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Photophysical Studies on the Benzophenones. Prompt and Delayed Fluorescences and Self-Quenching

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Abstract: The photophysical pathways of benzophenone and several 4,4′-disubstituted benzophenones (fluoro, chloro, methyl, methoxy, dimethylamino) in benzene at room temperature have been investigated using time-resolved laser spectroscopy. Prompt fluorescence spectra are reported for benzophenone and 4,4′-difluoro-, 4,4′-dichloro-, 4,4′-dimethyl- and 4,4′-dimethoxybenzophenone. The relative prompt fluorescence and absolute phosphorescence quantum yields at room temperature in benzene are reported. Both thermal ($T_1 \rightsquigarrow S_1$) and P type ($T_1 + T_1 \rightarrow S_1 + S_0$) delayed fluorescence are documented for these ketones. From variable temperature data on the thermal delayed fluorescence, the singlet-triplet splittings are estimated to be: benzophenone, 4.9 ± 0.5 kcal/mol; 4,4′-difluoro-, 3.9 ± 0.4 kcal/mol; 4,4′-dichloro-, 4.1 ± 0.4 kcal/mol; 4,4′-dimethyl-, 4.5 ± 0.5 kcal/mol; 4,4′-dimethoxy-, 5.1 ± 0.5 kcal/mol. All of these ketones and also 4,4′-bis(dimethylamino)benzophenone are shown to undergo self-quenching ($T_1 + S_0 \rightarrow 2S_0(k_{SQ})$). The k_{SQ}'s vary from ca. 10^5 to 10^9 M^{-1} sec^{-1} and correlate well with $\sigma_p{}^+$, $\rho = -1.7$. It is proposed that self-quenching involves formation of an exciplex wherein the half-filled n orbital of T_1 is directed toward the π electron density of an aromatic ring of S_0.

The photophysical and photochemical processes in aromatic carbonyl systems have been investigated extensively.[2] In the last few years, studies using recently developed technology[3] have allowed a more complete deciphering of the photophysical pathways in these systems. In this regard, we wish to report our results of a study of benzophenone and several derivatives using nitrogen laser excitation in conjunction with an electronically gated detection system.[3g]

The typically important photophysical processes in organic systems in fluid media are:

$$S_0 \xrightarrow{h\nu} S_1 \quad \text{excitation} \quad (1)$$

$$S_1 \xrightarrow{k_f} S_0 \quad \text{fluorescence} \quad (2)$$

$$S_1 \xrightarrow{k_{isc}} T_1 \quad \text{intersystem crossing} \quad (3)$$

$$T_1 \xrightarrow{k_p} S_0 \quad \text{phosphorescence} \quad (4)$$

$$T_1 \xrightarrow{k_d} S_0 \quad \text{nonradiative decay} \quad (5)$$

Many aromatic aldehydes and ketones have large rates of intersystem crossing ($k_{isc} \approx 10^{10}$–10^{11} sec^{-1})[4] with resulting low quantum efficiencies for prompt fluorescence ($\Phi_f \lesssim 10^{-4}$).[5] Recently, for such systems, we[3g] successfully time resolved the prompt fluorescence from the total emission, and elucidated delayed thermal fluorescence (DTF) (thermal activation of $T_1 \rightsquigarrow S_1$)[6] and P type delayed fluorescence ($T_1 + T_1 \rightarrow S_1 + S_0$)[7] in solution at room temperature.

In this paper, we utilize our method of time-resolved laser spectroscopy[3g] to identify the above and other photophysical pathways in a series of substituted benzophenones. Our approach is particularly suited for this study because of the (i) high intensity (100 kW) and short duration (~8 nsec) monochromatic (3371 Å) source and the (ii) variable time gating and signal averaging capabilities of the detecting system which lead to increased sensitivity and time resolution capabilities.

Specifically, the present study includes the time resolution of prompt fluoroscence from the total emission for benzophenone and 4,4′-difluoro-, 4,4′-dichloro-, 4,4′-dimethyl-, and 4,4′-dimethoxybenzophenone. Both DTF and P type delayed fluorescence are documented for all of the above ketones. The singlet-triplet energy splittings ($\Delta E_{S_1-T_1}$) for these compounds are calculated from variable temperature data on the DTF. Further, all of the above benzophenones and also 4,4′-bis(dimethylamino)benzophenone (Micheler's ketone) are shown to undergo self-quenching ($T_1 + S_0 \rightarrow 2S_0$)[8] with the magnitudes of the bimolecular rate constants for self-quenching increasing with electron-donating ability of the para substituent. Finally, relative prompt fluorescence and absolute phosphorescence yields at room temperature have been measured.

Experimental Section

Laser System. A 100 kW nitrogen laser (3371 Å, pulse width ~8 sec, repetition rate 10 pps) was used as the excitation source in all experiments except the phosphorescence quantum yield measurements. The sample emission was passed through a Bausch and Lomb 0.5 m grating monochromator onto either an RCA IP21 or IP28 photomultiplier tube. The signal from the photomultiplier tube was inputted into a Princeton Applied Research Model 160 Boxcar Integrator where a predetermined time segment was selectively sampled and signal averaged. The boxcar output was recorded on a Houston 2000 XY recorder.

We use the term "boxcar spectrum" below to mean the emission spectrum of some designated time segment following triggering of the laser. The length of time between triggering and the onset of the sampled segment is called the delay time, T_d, and the width of the sampled segment is called the gate, T_g. Emission spectra are obtained by establishing a stationary gate and varying the wavelength setting of the monochromator. The signal-averaged output from the boxcar integrator increases and decreases as the wavelength is varied as does the spectral distribution of the emission for the gated signal.

If a moving gate (meaning a fixed rate of increase in T_d) is used along with a fixed wavelength setting on the monochromator, the output from the boxcar integrator provides the emission decay, but with a much improved signal-to-noise ratio over conventional oscillographic techniques.

