probably due to the rigidity of the solvent. On the contrary, the reverse photochemical reaction induced by irradiation of II, that is, II* → I, occurs very effectively even in a rigid solution at 77 K.

The above results may be explained as follows. (a) It might be necessary for the intramolecular adduct formation of I that some solvent molecules are pushed out, and not for the reverse reaction, or (b) the excess energy corresponding to the difference between the S_1 states of II and I might be partly used for softening the surroundings.

References and Notes

(1) (a) Department of Chemistry, Faculty of Engineering Science; (b) Institute of Scientific and Industrial Research.

(2) T. Inoue, T. Kaneda, and S. Misumi, *Tetrahedron Lett.*, 2969 (1974).

(3) T. Inoue, T. Kaneda, and S. Misumi, to be published in *Bull. Chem. Soc. Jpn.*

(4) H. D. Hartzler, *J. Am. Chem. Soc.*, **93**, 4527 (1971).

Deactivation of Benzophenone Triplets via Exciplex Formation. Evidence for Dual Reaction Pathways

Monte W. Wolf, Ronald E. Brown, and Lawrence A. Singer*

Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90007.

Received July 2, 1976

Abstract: Self-quenching ($^3B^* + B \rightarrow 2B$, k_{SQ}) data in benzene and carbon tetrachloride are presented for a series of para,para′-disubstituted benzophenones: X = $(CH_3)_2N$, CH_3O, CH_3, F, Cl, H, $COOCH_3$, CF_3, and CN. The k_{SQ}'s correlate with $\sigma_p{}^+$'s but in a discontinuous manner resulting in a minimum for the cases of X = F, Cl, H. Thus, the correlation for the electron-donating X's gives a negative slope while the correlation for the electron-withdrawing X's gives a positive slope. Similar behavior is noted for phosphorescence quenching by a series of substituted benzenes of 4,4′-dimethoxybenzophenone, benzophenone, and 4,4′-bis(trifluoromethyl)benzophenone in 1,1,2-trichlorotrifluoroethane. These profiles are interpreted in terms of competing deactivation pathways via "n-type" and "π-type" exciplexes. The variation of the k_Q's with solvent for the benzophenone–anisole system indicates no dependence on solvent viscosity and only a modest (factor of ~6) variation between freon solvents and acetonitrile. A general kinetic scheme for reversible exciplex formation is presented and developed in terms of the present systems. The low temperature emission observed from the benzophenone-*N,N*-dimethylaniline system is reinvestigated and attributed as before to excitation of a ground state complex.

The deactivation scheme of aromatic aldehyde and ketone triplets in fluid aromatic media at room temperature is dominated by the nonradiative decay pathways (Scheme I) as evidenced by very low phosphorescence quantum yields ($\Phi_p \lesssim 10^{-3}$).[1] In the past few years, very significant photokinetic work in several laboratories has shown that the nonradiative decay path in aromatic solvents, in fact, is dominated by a bimolecular quenching process, step 5, that proceeds via a short-lived complex having some charge transfer character.[2]

Scheme I

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

(2) $S_1 \xrightarrow{k_{isc}} T_1$ intersystem crossing ($\Phi_{isc} \approx 1$)

(3) $T_1 \xrightarrow{-h\nu'} S_0$ phosphorescence

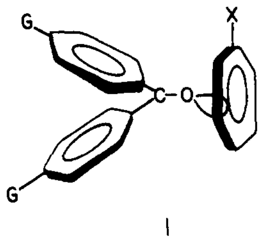
(4) $T_1 \xrightarrow{k_d} S_0$ nonradiative decay

(5) $T_1 + Q \xrightarrow{k_Q} S_0$ quenching

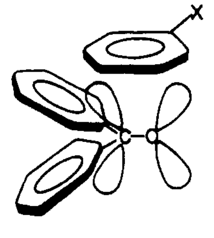
(6) $T_1 + S_0 \xrightarrow{k_{SQ}} 2S_0$ self-quenching

In addition to the above observations, a number of reports appeared in recent years of the self-quenching of aromatic aldehydes and ketones, step 6.[3] In the course of investigating a series of para,para′-disubstituted benzophenones, we noted an apparent linear correlation between log k_{SQ} and $\sigma_p{}^+$ ($\rho = -1.7$) for benzophenone and substituted benzophenones having *p*-Cl, F, CH_3, CH_3O, and $(CH_3)_2N$.[1] Previously, Cohen and Guttenplan[2a] reported that the quenching rates of benzophenone triplet by substituted benzenes increased with decreasing ionization potential of the latter. We found that a Hammett plot of their data also correlated well with $\sigma_p{}^+$ giving a negative ρ. We concluded that for benzophenone triplets both self-quenching and quenching by aromatic solvents proceed via exciplex **1** (hereafter called n-type exciplex) where there is some charge transfer character. In the n-type exciplex, the resulting charge polarization gives the triplet an acceptor role.

In contrast to the above results, Schuster, Weil, and Halpern[2b] found that electron-deficient benzenes quench benzophenone triplet *faster* than benzene. Accordingly, we found that a Hammett plot of their data tended towards a positive ρ. The apparent reversal of donor–acceptor roles is understandable if a different exciplex (**2**) (hereafter called π-type exciplex) were involved in these cases. Note that in the n-type exciplex electron transfer is facilitated between the π system of the aromatic ring and the half-filled n orbital of T_1 while in the π-type exciplex, electron transfer is facilitated between the half-filled π^* of T_1 and the unfilled π^* of Q.



