²³ This rate constant for energy transfer is also consistent with the rate constant measured for quenching of acetone triplet by toluene in acetonitrile solution ($3.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$).²⁴ Therefore, the lack of phosphorescence from acetone triplet in PS may reasonably be attributed to endothermic energy transfer from the acetone triplet to the pendant phenyl groups.

Direct Chemiluminescence from Polymer Films Containing DDD. The chemiluminescence spectrum produced by heating DDD in PS is shown in Figure 2. The maximum ($\sim 440 \text{ nm}$) is the same as that observed for photoexcited acetophenone phosphorescence, and is therefore assigned to emission from acetophenone triplets. In contrast to the situation with TMD, the chemiluminescence of DDD was sensitive to oxygen in both PS and PMMA films (Table I). Quenching of acetophenone triplet by phenyl groups is not expected since this energy transfer is $\sim 8 \text{ kcal/mol}$ endothermic. Quenching of DDD chemiluminescence by O_2 in both PS and PMMA demonstrates that O_2 quenches readily in both polymers. (The diffusion constants of O_2 are 1.1×10^{-7} and $1.4 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ in PS³⁰ and PMMA,³¹ respectively.)

Indirect Chemiluminescence of Energy Acceptors. Addition of certain energy acceptors (e.g., 9,10-diphenylanthracene (DPA), 9,10-dibromoanthracene (DBA) diphenylethynylanthracene (DPEA), 1,4-dibromonaphthalene (DBN)) to



polymer films containing TMD or DDD results in an enhancement of chemiluminescence intensity as a result of energy transfer to the acceptor which then emits its characteristic luminescence. Representative spectral results are shown in Figure 3.

Based on the spectral distribution and behavior of the emission intensity as a function of acceptor concentration (see below), we assign the indirect chemiluminescence to the fluorescence of DPA, DBA, and DPEA and to the phosphorescence of DBN.

The effect of oxygen on the indirect chemiluminescence of DBA and DBN was also investigated (Figures 3b and 3c). A slight decrease ($\sim 20\%$) from the emission intensity in an argon

atmosphere was observed when it was used to purge PS films containing TMD and DBA. Similar decreases in emission intensity in oxygen atmospheres were observed for TMD in PMMA or DDD in PS films (Table I). A more dramatic effect was observed for DBN in PS with TMD (Figure 3c).

Treatment of the Data. Models for Deriving Quantitative Energy Transfer Parameters from Intensity-Concentration Measurements. Investigation of the relationship between emission intensity of an energy acceptor and the concentration of the acceptor provides a means of quantifying energy transfer parameters in polymers.¹

Several models have been commonly employed to derive quantitative parameters (for systems involving energy transfer in solid solution or in polymers) from experimental measurements of donor (or acceptor) emission intensity as a function of acceptor concentration: (1) the Stern-Volmer model;³² (2) the exciton hopping model;³³ (3) the Perrin model;²⁵ (4) the Förster model;^{1,34} and (5) the Dexter model.^{3,35}

We feel that neither the Stern-Volmer nor the exciton hopping model is appropriate for analyzing our data, since both treatments require extensive molecular or exciton diffusion during the donor lifetime. The latter condition is not generally met in our systems.

The Perrin, Förster, and Dexter models may all be employed to derive quantitative energy parameters in systems such as those reported here, i.e., systems for which *molecular* diffusion is negligible during the lifetime of an excited donor molecule. Each model allows derivation of a so-called "critical radius" R_c . In the case of the Perrin model, R_c is the radius of a "quenching sphere" about the donor, whereas for the Förster and Dexter models R_c corresponds to that special distance of separation for which the rate of energy transfer from excited donor to acceptor is exactly equal to the rate of decay of the excited donor in the absence of acceptor. Values of R_c are derived from experimental measurement of emission intensity as a function of acceptor concentration.