Specific details of this system have been given elsewhere.[3g]

Sample Preparation. Benzophenone (Oxford Organic-Zone Refined) was used without further preparation. 4,4′-Dimethoxybenzophenone (Eastman Chemicals) was purified by several recrystallizations from ethanol and by vacuum sublimation. Both methods gave samples showing identical phosphorescence lifetimes in benzene at room temperature and were judged to be of equal purity. 4,4′-Dimethylbenzophenone (Eastman Chemicals), 4,4′-difluorobenzophenone (Aldrich Chemicals), 4,4′-dichlorobenzophenone (Aldrich Chemicals), and 4,4′-bis(dimethylamino)benzophenone (Aldrich Chemicals) were purified by several recrystallizations from ethanol. Benzene was distilled through a 60-cm glass column packed with glass beads and a center cut was taken.

Solutions of the ketones in benzene were degassed at $<10\ \mu$ by at least 6 freeze-pump-thaw cycles and sealed in 1-cm^2 Pyrex cuvettes. The low temperature phosphorescence samples were degassed in the same manner and sealed in lengths of 6-mm Pyrex tubing.

Procedures. Spectra. Both the prompt fluorescence and boxcar spectra were obtained using 10^{-1} *M* solutions of the ketones in benzene at room temperature. The sample emission was viewed at 180° (end-on) to the laser excitation. The prompt fluorescence spectra were obtained using a time gate of 10 nsec at a delay time of 0 nsec. The boxcar spectra were obtained using a time gate of 100 nsec and delay times ranging from 0 to 5 μsec.

Phosphorescence spectra were obtained from 10^{-4} *M* solutions of the ketones in benzene at 77°K. The frozen benzene matrix is transparent and cracking was not severe enough to preclude reasonable light levels. The low temperature phosphorescences were measured 90° to the excitation axis using a sampling gate of 10 μsec and delay times of $>30\ \mu$sec.

All reported spectra are uncorrected for photomultiplier response. Corrected fluorescence and phosphorescence spectra for benzophenone are reported elsewhere.[5]

Temperature Dependence of Delayed Thermal Fluorescence. The samples were placed in a dewar flask fitted with optically flat windows. The temperature within the dewar was regulated by passing a controlled temperature stream of heated nitrogen gas through the flask. The temperature in the dewar was monitored with an iron-constantan thermocouple.

Conditions were chosen to eliminate contributions from prompt fluorescence and P type delayed fluorescence to the observed emission. The emission spectra of $<10^{-2}$ *M* solutions of the ketones in benzene were measured 90° to excitation using sampling gates of 0.1-50 μsec with delay times sufficiently long so that the ratio of the residual delayed fluorescence-phosphorescence was constant.

The area of fluorescence was determined by normalizing the fluorescence spectral distribution to the high energy shoulder of the emission spectrum. The estimated fluorescence area was subtracted from the total area with the difference being the area of the phosphorescence. The ratio of the two areas = Φ_{DTF}/Φ_p.

Phosphorescence Lifetimes. The phosphorescence at room temperature from degassed samples of variable concentrations of the ketones in benzene was monitored 90° to the excitation axis through the monochromator set at the wavelength for maximum phosphorescence intensity. The signal from the photomultiplier was inputted into the boxcar integrator which was operated in the scanning gate mode. The emission decay was recorded on an XY recorder.

Fluorescence Quantum Yields. Relative prompt fluorescence quantum yields were estimated from the measured relative signal level at the wavelength of maximum fluorescence for each ketone. The measurements were performed using 180° viewing, with a boxcar sampling gate of 10 nsec at a time delay of 0 nsec, on 10^{-1} *M* solutions of the ketones in benzene under aerated conditions.

Phosphorescence Quantum Yields. Four solutions of each ketone in benzene were optically matched to quinine sulfate in 1.0 *N* sulfuric acid solutions with the latter having optical densities of 0.4, 0.8, 1.2, and 1.6 at the wavelength of excitation, 3130 Å. The emission spectra were recorded on an American Instrument Co. spectrofluorometer from degassed ketone solutions at room temperature. The phosphorescence quantum yields were calculated by comparing the integrated emission spectra of the ketones with the quinine sulfate standards and corrections were made for differences in refractive indices.[9] The limiting quantum yields were obtained by extrapolating plots of Φ_p^{-1} vs. OD to OD = 0.

Results and Discussion

Prompt Fluorescence and Phosphorescence. Previously, we reported that aryl ketones exhibit an ultrafast ($<10^{-9}$ sec), low yield ($\Phi \lesssim 10^{-4}$) emission which was identified as prompt fluorescence.[3g,5] While these results have been questioned by some,[10] they have been confirmed by others.[11] When a sampling gate of 10 nsec is established at a time delay of 0 sec (i.e., superimposed in time on the laser pulse), the emission spectrum obtained for this time regime corresponds to the fluorescence spectrum of the carbonyl. Figures 1-3 (upper) show the prompt fluorescence spectra obtained in this manner for 10^{-1} *M*, air saturated (to reduce the phosphorescence contribution) solutions of the ketones.[12] These spectra should be compared with the phosphorescence spectra (Figures 1-3, lower) obtained at 77°K using a T_g of 10 μsec and a T_d of $>30\ \mu$sec.

The prompt fluorescence spectra all appear as broad, structureless bands which severely overlap the phosphorescence spectra. Note that at the high concentrations used in obtaining these spectra, there is some self-absorption on the high energy side of the fluorescence band which precludes using these data for accurately estimating the S_0-S_1 transition energy.

The relative quantum yields of prompt fluorescence and the absolute quantum yields of phosphorescence of the benzophenones at room temperature in benzene were determined and appear in Table I. The phosphorescence yields are *limiting* quantum yields at the low concentration limit. (See section below on self-quenching.) The relative prompt fluorescence yields vary only slightly through the ketone series, and all, except for 4,4′-dimethoxybenzophenone, are within experimental error of one another. We cautiously and tentatively conclude that there are only small changes