1



2

If self-quenching and quenching by aromatic solvents are mechanistically similar, then we would also expect to find a changeover from the n- to the π-type exciplex at some point in the self-quenching mechanism for benzophenones having electron-withdrawing substituents. Further, the tendency of

Table I. Self-Quenching of Substituted Benzophenones in Benzene and Carbon Tetrachloride at Room Temperature

Benzophenone $(p\text{-X-}C_6H_4)_2CO$	Benzene: Limiting τ, μs^a	Benzene: k_{SQ}, $M^{-1}\ s^{-1}$	Carbon tetrachloride: Limiting τ, μs^a	Carbon tetrachloride: k_{SQ}, $M^{-1}\ s^{-1}$
$(CH_3)_2N$	28 ± 3^b	$2.8 \pm 0.2 \times 10^{8\ b}$		
CH_3O	47 ± 5	$2.2 \pm 0.2 \times 10^7$	3.6 ± 0.4	$1.7 \pm 0.2 \times 10^7$
CH_3	23 ± 1^c	$1.8 \pm 0.2 \times 10^6$	11 ± 1	$1.0 \pm 0.1 \times 10^6$
F	$3.0 + 0.3$	$3.9 \pm 0.4 \times 10^5$		
Cl	2.2 ± 0.2	$3.4 \pm 0.4 \times 10^5$		
H	$6.9 + 0.6^d$	$4.7 \pm 0.5 \times 10^{5\ d}$	16 ± 2	$2.6 \pm 0.3 \times 10^{5\ e}$
$COOCH_3$	0.8 ± 0.1	$2.3 \pm 0.4 \times 10^7$	77 ± 9	$4.2 \pm 0.7 \times 10^6$
CF_3	$(0.4)^f$		59 ± 6	$1.2 \pm 0.1 \times 10^7$
CN			74 ± 7	$4.3 \pm 0.4 \times 10^7$

[a] From $\tau_{obsd}^{-1} = \tau_L^{-1} + k_{SQ}[B]$. [b] To be compared with $\tau_L = 27$ s and $k_{SQ} = 1.25 \times 10^8\ M^{-1}\ s^{-1}$, ref 3f. [c] Note that this is a corrected value for that previously reported by us as 5.5 μs. [d] To be compared with $\tau_L = 10 \pm 1$ μs and $k_{SQ} = 1.6 \times 10^5\ M^{-1}\ s^{-1}$, ref 3g. [e] To be compared with $k_{SQ} = 3.25 \times 10^5\ M^{-1}\ s^{-1}$, ref 3g. [f] From benzene quenching data in Table II using the relationship $\tau_L^{-1} \simeq k_d \simeq k_Q(Q)$ where $(Q) \simeq 12$ M.

Table II. Quenching of Benzophenones by Substituted Aromatics in 1,1,2-Trichlorotrifluoroethane at Room Temperature[a]

Quencher	k_Q, $M^{-1}\ s^{-1}$: 4,4-Dimethoxybenzophenone	k_Q, $M^{-1}\ s^{-1}$: Benzophenone	k_Q, $M^{-1}\ s^{-1}$: 4,4′-Bis(trifluoromethyl)benzophenone
Anisole	$2.2 \pm 0.2 \times 10^5$	$3.1 \pm 0.3 \times 10^{6\ b}$	$1.7 \pm 0.2 \times 10^8$
Diphenyl ether	$3.8 \pm 0.4 \times 10^5$	$6.3 \pm 0.7 \times 10^{5\ c}$	$4.2 \pm 0.4 \times 10^7$
Toluene	$1.5 \pm 0.2 \times 10^5$	$5.8 \pm 0.6 \times 10^{5\ d}$	$7.6 \pm 0.8 \times 10^6$
Benzene	$3.5 \pm 0.4 \times 10^4$	$1.3 \pm 0.2 \times 10^{4\ e}$	$2.5 \pm 0.3 \times 10^5$
Chlorobenzene	$4.0 \pm 0.4 \times 10^4$	$2.0 \pm 0.2 \times 10^{4\ f}$	$2.1 \pm 0.2 \times 10^5$
Methyl benzoate	$1.4 \pm 0.2 \times 10^5$	$1.9 \pm 0.3 \times 10^4$	$1.5 \pm 0.2 \times 10^5$
α,α,α-Trifluorotoluene	$2.4 \pm 0.2 \times 10^5$	$9.4 \pm 0.9 \times 10^{4\ g}$	$2.8 \pm 0.3 \times 10^4$
Benzonitrile	$1.4 \pm 0.2 \times 10^6$	$4.9 \pm 0.5 \times 10^{5\ h}$	$1.0 \pm 0.1 \times 10^5$

[a] Using 10^{-3} M solutions of the benzophenones. Each kinetic entry determined from a plot according to eq 1 using at least 4 different concentrations of quencher. [b] $2.1 \times 10^6\ M^{-1}\ s^{-1}$ in benzene, ref 2a. [c] $7 \times 10^5\ M^{-1}\ s^{-1}$ in benzene, ref 2a. [d] $5.2 \times 10^5\ M^{-1}\ s^{-1}$ in benzene, ref 2a. [e] $1.8 \times 10^4\ M^{-1}\ s^{-1}$, in neat solvent, ref 2a. [f] $1.6 \times 10^4\ M^{-1}\ s^{-1}$, in neat solvent, ref 2b. [g] $7.2 \times 10^3\ M^{-1}\ s^{-1}$, in neat solvent, ref 2b. [h] $2.1 \times 10^5\ M^{-1}\ s^{-1}$, in neat solvent, ref 2b.

substituted benzophenones to be quenched by aromatics via n- or π-type exciplexes should depend on the substituent in the benzophenone. This manuscript reports on these and related experiments.