The Perrin model assumes no specific electronic mechanism for energy transfer, but postulates the existence of a volume (a "quenching sphere") at whose center the excited donor is located and whose radius is R_c^P . We should remember that the critical radii for Förster and Dexter energy transfer (R_c^F and R_c^D) will be derived (vide infra) from the "critical concentrations" for which energy transfer and excited donor decay occur at equal rates. In spite of this distinction and in spite of the fact that R_c^F and R_c^D are derived from different models, all three R_c parameters will be shown to be similar in magnitude. This result obtains because of the relatively short-range character of energy transfer in the systems studied (15–30 Å), and the fact that each of the models predicts similar dependences of the rate of energy transfer on distance for small separations of donor and acceptor. If the data can be fit to the Perrin model, the volume of a "quenching sphere" whose radius is R_c^P can be determined. Equation 2, a convenient quantitative form of the Perrin model, was employed to derive values of R_c^P in Å units:

$$R_c^P = - \left[\frac{3000 \ln (1 - I^A/I_\infty^A)}{4\pi N C_A} \right]^{1/3} \times 10^8 \quad (2)$$

where I^A = acceptor emission intensity at acceptor concentration, C_A ; I_∞^A = maximum acceptor emission intensity (further increases in C_A do not increase I^A); N = Avogadro's number; C_A = acceptor concentration in moles/liter. Figure 4 shows representative plots of experimental data for sensitization of *acceptor emission* in terms of eq 2. Since the concentration of acceptor was plotted vs. $\ln (1 - I^A/I_\infty^A)$, the slope of the plot (if linear) yields αR_c^3 where $\alpha = 4\pi N / (3000 \times 10^{24}) = 2.52 \times 10^{-3}$.

It is also possible to use the quenching of donor emission to

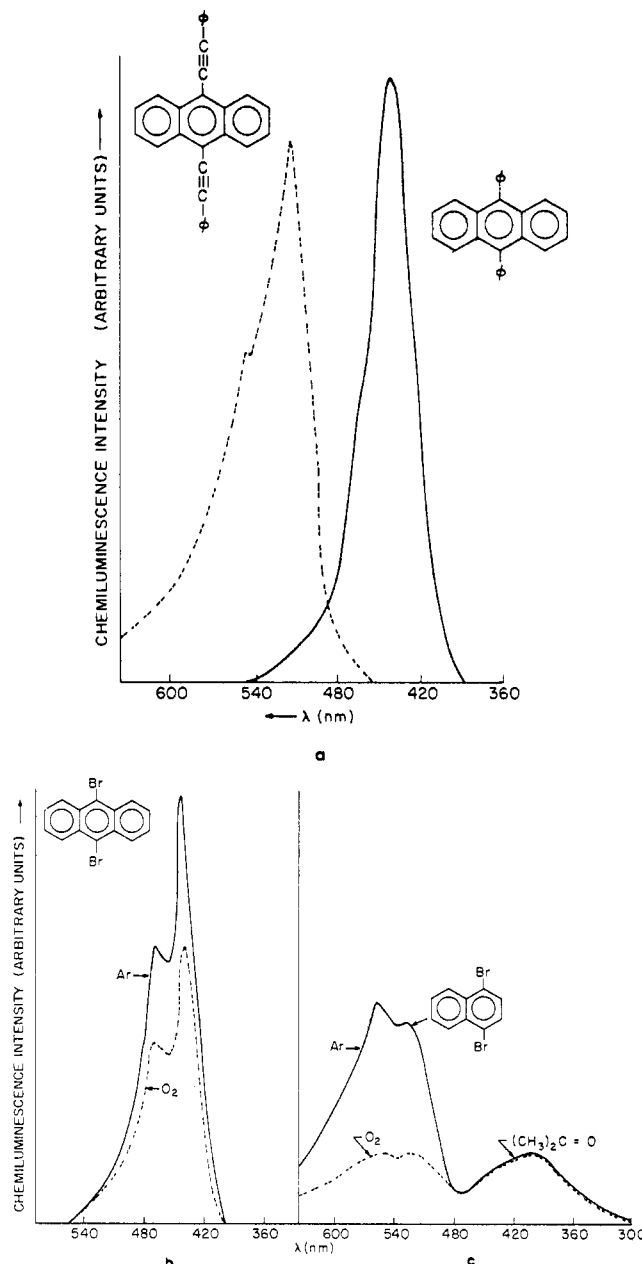


Figure 3. Indirect chemiluminescence from polymer films containing (a) DPA and DPEA, (b) DBA, and (c) DBN. For PS films containing TMD only the DBA and DBN chemiluminescences are oxygen sensitive. Emission slit, 3 ~ 15 nm; [DBA] = 1×10^{-2} M; [DPEA] = 1.8×10^{-2} M; [DPA] = 1.0×10^{-2} M; [DBN] = 2.5×10^{-2} M; [TMD] = 0.1 M; temperature = 50 °C.