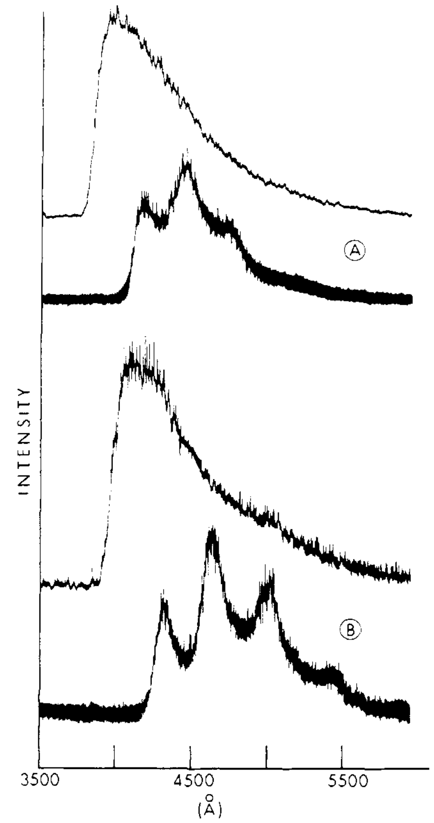


Figure 1. Emission spectra. (A) 4,4′-Dimethoxybenzophenone in benzene: upper, 10^{-1} M at room temperature, $T_d = 0$ nsec, $T_g = 10$ nsec; lower, 10^{-4} M at 77°K, $T_d = 5$ μsec, $T_g = 10$ μsec. (B) 4,4′-Dichlorobenzophenone in benzene: upper, 10^{-1} M at room temperature, $T_d = 0$ nsec, $T_g = 10$ nsec; lower, 10^{-4} M at 77°K, $T_d = 5$ μsec, $T_g = 10$ μsec.

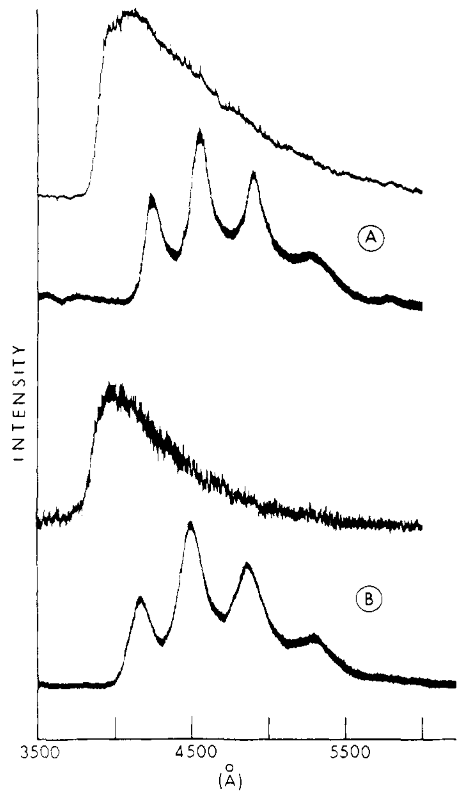


Figure 2. Emission spectra. (A) 4,4′-Dimethylbenzophenone in benzene: upper, 10^{-1} M at room temperature, $T_d = 0$ nsec, $T_g = 10$ nsec; lower, 10^{-4} M at 77°K, $T_d = 5$ μsec, $T_g = 10$ μsec. (B) 4,4′-Difluorobenzophenone in benzene: upper, 10^{-1} M at room temperature, $T_d = 0$ nsec, $T_g = 10$ nsec; lower, 10^{-4} M at 77°K, $T_d = 5$ μsec, $T_g = 10$ μsec.

in k_{isc} through this series since $\Phi_f = k_f/k_{isc}$. However, the correctness of this conclusion is dependent on the similar intensities of the n,π* absorption bands, and the further assumption of similar equilibrium geometries for the ground and excited states.[13] As a calibration point, we estimate the absolute quantum yield of the prompt fluorescence from benzophenone to be ca. 10^{-6}–10^{-5}.[3g] The benzophenone phosphorescence quantum yield (Table I) is in good agreement with previous measurements in benzene.[14]

Boxcar Spectra. A series of variable time gated boxcar spectra ($T_g = 100$ nsec, variable T_d) were obtained for the benzophenones in benzene at room temperature and appear in Figures 4–8. As expected, spectra recorded at $T_d = 0$ nsec show strong contributions from prompt fluorescence. At longer delay times, the prompt fluorescence no longer contributes to the recorded emission so the high energy shoulder observed in those spectra is due to *delayed* fluorescences. In all cases, the ratio of delayed fluorescence–phosphorescence drops rapidly during the early times until it reaches some constant value several μsec after triggering.

The delayed fluorescence observed at times less than several microseconds contains contributions from P type and thermal delayed fluorescences. Since P type delayed fluorescence results from a process that is second order in ketone triplet, it contributes strongly in early times but decays more rapidly than the first-order processes. The result is *a time-dependent delayed fluorescence-phosphorescence ratio whenever triplet-triplet annihilation is operative.*

The contribution from P type delayed fluorescence increases with increasing light intensity and benzophenone concentration since both these factors lead to higher triplet concentration. Note that, under our experimental conditions (ca. 10^{13} photons/pulse), P type delayed fluorescence in the benzophenones is negligible at concentrations <0.05 M in benzene, where the sum of all the first-order decays range from $k_1 \approx 2 \times 10^4$–$5 \times 10^5$ sec^{-1}.

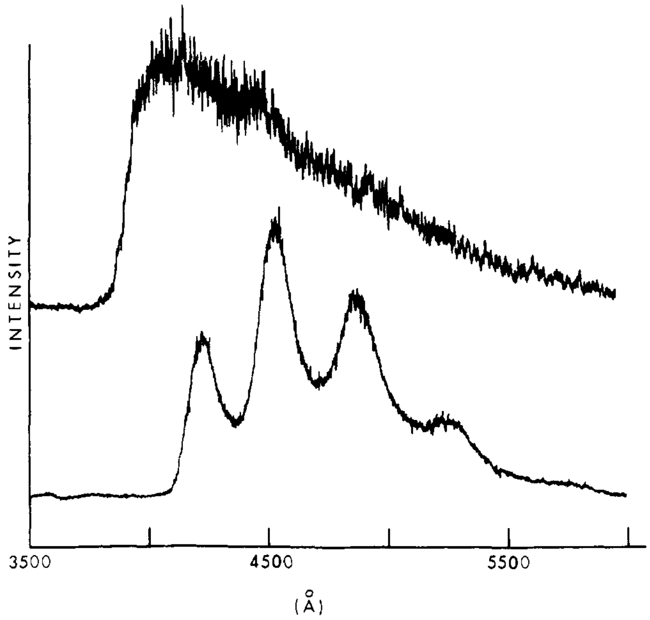


Figure 3. Emission spectra of benzophenone in benzene: upper, 10^{-1} M at room temperature, $T_d = 0$ nsec, $T_g = 10$ nsec; lower, 10^{-4} M at 77°K, $T_d = 5$ μsec, $T_g = 10$ μsec.