Results

Self-Quenching of the Benzophenones. Self-quenching data from direct lifetime measurements (eq 1, from Scheme I) for benzophenone, 4,4′-dichloro-, 4,4′-difluoro-, 4,4′-dimethyl-, 4,4′-dimethoxy-, and 4,4′-bis(dimethylamino)benzophenone in benzene at room temperature were previously reported.[1] In an extension to electron-deficient benzophenones, self-quenching data for 4,4′-dicarbomethoxy-, 4,4′-bis(trifluoromethyl)-, and 4,4′-dicyanobenzophenone were obtained. Because of very fast phosphorescence decays in benzene for the latter two benzophenones, self-quenching data for these and other benzophenones were obtained in carbon tetrachloride (Table I). The k_{SQ}'s were larger in all cases in benzene with the largest difference being a factor of 5 for 4,4′-dicarbomethoxybenzophenone. Figure 1 shows a plot of these k_{SQ}'s against σ_p^+.

$$\tau^{-1}{}_{obsd} = \tau^{-1}{}_L + k_Q[Q] \qquad (1)$$

where

$$\tau^{-1}{}_L = k_p + k_d$$

Quenching by Substituted Benzenes. The rate constants for quenching of the benzophenone, 4,4′-dimethoxy-, and 4,4′-bis(trifluoromethyl)benzophenone triplets by substituted benzenes in 1,1,2-trifluorotrichloroethane at room temperature were determined by direct lifetime measurements. These k_Q's appear in Table II and are plotted in Figure 2 against σ_p^+ values.

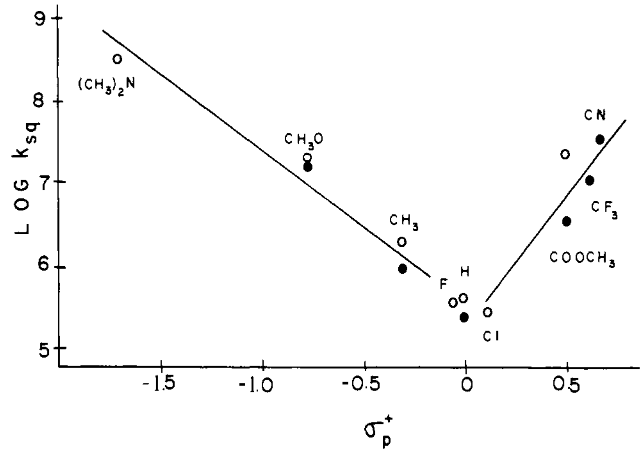


Figure 1. Hammett plot of the self-quenching rate constants vs. σ_p^+ values. ○, in benzene; ●, in carbon tetrachloride.

Solvent Effects. The effect of solvent variation on the benzophenone–anisole system was investigated. The entries in Table III were designed to probe effects due to solvent viscosity and polarity.

Exciplex Emissions. To date, we have not observed any new emissions that could be assigned to the transient exciplexes responsible for the above described phosphorescence

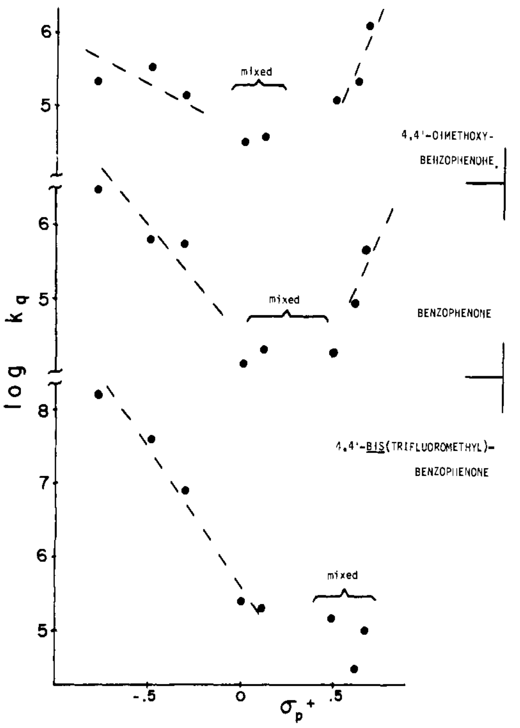


Figure 2. Hammett plot of the quenching rate constants vs. $\sigma_p{}^+$ for the phosphorescence quenching of three benzophenones by substituted benzenes.

Table III. Quenching of the Benzophenone Phosphorescence by Anisole in Various Solvents at Room Temperature

Solvent	Viscosity, cP[a]	Dielectric[a] constant	k_Q, $M^{-1}s^{-1}$
Carbon tetrachloride	0.97	2.2	$2.3 \pm 0.2 \times 10^6$
Trichlorofluoromethane	0.42[b]	2.3[c]	$1.3 \pm 0.1 \times 10^6$
1,1,2-Trichlorotrifluoromethane	0.71	2.41	$3.1 \pm 0.3 \times 10^6$
Methyl acetate	0.38	6.68	$1.8 \pm 0.2 \times 10^6$
Acetic anhydride	0.91	20.7	$7.1 \pm 0.7 \times 10^6$
Acetonitrile	0.36	37.5	$8.0 \pm 0.8 \times 10^6$

[a] At room temperature from J. Riddick and W. Bunger, "Organic Solvents", Wiley-Interscience, New York, N.Y., 1970, unless noted otherwise. [b] Supplied by E. I. du Pont de Nemours and Co., Freon Products Division. [c] A. Gordon and R. Ford, "The Chemist's Companion", Wiley-Interscience, New York, N.Y., 1972.

quenching. In our search, we examined a number of the systems in Table II using both steady state and pulsed (nitrogen laser) techniques. During the latter investigation, we employed our previously described gating techniques[1,4] and recorded emission spectra of narrow time segments between 0.5 and tens of μs after excitation. In all of these experiments, we could only document the phosphorescence of the benzophenone under study.

Discussion

General Description of the Exciplex. Numerous examples exist of quenching of aromatic aldehyde and ketone triplets under conditions where no observable product is formed and/or energy transfer is energetically unfavorable. These cases, as well as self-quenching, are believed to proceed via short-lived exciplexes (complex composed of excited and ground state components) which possess some degree of charge-transfer character.