derive values for R_c^P :

$$R_c^P = \left[\frac{3000 \ln (I_0^D/I^D)}{4\pi N C_A} \right]^{1/3} \times 10^8 \quad (3)$$

where I^D = donor emission intensity at acceptor concentration, C_A , and I_0^D = donor emission intensity in the absence of the acceptor.

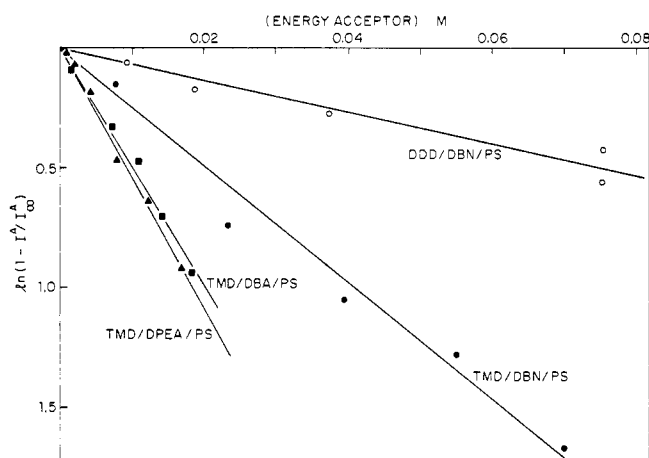
The R_c^P values, obtained by employing eq 2 or 3 for six energy acceptors in polymers containing TMD or DDD, are given in Table II.

The Förster model assumes a specific Coulombic (dipole-dipole) interaction mechanism for energy transfer. In this case for which the energy transfer rate is proportional to the inverse sixth power of the donor-acceptor distance, Förster showed that a quantitative relationship between acceptor emission intensity and acceptor concentration should obey the equation

Table II. Critical Radii, R_c , for Energy Transfer in Polymer Films^a

Donor	Acceptor	Polymer	R_c^P (Perrin), Å	R_c^F (Förster), Å	R_c^D (Dexter), Å	Transfer type
(CH ₃) ₂ CO	DPA	PS	26	23		S-S
(CH ₃) ₂ CO	DPEA	PS	29	26		S-S
(CH ₃) ₂ CO	DBA	PS	28	25		T-S
PhCOCH ₃	DBA	PS	28	25		T-S
(CH ₃) ₂ CO	DBN	PS	21		21	T-T
PhCOCH ₃	DBN	PS	16		15	T-T
(CH ₃) ₂ CO	DBN	PMMA	17		17	T-T
PhCOCH ₃	DBN	PMMA	17		17	T-T
(CH ₃) ₂ CO	Biphenyl	PMAN	12 ^b			
(CH ₃) ₂ CO	<i>t</i> -DCE	PMAN	13 ^b			

^a See text for explanation of derivation of R_c values. The latter were determined by measurement of acceptor emission at 50 °C except where noted. ^b Donor emission monitored to determine R_c .

**Figure 4.** Experimental relationship between the intensity of chemiluminescence of acceptor and acceptor concentration fit to the Perrin model (solid line). See Table II for R_c^P values.

$$I/I_{\max} = \sqrt{\pi}x(\exp x^2)[1 - \phi(x)] \quad (4)$$

where $x = \frac{1}{2}\sqrt{\pi}[A]/[A]_c$. In eq 4 I is the emission yield of acceptor at concentration $[A]$, I_{\max} is the maximum emission yield of acceptor (complete energy transfer), $[A]_c$ is the "critical concentration" for which the rates of energy transfer and donor decay are equal, and $\phi(x)$ is the error function. By definition, the Förster "critical radius," R_c^F , is evaluated by use of the equation