The benzophenone phosphorescence under conditions of high light intensity and concentrations ($\gtrsim$0.1 M) shows

Table I. Some Photophysical Parameters of the Benzophenones in Benzene

System	$\Phi_f^{rel\,a}$	Φ_p^{lim} (25°)^b	τ_p^{lim} (25°), μsec	k_{SQ}, M^{-1} sec^{-1}	$\Delta E_{S_1-T_1}$, kcal/mol	E_T,^{c} kcal/mol
4,4'-Difluoro-	1.2 ± 0.2	$1.3 \pm 0.1 \times 10^{-3}$	3.0 ± 0.3	$3.7 \pm 0.4 \times 10^5$	3.9 ± 0.4	68.9
4,4'-Dichloro-	1.3 ± 0.3	$0.93 \pm 0.09 \times 10^{-3}$	2.1 ± 0.2	$3.4 \pm 0.4 \times 10^5$	4.1 ± 0.4	66.8
Benzophenone	(1.0 ± 0.2)^d	$2.0 \pm 0.2 \times 10^{-3}$	7.7 ± 0.8	$4.4 \pm 0.4 \times 10^{5\,e}$	4.9 ± 0.5	67.6
4,4'-Dimethyl-	1.1 ± 0.1	$1.3 \pm 0.1 \times 10^{-3}$	5.5 ± 0.6	$1.9 \pm 0.2 \times 10^6$	4.5 ± 0.5	67.8
4,4'Dimethoxy-	2.1 ± 0.4	$9.9 \pm 1.0 \times 10^{-3}$	43 ± 4	$2.1 \pm 0.2 \times 10^7$	5.1 ± 0.5	68.1
4,4'-Bis(dimethyl-amino)-	1.3 ± 0.3		25 ± 2^f	$2.5 \pm 0.3 \times 10^{8\,g}$		

^{a} Essentially given by $(k_f/k_{isc})_X/(k_f/k_{isc})_B$ where X = substituted benzophenone and B is benzophenone. ^{b} Measured relative to quinine sulfate and corrected for differences in refractive indices.[9] ^{c} At room temperature as measured from the midpoint of the phosphorescence (0–0) transition. ^{d} Absolute Φ_f(prompt) $\approx 10^{-5}$–10^{-6} from a comparison of the integrated areas under the prompt fluorescence and phosphorescence emissions and using $\Phi_p \approx 10^{-3}$. ^{e} To be compared with $k_{SQ} = 1.6 \times 10^5\, M^{-1}$ sec^{-1}.[8g] ^{f} To be compared with τ_p^{lim} (25°) = 27 μsec.[8f] ^{g} To be compared with $k_{SQ} = 1.25 \times 10^5\, M^{-1}$ sec^{-1}.[8f]

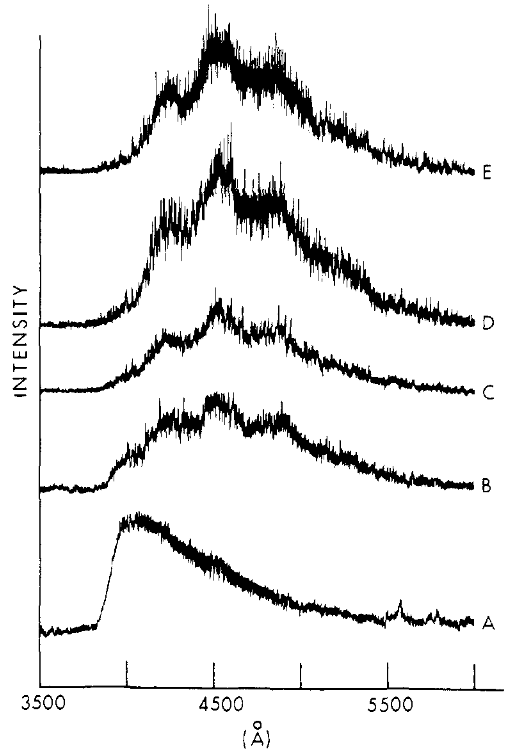


Figure 4. Boxcar spectra of 10^{-1} M benzophenone in benzene at room temperature, T_g = 100 nsec: (A) T_d = 0 nsec; (B) T_d = 200 nsec, rel sens = 4; (C) T_d = 500 nsec, rel sens = 4; (D) T_d = 1 μsec, rel sens = 10; (E) T_d = 1.5 μsec, rel sens = 10.

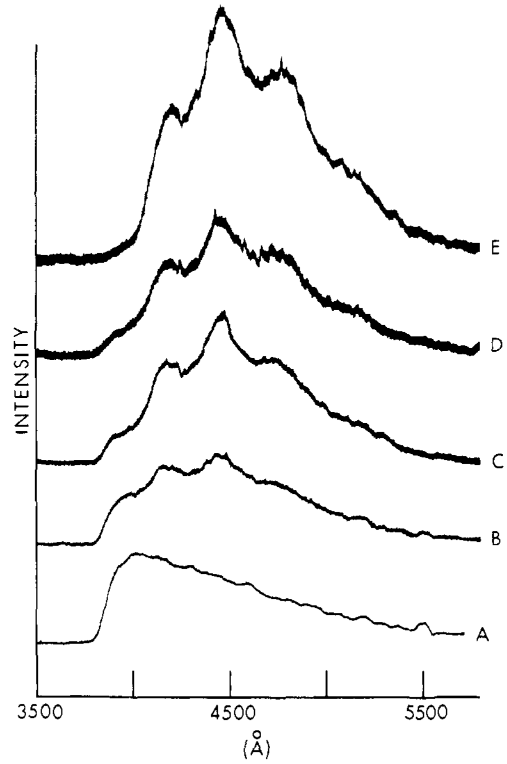


Figure 5. Boxcar spectra of 10^{-1} M 4,4'-dimethoxybenzophenone in benzene, T_g = 100 nsec: (A) T_d = 0 nsec; (B) T_d = 200 nsec, rel sens = 5; (C) T_d = 500 nsec, rel sens = 10; (D) T_d = 1 μsec, rel sens = 10; (E) T_d = 5 μsec, rel sens = 50.