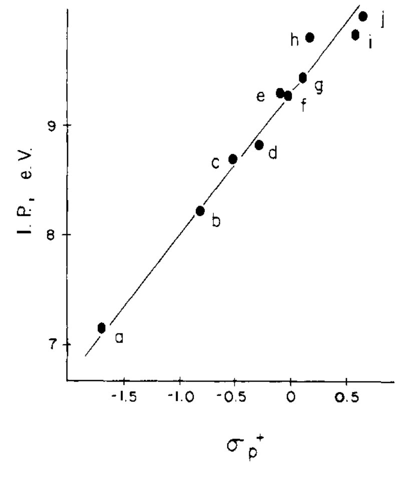


Figure 3. Correlation of the Hammett $\sigma_p{}^+$ values with the ionization potentials of substituted benzenes. X = (a) $-N(CH_3)_2$, (b) $-OCH_3$, (c) $-OC_6H_5$, (d) $-CH_3$, (e) -F, (*f*) -H, (g) -Cl, (h) -Br, (i) $-CF_3$, and (j) -CN.

An extension by Guttenplan and Cohen[2a] of a treatment developed by Weller and co-workers for cases of charge-transfer formation from excited singlet state reactions[5] led to

$$\Delta G_c \approx -{}^3\Delta E_{0,0} + \mathrm{IP_D} - E(A^-/A) + C \qquad (2)$$

where ΔG_c is the free-energy change for complex formation, ${}^3\Delta E_{0,0}$ is the triplet energy of the carbonyl (acceptor), $-E(A^-/A)$ is the reduction potential of the carbonyl, $\mathrm{IP_D}$ is the ionization potential of the quencher (donor), and C is a constant that includes entropy and solvation terms. For a series of donors with a constant acceptor, $\Delta G_c \approx \mathrm{IP_D} + C$. With this expression, they were able to correlate k_Q's for benzophenone phosphorescence quenching covering a range of almost 10^5. Separate correlations were noted for aliphatic and aromatic quenchers.

In our treatment, we use the Hammett substituent constant $\sigma_p{}^+$ [6] which inversely correlates well with IP's for a series of substituted benzenes (Figure 3). The $\sigma_p{}^+$'s have the advantage that they generally are more available than the IP data for specific compounds.

The general description of the wave function of the exciplex is[7]

$$\Psi_E = \alpha\Psi_1(A^+B^-) + \beta\Psi_2(A^-B^+) + \gamma\Psi_3(A^*B) + \delta\Psi_4(AB^*)$$

where α, β, γ, and δ have varying magnitude depending on the extent of mixing in of the charge resonance and exiton resonance states.

Substituent Effects and Charge Transfer Contribution to the Exciplex. The substituent effects in Tables I and II are explainable by charge transfer contributions to the exciplex responsible for phosphorescence quenching. However, a single exciplex is insufficient to explain the data because of the discontinuity observed in all of the plots correlating k_Q (or k_{SQ}) with $\sigma_p{}^+$. We suggest that n-type exciplexes (**1**) operate over regions of the Hammett plots where negative ρ's are observed while the π-type exciplexes operate over the regions wherever positive ρ's are seen. The changeover is not abrupt in any system and regions of mixed mechanism are implied. In fact, the data for the 4,4'-bis(trifluoromethyl) system (Figure 2) suggest that quenching via the π-type exciplex is never dominant.

The quenching data are consistent with the hypothesis that increasing charge resonance contribution to the exciplex increases k_Q (or k_{SQ}).[8] In Table II, the n-type exciplex systems (operating with anisole, diphenyl ether, and toluene as quenchers) show a relative reactivity order 4,4′-dimethoxybenzophenone > benzophenone > 4,4′-bis(trifluoromethyl)benzophenone which parallels the expected order of the electron affinities of the ketone triplets, $E(\mathrm{B}^-/{}^3\mathrm{B}^*)$.[9,10]

For those systems where the π-type exciplex appears to be dominating (α,α,α-trifluorotoluene and benzonitrile as quenchers), the reactivity order is reversed so that k_Q is largest for 4,4′-dimethoxy- and smallest for 4,4′-bis(trifluoromethyl)benzophenone. This reversal is understandable since the T_1 is now the donor in the π-type exciplex and the k_Q order should be inversely related to the order of the ionization potentials of the T_1's, $\mathrm{IP}(\mathrm{B}^+/{}^3\mathrm{B}^*)$.[11]

We note that for benzene, chlorobenzene, and methyl benzoate as quenchers, no trends are noted with the three benzophenones which again indicates regions of mixed mechanisms as suggested above from the overall profiles of the Hammett plots.

The analysis of the self-quenching data (Table I, Figure 1) is potentially more complicated than the benzene quenching data since the para substituents operate as variables on both components of the exciplex. Consideration of *only* the expected triplet substituent effect leads to the prediction of a Hammett plot showing a positive slope over the n-type exciplex region but a negative slope over the π-type exciplex region. This profile results from the expected positive correlation of the $E(\mathrm{B}^-/{}^3\mathrm{B}^*)$'s with $\sigma_p{}^+$ over the former region where T_1 has the acceptor role, but a negative correlation of the $\mathrm{IP}(\mathrm{B}^+/{}^3\mathrm{B}^*)$'s with $\sigma_p{}^+$ over the latter region where T_1 has the donor role. In contrast, the Hammett plot resulting from consideration *only* of the quencher substituent effect predicts a profile similar to that observed in Figure 2. Since this latter type profile is, in fact, observed for the self-quenching data, we conclude that the substituent variation in the quencher has the greater perturbing influence on exciplex stability.

Solvent Effects. The variation of k_Q with solvent for the benzophenone–anisole system (Table III) shows no correlation with solvent viscosity which is not unexpected since the observed rate constants are several orders of magnitude below the diffusion limit.[12] The correlation with solvent dielectric constant (ϵ) is modest (Figure 4) and of the same magnitude reported by Guttenplan and Cohen[2a] in their study. It is somewhat disconcerting that the k_Q spread among the halogenated solvents (essentially identical ϵ) is substantial relative to the k_Q difference between the low and high dielectric constant solvents. It strikes us that the modest variations of these k_Q's with solvent polarity must be cautiously interpreted as evidence for partial charge transfer character in the exciplex responsible for phosphorescence quenching.