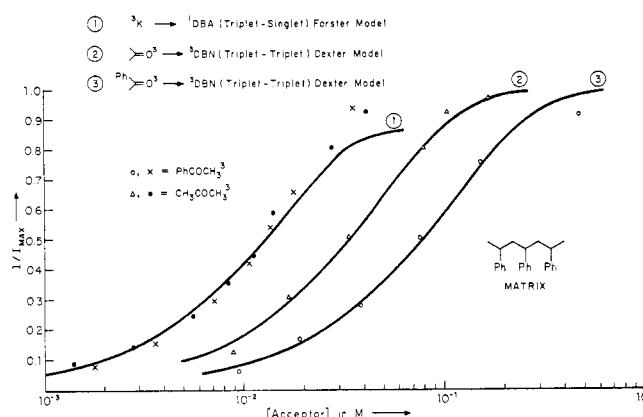
$$R_c^F = 7.35[A]_c^{-1/3} \quad (5)$$

where R_c^F has the units of Å when $[A]_c$ is given in M.

The Dexter model assumes that energy transfer occurs via an electron exchange mechanism. In this case, the rate constant for energy transfer is taken to have the form: constant $\exp(-2R/L)$, where R is the donor-acceptor distance and L is a parametric constant. Inokuti and Hirayama³⁵ showed that for an electron exchange mechanism a quantitative relationship between acceptor emission intensity and acceptor concentration is given by

$$I/I_{\max} = 1 - \left[\tau_0^{-1} \int_0^\infty \phi(t) dt \right] \quad (6)$$

where $\phi(t)$ is a function proportional to the donor emission intensity (and is treated as a parameter to be fit to experimental data), τ_0 is the lifetime of the donor emission in the absence of acceptor, I is the emission intensity of the acceptor at concentration $[A]$, and I_{\max} is the maximum intensity of acceptor emission (complete energy transfer). Inokuti and Hirayama provide a procedure by which use of a form of eq 6 (constructed

**Figure 5.** Experimental relationship between the intensity of chemiluminescence of acceptor and acceptor concentration in polystyrene. Curve 1: acetone triplet and/or acetophenone triplet to 9,10-dibromoanthracene singlet fit to the Förster model (solid line). Curve 2: acetone triplet to 1,4-dibromonaphthalene triplet fit to the Dexter model (solid line). Curve 3: acetophenone triplet to 1,4-dibromonaphthalene triplet fit to the Dexter model (solid line). See Table II for R_c values.

on analogy to the Förster eq 4) allows an evaluation of a "critical concentration" $[A]_c$ for which the rates of spontaneous donor decay (τ_0^{-1}) and energy transfer are equal. In analogy to the Förster model, the generation of $[A]_c$ is such that a "critical radius" R_c^D for Dexter energy transfer may be derived from knowledge of $[A]_c$ and application of eq 5.

Typical examples of treatment of our data by the various models are given in Figures 4 and 5. These and further data are summarized in Table II. In Figure 5, the triplet-singlet energy transfer from acetone triplet to DBA and for acetophenone triplet to DBA is shown by the Förster model. A calculation for the Dexter model gives a comparable fit to that data, but in this case a mechanistic interpretation of such a large value of R_c is problematic. We note that the parametric form of the Förster equation and the Dexter equation are similar and differ only by a numerical constant.^{34,35}

Simple visual inspection of the experimental data as presented in Figure 5 reveals that differences in values of $[A]_c$ must be generated by any theory.