nonexponential decay at shorter times (<2 μsec) and exponential decay thereafter.[3f] This decay behavior results from contributions from triplet-triplet annihilation at the early times (i.e., mixed first- and second-order decays), and correlates well with the observation of P type delayed fluorescence from benzophenone over that same time period. Previously, we compared the phosphorescence decay with a theoretical expression for the integrated light intensity based on mixed first- and second-order decays and extracted the bimolecular rate constant for triplet-triplet annihilation, $k_2 = 1.1 \pm 0.1 \times 10^{10}\, M^{-1}$ sec^{-1} [3f]

At times greater than several microseconds, the phosphorescence shows exponential decay and the ratio of delayed fluorescence-phosphorescence is constant. This residual delayed fluorescence is due to the thermal activation process $T_1 \rightsquigarrow S_1$. The several models developed to account for thermal delayed fluorescence are all based on an equilibrium between the T_1 and S_1 states that is maintained as the excited states decay via the radiative (fluorescence and phosphorescence) and nonradiative pathways.[6c] These models predict that the intensity ratio I_{DTF}/I_p will be time independent, so that similar lifetimes will be observed for the delayed fluorescence and phosphorescence.

Figure 9 illustrates a simplified but sufficient delayed thermal fluorescence scheme. Equation I shows the dependence of the quantum yield ratio of delayed thermal fluorescence/phosphorescence on the kinetic parameters in this scheme

$$\Phi_{DTF}/\Phi_p = \{[k_f k_{DTF}][k_p k_{isc}]\} e^{-\Delta E/RT} \qquad \text{(I)}$$

where k_{isc} is the rate constant for singlet to triplet intersystem crossing, $k_{DTF}e^{-\Delta E/RT}$ is the rate for triplet to singlet intersystem crossing with the Boltzmann factor providing the fraction of triplets to be found in the triplet level isoenergetic with the S_1, and where ΔE is the singlet-triplet splitting.

Determination of the Singlet-Triplet Splitting. According to eq I, the magnitude of ΔE can be assessed from a study

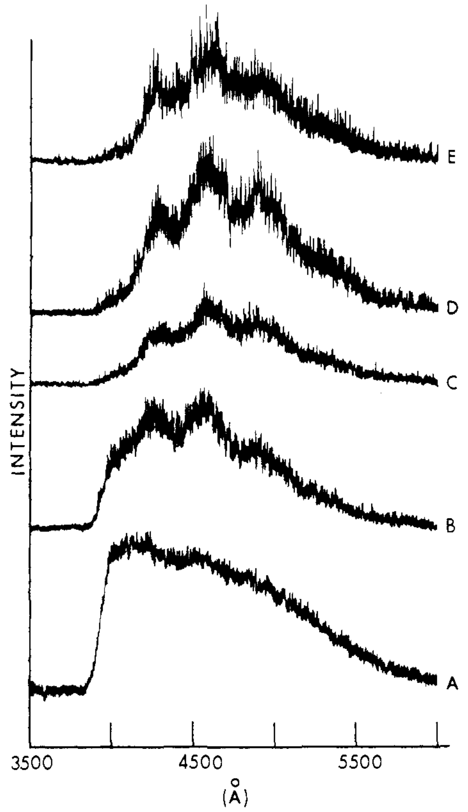


Figure 6. Boxcar spectra of 10^{-1} M 4,4′-dichlorobenzophenone in benzene; T_g = 100 nsec: (A) T_d = 0 nsec; (B) T_d = 200 nsec, rel sens = 4; (C) T_d = 500 nsec, rel sens = 4; (D) T_d = 1 μsec, rel sens = 10; (E) T_d = 1.5 μsec, rel sens = 10.

of the temperature dependence of Φ_{DTF}/Φ_P. Several such studies on aryl ketones have been carried out using the steady state approach.[6] In these systems, where there is severe overlap of the fluorescence and phosphorescence, the lack of knowledge of the complete spectral distribution of the fluorescence is a potential source of error in estimating Φ_{DTF}/Φ_P. Further, the steady state experiments provide a total emission spectrum that may incorporate prompt fluorescence and P type delayed fluorescence, as well as the desired thermal delayed fluorescence and phosphorescence, thereby further jeopardizing the validity of Φ_{DTF}/Φ_P.

Our approach to measuring the singlet-triplet splitting does not have the limitations cited above of the steady state method. In all of the systems we have studied to date, it has been possible to time resolve a good quality prompt fluorescence spectrum from the total emission. The isolation of thermal delayed fluorescence from the P type delayed fluorescence and prompt fluorescence is easily achieved by establishing a sampling gate at sufficiently long times so that the ratio Φ_{DF}/Φ_P has fallen to the residual value. This sampling gate is then held while variable temperature emission spectra are recorded for *that selected time segment of the total decay.*

A typical series of variable temperature boxcar spectra is shown in Figure 10 for 4,4′-dimethoxybenzophenone. The ratio Φ_{DTF}/Φ_P was readily obtained at each temperature by subtracting the area of the fluorescence spectrum, normalized to the observable high energy shoulder, from the area of the total emission spectrum. The resulting difference represents the phosphorescence. Good Arrhenius plots (log Φ_{DTF}/Φ_P vs. T^{-1}) were obtained in each case studied leading to estimates for ΔE. Figure 11 shows such a plot for 4,4′-dimethoxybenzophenone. The results are provided in Table I.