A General Kinetic Scheme. These quenching processes can be considered within the context of a general kinetic scheme that involves reversible exciplex formation.[13] In Scheme I, quenching via an irreversibly formed exciplex is implied. We show below that, under certain conditions, the expressions derived for a general scheme involving reversible exciplex formation lead to an expression that is kinetically equivalent to Scheme I. We will then point out several inconsistencies in our present data that become understandable by Scheme II.

Scheme II

(1) $\mathrm{S}_0 \xrightarrow{h\nu} \mathrm{S}_1$	excitation
(2) $\mathrm{S}_1 \xrightarrow{k_\mathrm{isc}} \mathrm{T}_1$	intersystem crossing
(3) $\mathrm{T}_1 \xrightarrow{k_\mathrm{d}'} \mathrm{S}_0$	all unimolecular decays
(5′) $\mathrm{T}_1 + \mathrm{Q} \underset{k_{-e}}{\overset{k_e}{\rightleftharpoons}} [\mathrm{E}]$	exciplex formation
(6′) $[\mathrm{E}] \xrightarrow{k_\mathrm{r}} \mathrm{S}_0 + \mathrm{Q}$	deactivation of exciplex

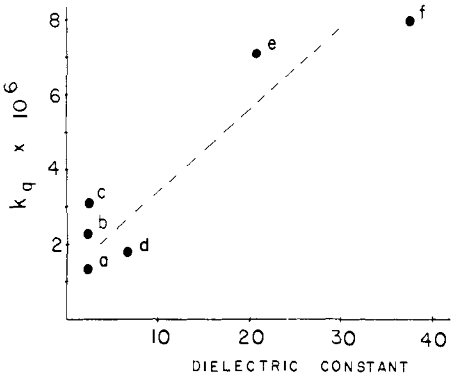


Figure 4. Correlation of the quenching rate constants for the benzophenone–anisole system with solvent dielectric constant. Solvent: (a) trichlorofluoromethane, (b) carbon tetrachloride, (c) 1,1,2-trichlorotrifluoroethane, (d) methyl acetate, (e) acetic anhydride, (f) acetonitrile.

According to Scheme II, the phosphorescence intensity, $I_\mathrm{p}(t)$, decays with time according to[14]

$$I_\mathrm{p}(t) = [k_\mathrm{p}(\lambda_2 - X)/(\lambda_2 - \lambda_1)](e^{-\lambda_1 t} + Ae^{-\lambda_2 t}) \qquad (3)$$

where

$$2\lambda_{1,2} = X + Y \mp [(Y - X)^2 + 4k_{-e}k_e(\mathrm{Q})]^{1/2} \qquad (4)$$

and

$$X = (k_\mathrm{d}' + k_\mathrm{e}[\mathrm{Q}]),\ Y = (k_{-e} + k_\mathrm{r})$$

$$A = (X - \lambda_1)/(\lambda_2 - X)$$

Nonexponential decays are predicted from eq 3 when λ_1 and λ_2 are comparable in magnitude while exponential decays will result when $\lambda_1 \gg \lambda_2$ or $\lambda_2 \gg \lambda_1$. However, an inspection of eq 4 shows that the first condition is precluded so that exponential decay (such as noted in our study) means that $\lambda_2 \gg \lambda_1$. Thus, for exponential decays, eq 3 simplifies to

$$I_\mathrm{p}(t) = [k_\mathrm{p}(\lambda_2 - X)/(\lambda_2 - \lambda_1)]e^{-\lambda_1 t} \qquad (5)$$

where λ_1^{-1} is defined in classical terms as the "phosphorescence lifetime".

A further condition of our experiments is that linear Stern–Volmer plots are observed. Note that in this treatment, Stern–Volmer plots are plots of λ_1 vs. [Q]. Equation 4 for λ_1 can be rewritten as

$$2\lambda_1 = X + Y - \{[(Y - X)^2/(Y - X)^2][(Y - X)^2 + 4k_{-e}k_e(\mathrm{Q})]\}^{1/2}$$

so that

$$2\lambda_1 = X + Y - (Y - X)\{1 + [4k_{-e}k_e(\mathrm{Q})]/(Y - X)^2\}^{1/2}$$

Under conditions where $[4k_{-e}k_e(\mathrm{Q})]/(Y - X)^2 < 1$, the following expansion holds[15]

$$2\lambda_1 = X + Y - (Y - X)\{1 + [2k_{-e}k_e(\mathrm{Q})]/(Y - X)^2 \ldots\}$$

so that

$$\lambda_1 = X - [k_{-e}k_e(\mathrm{Q})/(Y - X)] \qquad (6)$$

If the exciplex is much shorter lived than the triplet, $Y \gg X$ and eq 6 simplifies to

$$\lambda_1 = k_{\mathrm{d}'} + k_e[k_\mathrm{r}/(k_{-e} + k_\mathrm{r})](\mathrm{Q}) \qquad (7)$$

so that in eq 1 $k_\mathrm{Q} = k_e[k_\mathrm{r}/(k_{-e} + k_\mathrm{r})]$. The major condition that leads to the simplification above is $Y \gg X$ which is the basis for $[4k_{-e}k_e(\mathrm{Q})]/(Y - X)^2 \ll 1$ and $\lambda_2 \gg \lambda_1$. This condition is consistent with the experimental observation of exponential decays which requires $\lambda_2 \gg \lambda_1$.

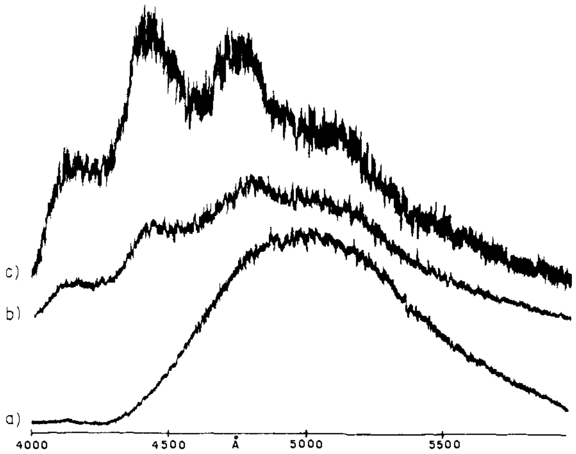


Figure 5. Time-gated emission spectra for the benzophenone-*N,N*-dimethylaniline system at 77 K in 1,1,2-trichlorotrifluoroethane. Excitation at 3371 Å. All with sampling gate of 5 μs and with time delays of (a) 3, (b) 50, and (c) 160 μs.