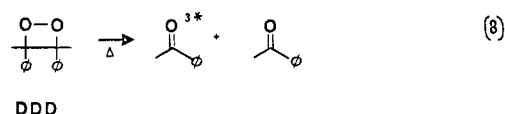
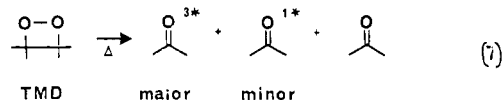
Emission Quenching by Acetone in PS Films. To determine if acetone triplet molecules could diffuse in PS films and significantly affect the R_c values, acetone was used as a quencher in PS films. The donor was naphthalene singlet generated by photoexcitation as described in the Experimental Section. The naphthalene fluorescence was quenched by both TMD and acetone generated from TMD in PS films. The quenching radius for TMD was 14 Å. The points on a Perrin plot with acetone as the acceptor fell on about the same line as those

using TMD. However, R_c cannot be calculated unambiguously for acetone since the absolute concentration of acetone is two times that of TMD (assuming 100% conversion of TMD into two acetone molecules) although the acetone molecules presumably exist as pairs. Considering these factors, R_c for acetone quenching of naphthalene fluorescence in PS must be considered to be less than or equal to that for TMD.

Trivial Energy Transfer via Donor Emission-Acceptor Absorption. The contribution of trivial energy transfer (donor emission followed by acceptor reabsorption) was minimized by the use of very thin films. However, experimental tests demonstrated the lack of a significant contribution of the trivial mechanism under our experimental conditions. First, the absolute number of photons emitted in the indirect chemiluminescence experiments was always 10–1000 times greater than that for direct chemiluminescence. Thus, the maximum contribution of the trivial mechanism is less than a few percent since the maximal OD of acceptor absorption did not exceed 0.1. Second, in the case of DBN as acceptor, only phosphorescence was observed via chemiexcitation whereas *both* fluorescence and phosphorescence are observed via photoexcitation.

Discussion

The Use of Chemiluminescence Techniques to Study Energy Transfer in Polymer Films. The chemiluminescent decomposition of TMD and DDD (eq 7 and 8) provides a very sensitive



and convenient analytical technique for the study of energy transfer in polymer films. This technique completely avoids two major disadvantages which are inherent in photoexcitation, namely, a decrease in signal/noise due to light scattering from the exciting lamp and competitive light absorption by donor and acceptor of incident light. The chemiluminescence technique is particularly suited for studying singlet-singlet or triplet-singlet energy transfer processes.

It is important to clearly distinguish the experimental data points in Figures 4 and 5 from the R_c values derived from eq 2, 3, and 5. Simple visual inspection of the figures reveals that qualitative trends in intensity-concentration profiles are clear, irrespective of any quantitative theoretical interpretation. For example, from Figure 5 it is clear that R_c must be larger for the acetone triplet-DBA system than for the acetone triplet-DBN system. Similarly, R_c must be larger for the acetone triplet-DBN system than for the acetophenone triplet-DBN system in polystyrene.

Singlet-Singlet Energy Transfer in Polystyrene. From the Perrin model analysis (Figure 4, Table II), R_c^P values of 26 and 29 Å were derived for energy transfer from acetone singlet to DPA and DPEA, respectively and the Förster model yields R_c^F values of 23 and 26 Å, respectively. The differences in R_c values is partially due to the different definitions of critical radii in the Perrin and Förster models. The important point we wish to make is that both models yield values of R_c much larger than collisional radii. The larger value of R_c for DPEA is consistent with the greater overlap of the acetone emission with DPEA absorption spectrum than with that of DPA. We have shown earlier¹⁰ that there is no significant component of energy transfer involving triplet acetone to singlet DPA or singlet DPEA.

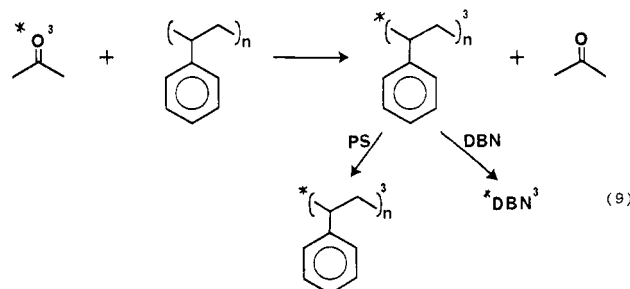
The relatively large values of R_c obtained indicate that the long-range Förster mechanism for energy transfer is dominant. Participation of the pendant phenyl groups in the singlet-singlet energy transfer is ruled out by energetic considerations (acetone singlets, $E \approx 82$ kcal/mol; benzene singlets, $E \approx 105$ kcal/mol).