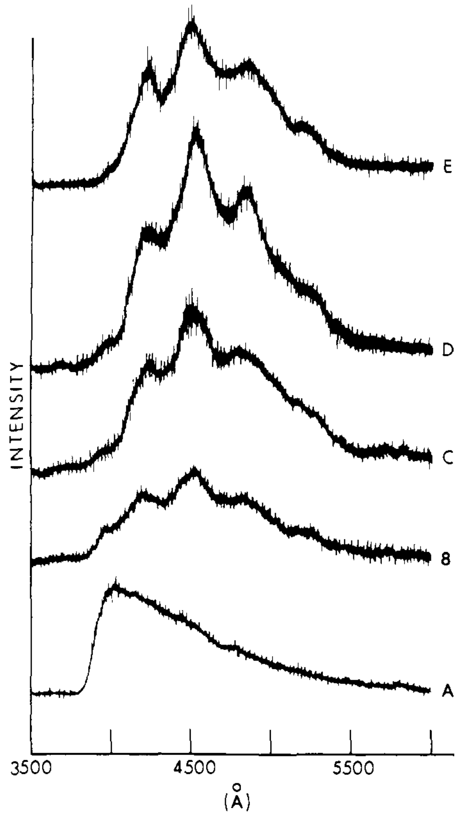


Figure 7. Boxcar spectra of 10^{-1} M 4,4′-dimethylbenzophenone in benzene, T_g = 100 nsec: (A) T_d = 0 nsec; (B) T_d = 200 nsec, rel sens = 4; (C) T_d = 500 nsec, rel sens = 10; (D) T_d = 1 μsec, rel sens = 20; (E) T_d = 1.5 μsec, rel sens = 20.

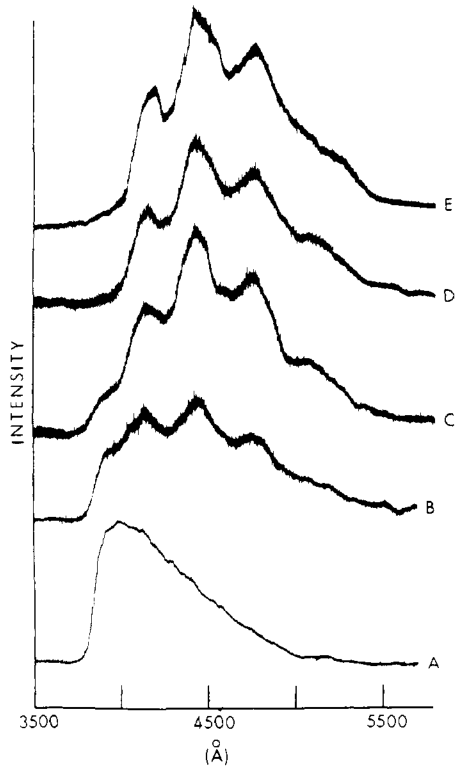


Figure 8. Boxcar spectra of 10^{-1} M 4,4′-difluorobenzophenone in benzene, T_g = 100 nsec: (A) T_d = 0 nsec; (B) T_d = 200 nsec, rel sens = 2; (C) T_d = 500 nsec, rel sens = 5; (D) T_d = 1 μsec, rel sens = 5; (E) T_d = 5 μsec, rel sens = 50.

Table II. Self-Quenching Data

Concn, *M*	τ, μsec	Concn, *M*	τ, μsec
4,4'-Difluorobenzophenone		4,4'-Dichlorobenzophenone	
0.010	2.92 ± 0.03	0.01	2.07 ± 0.02
0.050	2.80 ± 0.04	0.050	2.03 ± 0.02
0.10	2.64 ± 0.03	0.075	2.00 ± 0.02
0.15	2.54 ± 0.03	0.10	1.92 ± 0.02
0.20	2.40 ± 0.03	0.15	1.89 ± 0.02
τ^{lim}	3.0 ± 0.3	τ^{lim}	2.1 ± 0.2
4,4'-Dimethylbenzophenone		4,4'-Dimethoxybenzophenone	
0.010	4.9 ± 0.1	0.00050	28 ± 1
0.020	4.5 ± 0.1	0.0050	7.8 ± 0.2
0.040	3.8 ± 0.1	0.0075	5.5 ± 0.1
0.080	3.0 ± 0.1	0.010	4.1 ± 0.1
τ^{lim}	5.5 ± 0.6	τ^{lim}	43 ± 4
4,4'-Bis(dimethylamino)-benzophenone		Benzophenone	
		0.0048	7.7 ± 0.2
0.000010	29.0 ± 1	0.0100	7.6 ± 0.1
0.000050	19.0 ± 1	0.021	6.9 ± 0.2
0.00010	14.5 ± 0.5	0.050	6.7 ± 0.1
0.00015	13.0 ± 0.5	0.10	5.6 ± 0.1
0.00020	11.0 ± 0.5	0.15	5.1 ± 0.1
τ^{lim}	25 ± 2	τ^{lim}	7.7 ± 0.8

Table III. Variable Temperature Data

Temp, °K	$\Phi_{\text{DTF}}/\Phi_{\text{p}}$	Temp, °K	$\Phi_{\text{DTF}}/\Phi_{\text{p}}$
4,4'-Difluoro-benzophenone		4,4'-Dichloro-benzophenone	
294	0.078	303	0.12
303	0.099	313	0.15
315	0.11	326	0.19
328	0.16	336	0.24
340	0.18	348	0.28
353	0.23	Benzophenone	
360	0.27	293	0.10
4,4'-Dimethyl-benzophenone		295	0.09
296	0.13	304	0.12
313	0.18	310	0.15
328	0.30	318	0.18
339	0.34	329	0.21
352	0.42	4,4'-Dimethoxy-benzophenone	
362	0.54	295	0.059
		305	0.085
		317	0.12
		330	0.17
		343	0.22
		354	0.28

Phosphorescence Self-Quenching. We[8h] and others[8g] have noted self-quenching (step 6 below) of the benzophenone phosphorescence in fluid media at room temperature. This process also has been observed with a number of other ketone and aldehyde triplets.[8]

$$T_1 + S_0 \xrightarrow{k_{SQ}} 2S_0 \qquad (6)$$

In the absence of triplet-triplet annihilation (lower concentration and times greater than several microsecond), the ketone triplet decays by steps 4, 5, and 6 so that $\tau^{-1} = k_p + k_d + k_{SQ}[S_0]$. A reasonably accurate measure of k_{SQ} can be obtained from a study of the concentration dependence of the phosphorescence lifetime. In a plot of the observed reciprocal phosphorescence lifetimes vs. $[S_0]$ the slope directly defines k_{SQ} and the intercept provides the *limiting lifetime* ($\tau_L^{-1} = k_p + k_d$) which is solvent and temperature dependent.[15] Accordingly, the self-quenching data are han-

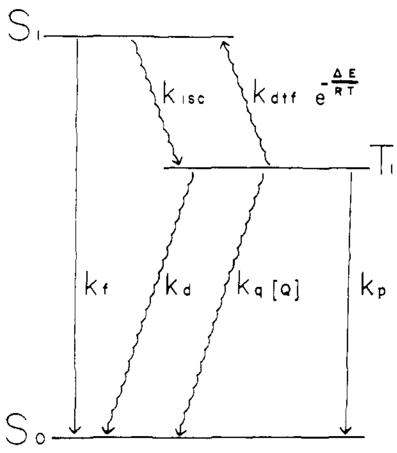


Figure 9. Delayed thermal fluorescence scheme.