In cases where simplification of the expression to eq 7 does not hold, nonlinear Stern-Volmer plots ("λ plots") are observed with slope decreasing at higher [Q]. The classical example is the pyrene monomer-excimer system.[14a] More recent and closer examples are the gas-phase quenching of glyoxal triplet by ethylene,[14b] the quenching of cyanonaphthalene by olefins,[14c] and the quenching processes in the 9,10-dichloroanthracene-2,5-dimethyl-2,4-hexadiene system.[14d] In our own laboratory, we note nonlinear Stern-Volmer behavior for the self-quenching of benzil triplet in benzene and cyclohexane.[13]

A few inconsistencies exist among the data in Tables I and II that are worth noting within the context of the present discussion. The k_Q reported in Table II for the 4,4′-dimethoxybenzophenone-benzene system predicts a limiting lifetime of ca 2.6 μs in neat benzene in sharp disagreement with the observed value of 47 μs. Also, discrepancies are noted between our k_Q's determined by Stern-Volmer quenching experiments (Table II) and those obtained from lifetime measurements in neat solvents for the benzophenone-α,α,α-trifluorotoluene and benzophenone-benzonitrile systems.[2b,16] In all three examples, the k_Q's determined from lifetime measurements in neat solvents are significantly lower.

A possible explanation for this disagreement is that Stern-Volmer plots become nonlinear in these systems at very high [Q]. Thus, lifetimes obtained in neat quenching media are substantially higher than those predicted by extrapolating lower [Q] Stern-Volmer data to high [Q] (i.e., neat media).

Exciplex Emission. As mentioned earlier, we have not yet observed any emission attributable to an exciplex responsible for phosphorescence quenching. In the course of this search, we examined the very interesting benzophenone-*N,N*-dimethylaniline system. Cohen and Guttenplan[2a] report the efficient quenching of the benzophenone phosphorescence by *N,N*-dimethylaniline ($k_Q = 2.7 \times 10^9\ M^{-1}\ s^{-1}$ in benzene) at room temperature. Arimutsu and Tsubomura[17] report a new emission at 77 K from a rigid glass containing high concentrations of *N,N*-dimethylaniline. In a steady state experiment, these authors cleverly determined the new emission to be a broad, structureless band centered at 5000 Å by comparison of the total emission spectrum from the benzophenone-*N,N*-dimethylaniline system with the pure benzophenone phosphorescence spectrum. Further, these authors noted a new band in the absorption spectrum of these solutions at room temperature. This new band is red-shifted from the benzophenone n,π* absorption and they concluded that it was due to a ground state complex which was the source of the new emission band in the low temperature experiment.

Our preliminary results from the reexamination of this system confirm the observations above. We measure $k_Q = 7.2 \pm 0.6 \times 10^9\ M^{-1}\ s^{-1}$ for quenching of the benzophenone phosphorescence by *N,N*-dimethylaniline in 1,1,2-trichlorotrifluorethane. Solutions of 5×10^{-3} M benzophenone containing high concentrations of *N,N′*-dimethylaniline (2 M) showed enhanced absorption to the red of the benzophenone n,π* absorption maximum. While the new band is not red-shifted sufficiently to provide a complete absorption profile, we estimate its maximum to be near 3600 Å. At 77 K, a new structureless emission band centered near 5000 Å is nicely revealed from a series of time-gated spectra (Figure 5). The time-gated spectrum recorded with a sampling gate of 5 μs, and a time delay for the onset of the gate of 3 μs, appears to be essentially pure complex emission. From time-gated spectra recorded at longer delay times which show decreased complex emission, we estimate the lifetime of the new emission under low temperature matrix conditions to be tens of μs. Variable low temperature work shows that all emission yields tend to decrease slowly with increasing temperature with an abrupt disappearance of all emission just above 200 K. We associate this discontinuity with the matrix melt point. Pure 1,1,2-trichlorotrifluorethane melts at 232 K.

It is our opinion that the new emission results from excitation of the ground state complex. We believe that this complex is probably a π-type charge transfer complex (similar to **2**) with benzophenone and *N,N*-dimethylaniline being acceptor and donor, respectively. In the low temperature matrix, molecular motions are restricted so that the excited complex is preserved in a π-type structure and emission is noted. When the matrix softens and then melts with increasing temperature, the excited complex could either (i) dissociate into excited benzophenone and *N,N*-dimethylaniline which then would recombine as a more stable n-type exciplex with resulting quenching or (ii) undergo an intramolecular transformation into the n-type structure with resulting rapid quenching. We have no evidence that this new emission is observable *except under matrix imposed conditions.* In our opinion, it is misleading to consider this emission an example of exciplex emission within the context of the exciplexes responsible for phosphorescence quenching.

Experimental Section

Materials. The Benzophenones. Benzophenone (Oxford Organic-Zone refined) was used without further purification. **4,4′-Dimethoxybenzophenone** (Eastman Organics) was purified by several recrystallizations from ethanol and 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 Organics), **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.

4,4′-Carbonylbis(dimethyl benzoate) was prepared by conventional procedures from 4,4′-carbonylbis(benzoyl chloride), mp 132-134 °C (lit. 133-134 °C[18]), which was readily obtained from 4,4′-carbonylbis(benzoic acid), mp 360 °C dec (lit. 367-369 °C[18]) using phosphorus pentachloride. The dicarboxylic acid was synthesized as follows. A mixture of 20 g (0.96 mol) of 4,4′-dimethylbenzophenone, 140 g (0.89 mol) of potassium permanganate, and 18 cm^3 of 10% aqueous sodium hydroxide in 1 l. of water was refluxed for 3 h. The hot solution was suction filtered through filter aid and acidified with concentrated hydrochloric acid. The white suspension was suction filtered and washed several times with water. The dried product weighed 15.4 g (60%).

