

Photokinetic Studies on Benzophenone. Photocycloaddition to Ketenimines and Self-Quenching of the Benzophenone Triplet

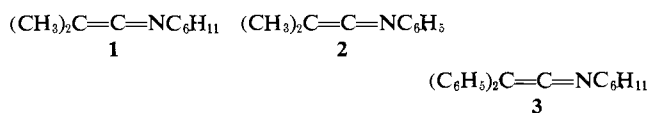
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Abstract: The kinetics of the photocycloaddition of benzophenone to three ketenimines (**1**, dimethyl-*N*-(cyclohexyl)-; **2**, dimethyl-*N*-(phenyl)-; **3**, diphenyl-*N*-(cyclohexyl)ketenimine) in benzene at room temperature were investigated by adduct quantum yield measurements in the absence and presence of di-*tert*-butyl nitroxide (DTBN), and by direct benzophenone phosphorescence lifetime measurements. It is observed that (i) the limiting quantum efficiencies for adduct formation decrease in the order $1 > 2 > 3$, and (ii) that **1**, **2**, **3** and DTBN all quench the benzophenone phosphorescence at rates close to the diffusion limit. These results are interpreted in terms of a scheme which takes into account the reversible formation of a diffusion encounter pair between the benzophenone triplet and ketenimine. For each system, it is estimated that the combined efficiencies (P_E) of adduct formation and energy transfer from the encounter pair are between 0.11 and 0.19. A modified scheme also is proposed wherein the previously mentioned processes of adduct formation and energy transfer are preceded by exciplex formation so that P_E measures the efficiency of exciplex formation. The competition between adduct formation and energy transfer from the encounter pair or exciplex governs the limiting quantum efficiencies of adduct formation which are estimated to be $\Phi = 1.00, 0.40,$ and 0.05 for **1**, **2**, and **3**, respectively. The phosphorescence lifetimes and quantum yields from benzophenone decrease with increasing benzophenone concentration in benzene solution. A self-quenching process involving ground-state benzophenone is proposed and the rate constant, k_B , of this quenching process is estimated to be $4.3 \times 10^5 M^{-1} \text{sec}^{-1}$.

Earlier work showed the synthetic potential of the photocycloaddition of aldehydes and ketones to ketenimines² which is a special case of the Paterno-Buchi reaction.³ This photochemical reaction also has served as a vehicle for the study of photophysical processes. Detailed photokinetic results have been reported on the fluorenone-dimethyl-*N*-(cyclohexyl)ketenimine system^{2c} while preliminary results have been published on the benzophenone-ketenimine reaction.^{2b}

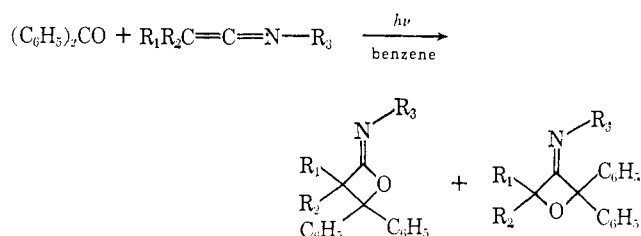
We now report a more complete photokinetic study of the cycloaddition of benzophenone triplet to three ketenimines.¹⁻³ Systematic structural change in the latter provides an opportunity to probe the partitioning between the competing processes of adduct formation and electronic deactivation of benzophenone triplet by ketenimine. Also we report phosphorescence lifetime and yield measurements for benzophenone in benzene that clearly reveal the importance of a self-quenching step.



Results

Ketenimines **1**, **2**, and **3** were prepared by dehydration of the corresponding amides.^{2b} The photoad-

ducts (α - and β -iminooxetanes)⁴ were prepared by irradiation of equimolar mixtures of benzophenone and the ketenimines in benzene (excitation between 3200 and 4000 Å). The α - and β -iminooxetane product mixtures as determined by nmr analyses of the crude photolysis mixtures were benzophenone-**1**, 100% α ; benzophenone-**2**, 40% α /60% β ; benzophenone-**3**, 100% α . In all three cases the isolated yields of photoadduct were $\geq 50\%$. These low recoveries are due, in part, to secondary photolysis of the α adducts to alkenes and isocyanates during the latter stages of the photo-reaction. Infrared analysis of the reaction mixtures carried to 25% conversion under photokinetic conditions (see below) indicates quantitative adduct formation in benzophenone-**1** and -**3**, but only 80% of the theoretical yield of adduct in benzophenone-**2** based on ketenimine disappearance. Accordingly, the rate data (based on ketenimine disappearance) for the latter were corrected for side reaction.