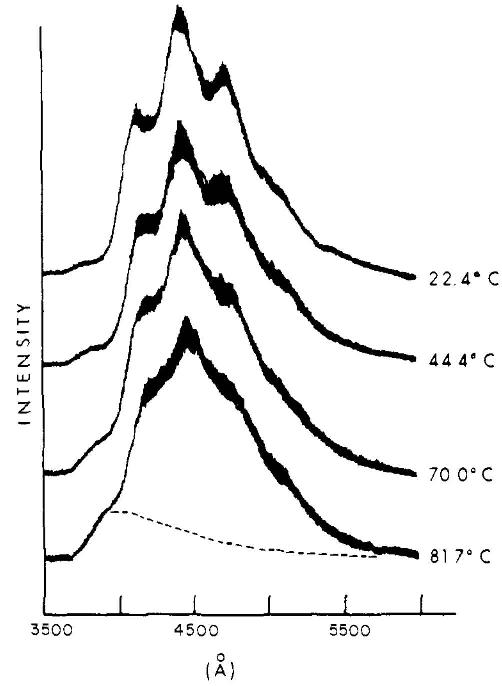


Figure 10. Temperature dependent emission spectra of 10^{-3} *M* 4,4'-dimethoxybenzophenone in benzene: T_d = 5 μsec, T_g = 50 μsec.

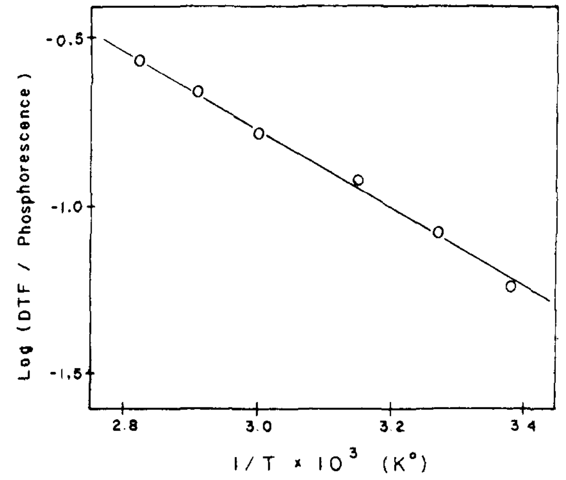


Figure 11. Arrhenius plot of delayed thermal fluorescence data for 4,4'-dimethoxybenzophenone. (See Tables II and III for data.)

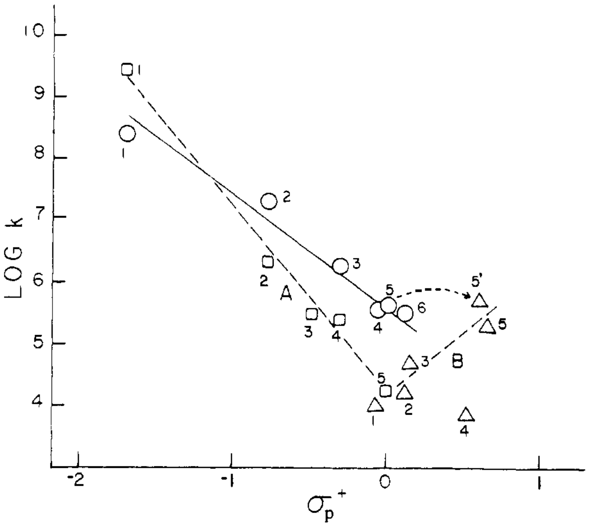


Figure 12. Correlation of benzophenone phosphorescence quenching rate constants in benzene with σ_p^+. (○) Self-quenching of benzophenone phosphorescence (this work): 1, 4,4′-bis(dimethylamino)-; 2, 4,4′-dimethoxy-; 3, 4,4′-dimethyl-; 4, 4,4′-difluoro-; 5, benzophenone; 6, 4,4′-dichloro. (□) Quenching of benzophenone phosphorescence by substituted benzenes (from ref 17): 1, dimethylamino; 2, methoxy-; 3, phenoxy-; 4, methyl-; 5, benzene. (△) Quenching of benzophenone phosphorescence by substituted benzenes (from ref 3e): 1, fluoro-; 2, chloro-; 3, bromo-; 4, trifluoromethyl-; 5, cyano-.

dled through the Stern-Volmer relationship in eq II. We have observed self-quenching with all of the benzophenones studied to date in our laboratory.

$$\tau^{-1} = \tau_L^{-1} + k_{SQ}[S_0] \qquad \text{(II)}$$

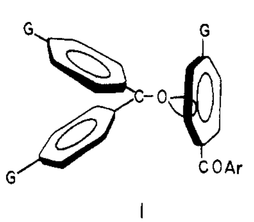
The phosphorescence yields also are concentration dependent because of the relationship $\Phi_p = k_p\tau_p$, where k_p is the radiative rate constant.

The bimolecular rate constants for self-quenching of the benzophenone triplets differ by almost a factor of 10^3 with benzophenone and the 4,4′-dihalobenzophenones clustered on the low side and Micheler's ketone being on the high side. A good correlation is found between the log k_{SQ}'s and the Hammett σ_p^+ [16] (Figure 12) with $\rho = -1.7$. This correlation suggests that quenching of the benzophenone triplet involves formation of some species stabilized by electron-donating substituents.