4,4′-Bis(trifluoromethyl)benzophenone was prepared by the Seyferth ketone synthesis.[19] A solution of 10.8 g (0.048 mol) of 4-bromo-α,α,α-trifluorotoluene in 75 cm^3 of dry tetrahydrofuran was added over 15 min to 1.17 g (0.048 mol) of magnesium metal in 55 cm^3 of dry tetrahydrofuran under a nitrogen atmosphere. The mixture was refluxed for 1.5 h and 13 g (0.48 mol) of mercuric chloride in 50 cm^3 of dry tetrahydrofuran was added dropwise at room temperature. A white precipitate formed and the mixture was refluxed for 0.5 h. The decanted solution was added dropwise at room temperature to a solution of 16.4 g (0.048 mol) of dicobalt octacarbonyl (Pressure Chemical Co., Pittsburgh, Pa.) in 100 cm^3 of dry tetrahydrofuran. The resulting solution was stirred for 1 h and concentrated *in vacuo*. The residue was extracted with 500 cm^3 of hot benzene. The benzene washing was treated with 44 g of triphenyl phosphine, stirred, and filtered. The solution was then treated with 44 cm^3 of methyl iodide, allowed to sit for 1 h, and then filtered. The benzene layer was concentrated in vacuo and the resulting solid vacuum sublimed to give 3.3 g (43%) of product, mp 107-109 °C. Infrared, ultraviolet, and NMR spectroscopic data were all consistent with the structure. Anal. Calcd for $C_{15}H_8F_6O$: C, 56.65; H, 2.53. Found: C, 57.02; H, 2.70.

4,4′-Dicyanobenzophenone was prepared by modification of a previously reported synthesis.[20] A solution of 6.9 g (0.1 mol) of sodium nitrite in 20 cm^3 of water was added to a cold (0-5 °C) solution containing 10 g (0.047 mol) of 4,4′-diaminobenzophenone (Eastman Organics, practical) and 25 cm^3 of concentrated hydrochloric acid in 100 cm^3 of water. After 15 min, the mixture was neutralized with ca. 5 g of sodium carbonate. The cold mixture was added slowly (30 min) to a cold solution of 10.2 g (0.125 mol) of cuprous cyanide and 9.8 g (0.20 mol) of sodium cyanide in 50 cm^3 of water. The mixture was allowed to slowly warm to room temperature and was then heated to bring the temperature to 50 °C. The water was removed in vacuo and the residue was continuously washed with hot toluene in a Soxhlet extractor overnight. The toluene solution was dried with anhydrous sodium sulfate, filtered, and concentrated in vacuo. The solid residue was vacuum sublimed and then recrystallized from ethanol to give 1.2 g (11%) of product, mp 157-159 °C (lit. 162 °C[21]).

Solvents. Benzene (Mallinckrodt, analytical reagent, thiophene-free) was distilled through a 60-cm glass column packed with glass beads. A center cut was taken. **Carbon tetrachloride** (Mallinckrodt, analytical reagent) was distilled through a 15-cm glass column packed with glass beads. A center cut was taken. **1,1,2-Trichlorotrifluoroethane** (Matheson Coleman and Bell, spectroquality), **trichlorofluoromethane** (Matheson Gas Products), **acetonitrile** (Burdick and Jackson), **acetic anhydride** Mallinckrodt, analytical reagent), and **methyl acetate** (Matheson Coleman and Bell, 98%) were used as received.

Quenchers. Anisole (Matheson Coleman and Bell), **toluene** (Mallinckrodt, analytical reagent), **chlorbenzene** (Mallinckrodt, analytical reagent), **methyl benzoate** (Matheson Coleman and Bell), ***α,α,α*-trifluorotoluene** (Matheson Coleman and Bell, practical), and **benzonitrile** (Matheson Coleman and Bell, practical) were purified by four distillations through a 15-cm glass column packed with glass beads. A center cut was taken after each distillation. **Diphenyl ether** (Matheson Coleman and Bell) was purified by three recrystallizations from absolute ethanol. ***N,N*-Dimethylaniline** (Matheson Coleman and Bell, free from mono) was used as received.

Sample Preparation. Solutions of the ketones and quenchers, where appropriate in the various solvents, were degassed at $<10\ \mu$ by at least six freeze-pump-thaw cycles and sealed in 1-cm^2 Pyrex cuvettes. The low temperature emission spectra were obtained on samples similarly degassed in sealed lengths of 6-mm Pyrex tubing.

Lifetime Measurements. The basic instrumentation comprising our nitrogen laser system (excitation 3371 Å) has been described previously.[4] In the self-quenching experiments, emission decays were obtained by using a moving gate in conjunction with a fixed wavelength on the sampling monochromator which was set at a wavelength near the phosphorescence maximum. Exponential decays were observed over at least two lifetimes and lifetimes were obtained from a semilogarithmic plot of intensity vs. time.

In the substituted benzene quenching experiments, the sampling monochromator was bypassed and the emission was sent through a sharp cut-off glass filter (transmission >4500 Å) (Optical Industries, Inc., Schott No. GG 395) onto the photomultiplier tube. This procedure was justified since the only emission noted over the period of the experiments is the characteristic emission of the benzophenone.

Benzophenone–*N,N*-Dimethylaniline System. UV-visible absorption spectra of separate and combined solutions of 5×10^{-3} M benzophenone and 2 M *N,N*-dimethylaniline in 1,1,2-trichlorotrifluoroethane were recorded on a Beckman Acta M VI spectrophotometer at room temperature. Time gated emission spectra of the mixture at 77 K were recorded using a sampling gate of 5 μs and delay times of 3, 50, and 160 μs. A new structureless emisson was noted at the earlier times (Figure 5). Time gated spectra were recorded at several temperatures between 77 and 200 K. The new band was observed along with the characteristic phosphorescence emission but with decreasing signal intensity as the temperature increased. All emission abruptly disappeared slightly above 200 K.