Triplet-Triplet Energy Transfer in Polymer Films. Energy transfer from acetone and acetophenone triplets to several energy acceptors was studied in PS and PMMA films in order to determine the variation in R_c for triplet-triplet energy transfer processes in polymer films. The R_c values derived by the Perrin and Dexter models are summarized in Table II.

Triplet-triplet energy transfer in solid solution (77 K) has been studied for numerous donor-acceptor pairs (e.g., benzophenone-naphthalene,²⁷ carbazole-naphthalene³⁷) and measured R_c values range in the order of 13–15 Å. For polymer films in which energy migration is possible (e.g., polyvinylbenzophenone,⁸ polyvinylcarbazole⁹) R_c values greater than 20 Å have been reported.

Notice that both the Perrin model and the Dexter-Inokuti-Hirayama model yield essentially the same R_c values (Table II). This result is expected since both models basically assume a sharp, short-range cutoff for energy transfer. For all T-T transfer the R_c values (11–21 Å) are significantly smaller than the values for singlet-singlet energy transfer processes.

Transfer to DBN was studied in both polymers. The largest R_c value (21.0 Å) was found in PS for the transfer from acetone triplet to DBN. This result can be explained by postulating that in polystyrene acetone triplets transfer energy to a nearby phenyl group which in turn passes on the energy to other phenyl groups or to DBN molecules (eq 9). Evidence in support of this



proposal includes (1) $R_c = 16$ Å for transfer from acetophenone triplet to DBN in PS. *In this system the phenyl groups cannot participate in the energy transfer process* owing to the energy gap between the acetophenone triplet level (73 kcal/mol) and that of polystyrene (~ 81 –83 kcal/mol). (2) $R_c = 17$ Å for the acetone triplet to DBN transfer in PMMA. This polymer does not possess pendant groups with sufficiently low triplet levels to participate in triplet energy transfer from ketones to DBN. (3) Values of R_c in the range 11–16 Å are consistent with literature reports for triplet-triplet energy transfer by the exchange mechanism in solid solution^{27,35,36} or polymers.⁵ Our results for two other quenchers in PMAN also show values in this range (Table II).

It thus appears that, although triplet energy transfer³⁶ from acetone triplets to the substituted benzene group of polystyrene is endothermic by ~ 3 –5 kcal/mol, energy transfer from acetone triplet to polystyrene may compete with decay of the acetone triplet at 50 °C. Thus, the phenyl groups can directly participate in the energy transfer step between acetone triplet and DBN.

Alternative explanations for the large R_c for transfer between acetone triplets and DBN in PS have been considered and tested experimentally. One explanation is that TMD and DBN molecules complex or aggregate in the PS films. Evidence against this proposal was derived from two sources. First, as mentioned above, energy transfer in PS from acetophenone

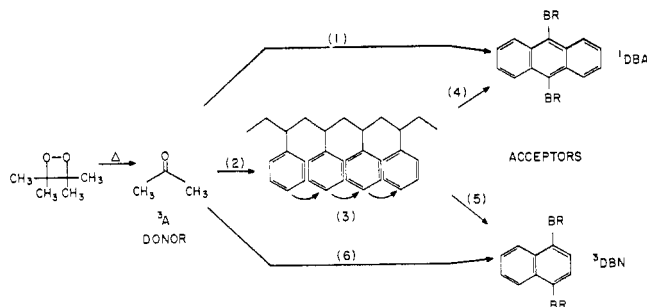


Figure 6. Triplet-singlet and triplet-triplet energy transfer in polystyrene: (1) triplet-singlet energy transfer; (2) energy transfer to polymer; (3) triplet exciton migration in polymer; (4) triplet energy transfer to singlet acceptor; (5) triplet energy transfer to triplet acceptor; (6) direct energy transfer from triplet excited acetone (3A) to triplet excited DBN.

triplet derived from DDD did not show an abnormally large R_c demonstrating that if complexing between TMD and DBN occurs it is not a property common to all dioxetanes. In the same vein, in PMMA, TMD and DBN apparently did not complex and there does not appear to be any unique feature of PS which would favor this interaction over a random distribution of molecules in the matrix.