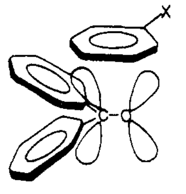
Guttenplan and Cohen[17] correlated the bimolecular rate constant for quenching of the benzophenone phosphorescence (k_Q) with the ionization potential of a large number of compounds. These k_Q's range from ca. 10^6 (toluene, anisole) to ca. 10^9 M^{-1} sec^{-1} (amines). From their data and other considerations, they conclude that the quenching process involves a complex where there is partial charge transfer from the quencher (donor) to the benzophenone triplet (acceptor).

Schuster, Weil, and Halpern[3e] observed decreased lifetimes for benzophenone phosphorescence in electron-deficient aromatic solvents and, from the correlation with solvent ionization potentials, conclude that quenching involves partial charge transfer from the ketone triplet (donor) to the solvent (acceptor). Note that this direction of charge polarization is opposite to that observed by Guttenplan and Cohen.

These types of quenching processes which do not involve any observable photochemistry or energy transfer are thought to proceed via exciplex formation, i.e., a complex formed between excited and ground state components. The general description of the wave function for an exciplex is[18]



1



2

where the coefficients α, β, γ, and δ have varying magnitudes depending on the extent of mixing in of the charge resonance (D^+A^- and D^-A^+) and exciton resonance (D^*A and DA^*) states. The special case of excimer involves identical partners for D and A with the additional requirement that $|\alpha| = |\beta|$ and $|\gamma| = |\delta|$.[18]

$$\psi_E = \alpha\Psi_1(D^+A^-) + \beta\Psi_2(D^-A^+) + \gamma\Psi_3(D^*A) + \delta\Psi_4(DA^*) \qquad \text{(III)}$$

We do not believe that self-quenching of the benzophenone triplets involves excimer formation. In the excimer, the two components are usually assumed to form a symmetrical sandwich with the molecular planes (in this case as well as they can be defined) and axes parallel.[19] While such a structure would allow electron transfer between the π and π^* orbitals, electron transfer between the π and n orbitals would be difficult since the former is normal to the molecular plane while the latter is in the molecular plane (more properly the carbonyl plane).

Rather, we propose that the self-quenching of the benzophenone triplets occurs via formation of an AD exciplex ($|\alpha| > |\beta|$) where the triplet molecule is the acceptor and the ground state molecule is the donor. A possible structure that provides for the necessary orbital overlap is shown in **1** where the half-filled n orbital of T_1 is directed toward the π electron density of one of the aromatic rings of S_0. The electron-donating ability of the benzene ring of S_0 would be enhanced if the carbonyl is out-of-plane with the donating aromatic ring. As the electron-donating ability of the substituent in S_0 increases, the degree of charge transfer in the exciplex increases (i.e. α increases with respect to γ and δ) leading to enhanced radiationless decay to the ground state.[20]

A possible kinetic scheme for quenching of triplets via exciplex formation as described is

$$^3A^* + D \underset{k_{-e}}{\overset{k_e}{\rightleftharpoons}} \underset{\text{exciplex}}{[^3A, D \longleftrightarrow A\cdot^-, D^+]} \xrightarrow{k_r} A + D$$

where the rate constant for self-quenching would be $k_{SQ} = k_e k_r/[k_{-e} + k_r]$. The observed increase in k_{SQ} with electron-donating groups could result from an increase in k_e and/or k_r relative to k_{-e} as the charge transfer character of the exciplex increases. An increase in k_e would reflect an increase in the binding energy of the exciplex, whereas k_r (nonradiative decay) would increase from enhanced spin-orbit coupling.[20]

Figure 12 shows the data of Guttenplan and Cohen[17] for quenching of the benzophenone triplet by several substituted benzenes. These quenching rate constants correlate reasonably well with σ_p^+ as was observed with our self-quenching data. We suggest that both of these quenching processes involve formation of an exciplex of the type shown in **1**.[21]

In contrast, some quenching data selected from the work of Schuster, Weil, and Halpern[3e] (benzophenone triplet and electron-deficient aromatic solvents) correlates poorly, and may even be interpreted as showing an inverse correlation with σ_p^+. If the benzophenone triplet *is* the donor in these cases,[3e] quenching may involve formation of an exciplex as shown in **2** where the donor and acceptor are in parallel planes so as to facilitate electron transfer from π^* of T_1 to the π^* of the acceptor.[22] Accordingly, from the data currently available, it appears that there may be at least two different mechanisms for phosphorescence quenching via exciplex formation as depicted by **1** and **2**. Quenching via exciplex **1** may operate in the region covered by curve A in Figure 12 (electron-donating substituents) while quenching via **2** may hold in the region covered by curve b (electron-withdrawing substituents). Interestingly, if one considers benzophenone as a substituted benzene,[23] then our self-quenching data for benzophenone correlates with the data of Schuster, Weil, and Halpern[3e] as the triangle labeled 5′.[24] Note that here benzophenone self-quenching is being viewed as the quenching of benzophenone triplet by an electron-deficient benzene. The implication of the result of this analysis is that the benzophenone self-quenching appears to be occurring via **2** rather than, or as well as, via **1**. Possibly, the cluster of points in our self-quenching data (circles 4, 5, 6) represents a minimum in quenching efficiency similar to that seen in the benzophenone/substituted benzene systems.

If this interpretation is correct, then the rate constants for self-quenching of benzophenones with electron-withdrawing substituents will not correlate with the self-quenching data in Figure 12. We would anticipate a discontinuity in the Hammett plot of self-quenching efficiency to appear at the point of changeover or duality of mechanism. Experiments to test out this hypothesis are now in progress.

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(22) See N. J. Turro, J. C. Dalton, G. Farrington, M. Niemczyk, and D. M. Pond, *J. Am. Chem. Soc.*, **92**, 6978 (1970), and references therein for a study of alkanone fluorescence quenching by electron-rich and electron-deficient alkenes which indicates modes of reaction similar to the structures shown in **1** and **2**, respectively.

(23) We thank Professor P. J. Wagner for pointing out to us this interpretation.

(24) We are using a σ_p^+ for C_6H_5CO- of 0.6 based on the value of 0.56 reported for CH_3CO-: C. G. Swain and E. C. Lupton, Jr., *J. Am. Chem. Soc.*, **90**, 4328 (1968).