Acknowledgment. We thank the U.S. Army Research Office—Durham for support of this work.

References and Notes

(1) For example, see M. W. Wolf, K. D. Legg, R. E. Brown, L. A. Singer, and J. H. Parks, *J. Am. Chem. Soc.*, **97**, *4490* (1975).

(2) (a) J. B. Guttenplan and S. G. Cohen, *J. Am. Chem. Soc.*, **94**, 4040 (1972); (b) D. E. Schuster, T. M. Weil, and A. M. Halpern, *ibid.*, **94**, 8248 (1972); (c) J. P. Blanchi and A. R. Watkins, *J. Chem. Soc.*, *Chem. Commun.*, 265 (1974).

(3) (a) J. A. Bell and H. Linschitz, *J. Am. Chem. Soc.*, **85**, 528 (1963); (b) O. L. Chapman and G. Wampfler, *ibid.*, **91**, 5390 (1969); (c) C. A. Parker and T. A. Joyce, *Trans. Faraday Soc.*, **65**, 2823 (1969); (d) T. H. Koch and A. H. Jones, *J. Am. Chem. Soc.*, **92**, 7503 (1970); (e) C. D. DeBoer and R. H. Schlessinger, *ibid.*, **94**, 655 (1972); (f) D. I. Schuster and M. D. Goldstein, *ibid.*, **95**, 986 (1973); (g) D. I. Schuster and T. M. Weil, *ibid.*, **95**, 4091 (1973); (h) L. A. Singer, R. E. Brown, and G. A. Davis, *ibid.*, **95**, 8639 (1973).

(4) R. E. Brown, K. D. Legg, M. W. Wolf, L. A. Singer, and J. H. Parks, *Anal. Chem.*, **46**, 1690 (1974).

(5) A. Leonardt and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **67**, 791 (1963).

(6) (a) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80** 4979 (1958); (b) C. D. Richie and W. F. Sager, *Prog. Phys. Org. Chem.*, **2**, 323 (1964).

(7) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, N.Y., 1960, p 378.

(8) According to the kinetic scheme presented below based on reversible exciplex formation, an increase in charge transfer character in the exciplex could increase k_e and k_r. An increase in k_e would result from greater binding energy in the exciplex while an increase in k_r would result from increased spin–orbit coupling. For a discussion of this latter point see S. P. McGlynn, T. Azumi, and M. Komoshita, "Molecular Spectroscopy of the Triplet State", Prentice-Hall, Englewood Cliffs, N.J., 1969, p 284.

(9) From the relationship $-E(B^-/{}^3B^\bullet) = -E(B^-/B) - {}^3\Delta E_{0,0} + C$, where $E(B^-/{}^3B^\bullet)$ is the electron affinity of the ketone triplet. Since the ${}^3\Delta E_{0,0}$'s are all very close in energy, the $E(B^-/{}^3B^*)$ order will parallel the $E(B^-/B)$ order which in turn parallels the $\sigma_p{}^+$'s.

(10) A series of para-substituted trifluoroacetophenones shows a quenching order in acetonitrile for the ketone triplets with toluene: *p*-CH_3O < *p*-CH_3 < H < *p*-CF_3, *m*-CF_3. The quenching order for triplet trifluoroacetophenone with substituted benzenes is *p*-dimethoxy > CH_3O > CH_3 > *p*-dichloro > Cl > F > CF_3 > CN. These trends suggest acceptor–donor roles for the ketone triplet and aromatic quencher. H. Lam, M.S. Thesis, Michigan State University, 1975. We thank Professor P. Wagner for making these data available to us.

(11) From $IP(B^+/{}^3B^*) = IP(B^+/B) - {}^3\Delta E_{0,0} + C$. Since the ${}^3\Delta E_{0,0}$'s are all close in energy, the $IP(B^+/{}^3B^*)$ order will parallel the $IP(B^+/B)$ order which should show an inverse correlation with the $\sigma_p{}^+$'s.

(12) See A. M. North, *Q. Rev.*, *Chem. Soc.*, **20**, 421 (1966), for a discussion of diffusion-limited rates.

(13) This scheme will be discussed in a future publication on the photophysics of benzil in fluid media. T.-S. Fang, unpublished results.

(14) Similar kinetic schemes have been presented by (a) J. B. Birks, ref 7, p 403; (b) J. T. Yardley, *J. Am. Chem. Soc.*, **94**, 7283 (1972); (c) W. R. Ware, D. Watt, and J. D. Holmes, *ibid.*, **96**, 7861 (1974); (d) J. Saltiel, D. E. Townsend, B. D. Watson, and P. Shannon, *ibid.*, **97**, 5688 (1975).

(15) This expansion is of the form $(1 + X)^{1/2} = 1 + (1/2)X - (1/8)X^2 \ldots\ldots$ and is valid for $|X| < 1$.

(16) D. E. Schuster and T. M. Weil, *Mol. Photochem.*, **4**, 447 (1972), also noted that benzophenone triplet lifetimes in neat aromatic solvents were somewhat greater than lifetimes calculated from quenching results.

(17) S. Arimutsu and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, **45**, 1357 (1972).

(18) I. K. Kozinenko and A. F. Lebedev, *Vestn. Kiev Politekh. Inst., Ser. Khim.-Tekhnol.*, **2**, 54 (1966); *Chem. Abstr.*, **68**, 30210g (1968).

(19) D. Seyferth and R. Spohn, *J. Am. Chem. Soc.*, **91**, 3027 (1969).

(20) A. H. Blatt, Ed., "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1941, p 514.

(21) W. Tadros, Y. Akhnookh, and G. Azia, *J. Chem. Soc.*, 186 (1953).