Photokinetic Experiments. Degassed and sealed Pyrex ampoules containing benzene solutions of 1.0 *M* benzophenone, variable concentrations of ketenimine, and with and without variable concentrations of di-

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(2) (a) L. A. Singer and G. A. Davis, *J. Amer. Chem. Soc.*, **89**, 158 941 (1967); (b) *ibid.*, **89**, 598 (1967); (c) L. A. Singer, G. A. Davis, and V. P. Muralidharan, *ibid.*, **91**, 897 (1969); (d) L. A. Singer, G. A. Davis, and R. L. Knutsen, *ibid.*, **94**, 1188 (1972).

(3) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968), and references therein.

(4) The structure proofs for the benzophenone-**1** and -**2** adducts were reported in ref 2b. The structure proof for the benzophenone-**3** α adduct appears in the Experimental Section.

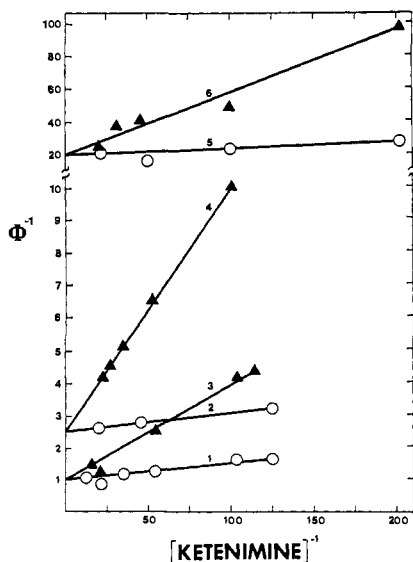


Figure 1. The dependence of the quantum yields for adduct formation on the ketenimine concentrations: (O) no DTBN added; (\blacktriangle) with 0.010 M DTBN. Ketenimine 1: curve 1, slope (m) = 0.0042 M, intercept (α) = 1.0; curve 3, $m = 0.031$ M, $\alpha = 1.0$. Ketenimine 2: curve 2, $m = 0.010$ M, $\alpha = 2.5$; curve 4, $m = 0.080$ M, $\alpha = 2.5$. Ketenimine 3: curve 5, $m = 0.0415$ M, $\alpha = 19$; curve 6, $m = 0.385$ M, $\alpha = 19$.

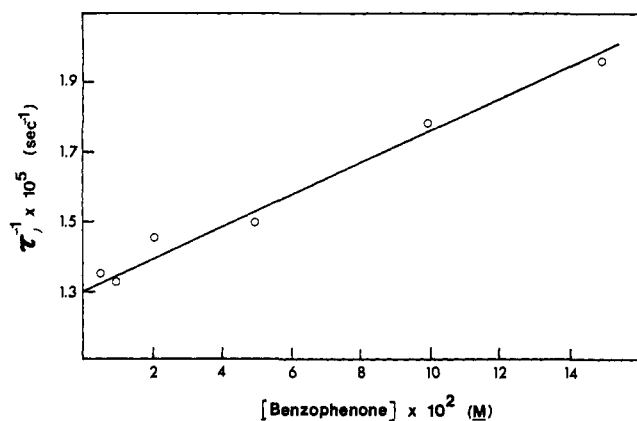


Figure 2. Concentration dependence of the lifetime of the benzophenone triplet in benzene.

tert-butyl nitroxide (DTBN)⁵ were irradiated at room temperature along with actinometer tubes, benzophenone-benzhydrol⁶ or potassium ferrioxalate,⁷ in a rotating photochemical assembly. The light from a 450-W Hanovia lamp was filtered through either Corning 7-39 or 7-51 filters. The rates of disappearance of ketenimine were followed by infrared spectroscopy from 0 to 25% reaction and were adjusted to molar conversion rates for comparison with the actinometer samples.