Another alternative explanation for the large acetone triplet-DBN transfer distance is that the acetone triplet diffuses significantly during its lifetime in PS at 50 °C. However, simple calculations along with experimental results indicate that this explanation is not valid. In general, the root mean square distance, \bar{r} , traveled by a molecule in a given time can be calculated from the equation²⁸

$$\bar{r} = \sqrt{2Dt} \quad (10)$$

where \bar{r} = the root mean square distance the molecule has traveled (cm), D = diffusion coefficient (cm^2/s), and t = time (s).

Diffusion coefficients of many small organic molecules in PS matrix have been determined experimentally.²⁹ The values at 25 or 50 °C are in the range $1\text{--}10 \times 10^{-10} \text{ cm}^2/\text{s}$, about three orders of magnitude lower than those for O_2 and N_2 and about five orders of magnitude less than for organic molecules in fluid solution. The lifetime of acetone triplet in PS is not known but the absence of phosphorescence requires that it must be shortened from its solution value ($\sim 5\text{--}10 \mu\text{s}$ at 50 °C) by quenching processes. These processes are expected to be at least as rapid as quenching of triplet acetone by toluene in solution,²⁴ which has a rate constant of $3.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Using an acetone triplet lifetime of 30 ns and $D = 10 \times 10^{-10} \text{ cm}^2/\text{s}$, the maximum \bar{r} traveled by acetone triplet during its lifetime is calculated to be 0.8 Å. Thus, within the validity of this calculation, diffusion of acetone triplet should not contribute significantly to the \bar{r} value in triplet energy transfer from acetone triplet in PS. To determine experimentally if acetone triplet can diffuse significantly in 50 ns, acetone was used to quench naphthalene fluorescence at 50 °C in polystyrene films. Naphthalene singlet lifetime in solution is ~ 50 ns. Acetone was generated in these films from TMD as described in the Experimental Section. A quenching radius of ~ 13 Å was calculated from the data, a value significantly below that expected if acetone was able to diffuse readily in PS at 50 °C.

Therefore, from calculations and experiments it appears that neither aggregation nor diffusion of acetone triplet can account for the quenching radius of 21 Å calculated for triplet energy transfer from acetone to DBN in PS. Thus we conclude that energy hopping among phenyl groups of polystyrene still appears to be the most tenable explanation.

Triplet-Singlet Energy Transfer. Considering the results obtained for triplet-triplet energy transfer it appeared possible

that triplet-singlet energy transfer from acetone triplet to suitable acceptors in polystyrene might also involve energy migration through the phenyl groups. This effect would be added to the long-range induced dipole character of T-S energy transfer to produce a net R_c value which is a composite of two factors. From the experimental results (Figure 5), however, the data fit to the Förster model quite well up to very high concentrations of acceptor. Thus, the phenyl groups do not appear to participate significantly in this energy transfer except perhaps at high concentrations. The quenching radii for acetone and acetophenone triplets by dibromoanthracene (DBA) in polystyrene were both 28 Å. Therefore, the rate of transfer from acetone triplet to DBA must be greater than that to the nearby phenyl groups.

Summary

The most significant conclusions concerning energy transfer from ketone triplets to various energy acceptors in polymer films may be summarized with reference to Figure 6. Triplet-triplet and triplet-singlet energy transfer can be readily observed and parametrized by the chemiluminescent technique. With DBA, DPEA, and DPA as singlet energy acceptors, the major pathway appears to be a long-range, Förster type of mechanism. With DBN as a triplet energy acceptor in PS, a major mechanism involves an initial energy transfer to a pendant phenyl group followed by hopping and eventual quenching of an excited phenyl group by energy transfer to DBN. In PMMA only the short-range, collisional mechanism for triplet-triplet energy transfer occurs.

It is also significant that the Perrin, Dexter, and Förster models are *not* useful for mechanistic interpretations for the range of transfer distances involved in the systems reported here.

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Photophysics of Phenylcyclopropanes, Styrenes, and Benzocycloalkadienes¹

Arthur L. Lyons, Jr., and Nicholas J. Turro*

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. Received August 12, 1977

Abstract: The fluorescent and phosphorescent properties of several styrenes, phenylcyclopropanes, and benzoalkadienes were investigated. The effect of the varying orientation of the alkenyl or cyclopropyl group with respect to the π system of the benzene chromophore on the photophysics of the molecules was examined. The photophysics of several phenylcyclopropanes in which the geometry between the cyclopropane ring and the aryl moiety is either not fixed or fixed, in one case, to maximize a conjugative interaction between the two groups, in the other case, to minimize the effect, confirmed a stereoelectronic requirement for an excited state interaction between the aromatic and cyclopropane rings. The phenylcyclopropane with the poorest overlap of the cyclopropane bonds to the adjacent aromatic ring was the most highly phosphorescent of the phenylcyclopropanes studied; presumably the ineffective interaction negates a fast triplet radiationless process, e.g., α,β C-C bond cleavage, and allows triplet emission to compete more favorably. Alkenylbenzenes, in which the styryl double bond is fixed by steric constraints to be out of plane (at an angle close to 90°) with the phenyl ring, exhibited extremely low fluorescent yields attributable to enhanced internal conversion arising from a closing of the S_1 - S_0 energy gap as this highly twisted conformation is reached. A similar mechanism may operate in the triplet states of all the alkenylbenzenes rendering them nonemissive.

Although the electronic absorption spectra of arylcyclopropanes² and arylalkenes³ have been extensively studied, conclusive information regarding emission characteristics of these molecules⁴ is lacking. This is surprising in view of the photochemical interest in these systems. Arylcyclopropane photochemistry has been highly explored, and is known to include many processes, of which cis-trans isomerization and ring opening leading to olefin formation are most important.⁵ The photoreactions of conjugated arylalkenes have been investigated to a lesser extent, but dimerization, geometric isomerization, and rearrangements are known to be major pathways of reaction for these molecules.⁶

O'Connell et al.^{4a} reported that the luminescence of phenyl and naphthyl chromophores is quenched by adjacent cyclopropyl groups. Specifically, they noted that the phosphorescence quantum yield of phenylcyclopropane was ca. 50 times less than that of a model alkylbenzene. Becker et al.^{4c} noted that phenylcyclopropane exhibits a benzenelike fluorescence, but no phosphorescence. Salisbury^{4b,d} investigated the fluorescence of several phenylcyclopropanes in conjunction with photochemical studies. Contrary to some of O'Connell's results, these phenylcyclopropanes showed enhanced fluorescence quantum yields over those of model alkylbenzenes.

Reports of studies on the luminescence of alkenylbenzenes are slightly more numerous. Heckmann^{4e} reported that indene in EPA solvent at liquid air temperature phosphoresced weakly

in the 400–500-nm spectral region. Recently, however, it has been noted that the emission may be due to an impurity.^{4g,i,k} Examination of the recombination luminescence of styrene in a methylcyclohexane glass at 77 K revealed only styrene fluorescence.^{4f} The lack of phosphorescence can be attributed to either a negligible triplet population and/or nonradiative triplets. The evidence suggested that styrene triplets, although generated, were deactivated by a radiationless process(es). Recently, Salisbury and Crosby^{4m} found through fluorescence studies that nonradiative processes make important contributions to the photophysics and photochemistry of styrenes. Zimmerman et al.^{4j,l} observed in a series of 1-phenylalkenes excited state decay processes which correlate with molecular flexibility. Both the Salisbury and Zimmerman studies revealed that the contribution of radiationless decay to the deactivation of the excited states in these systems is strongly structurally dependent.

We undertook a study of the luminescence, fluorescence and phosphorescence, of a series of phenylcyclopropanes, styrenes, and benzocycloalkadienes. The intention was to correlate the radiative and radiationless processes in these molecules with the varying orientation of either a cyclopropyl or alkenyl moiety with respect to the aromatic chromophore. The phenylcyclopropanes included the parent compound **1** as well as the conformationally rigid phenylcyclopropanes **2** and **3**. The alkenylbenzenes included styrene (**4**), 2,5-dimethylstyrene (**5**),