Based on uv absorption at 3660 Å, corrections were made for light filtering by the ketenimines where necessary. In benzophenone-1, no correction was necessary. In benzophenone-2 and -3, at the maximum ketenimine concentration (0.050 M), corrections of 9 and 14%,

(5) A. K. Hoffman, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *J. Amer. Chem. Soc.*, **86**, 639 (1964).

(6) W. M. Moore, G. S. Hammond, and R. P. Foss, *ibid.*, **83**, 2789 (1961).

(7) C. A. Parker, "Photoluminescence of Solutions," Elsevier, New York, N. Y., 1968, p 208.

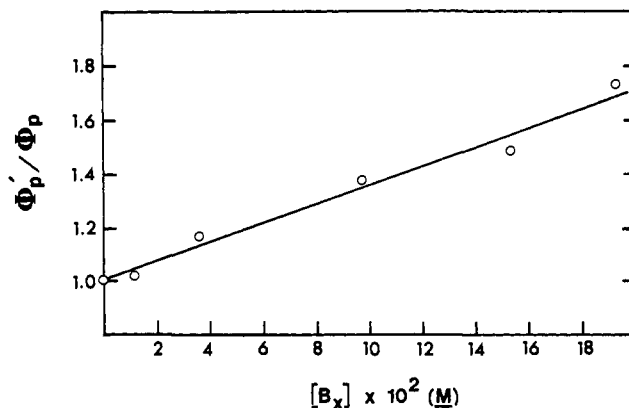


Figure 3. Concentration dependence of the benzophenone phosphorescence quantum yield.

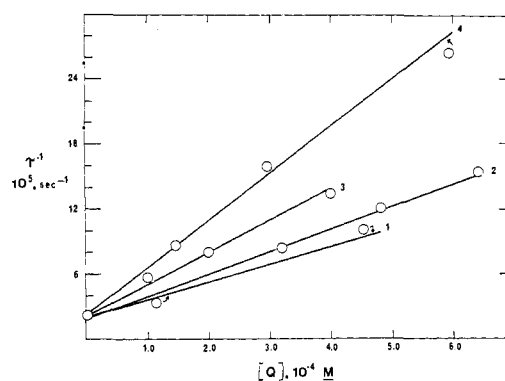


Figure 4. The dependence of the lifetime of the benzophenone phosphorescence on quencher concentration: curve 1, ketenimine 1, slope (m) = 1.7×10^9 M⁻¹ sec⁻¹; curve 2, ketenimine 2, $m = 2.1 \times 10^9$ M⁻¹ sec⁻¹; curve 3, ketenimine 3, $m = 2.9 \times 10^9$ M⁻¹ sec⁻¹; curve 4, DTBN, $m = 4.3 \times 10^9$ M⁻¹ sec⁻¹.

respectively, were made. Figure 1 shows the dependence of the reciprocal of the quantum yield for adduct formation on the reciprocal of the ketenimine concentration for the three systems.

Concentration Dependence of the Benzophenone Phosphorescence Lifetime and Yield. Phosphorescence lifetimes of benzophenone in benzene solutions at room temperature were determined using a pulsing 50-kW nitrogen laser. The phosphorescence decays of degassed samples were monitored at 4500 Å with exposure limited to 20 pulses or less from the laser. The lifetime of the phosphorescence decay was concentration dependent over the range 0.0048–0.15 M benzophenone as shown in Figure 2. Exponential decays were observed under these conditions. Similarly, the benzophenone phosphorescence yield is concentration dependent over this same range (Figure 3). These results are reproducible with benzophenone samples purified either by recrystallization or zone refining (Princeton Organics PAR Grade) so that impurity quenching is not thought to be responsible. Instead, we attribute this concentration dependence to self-quenching, *i.e.*, quenching of the benzophenone triplet by ground-state benzophenone. These results will be discussed more fully later.

Quenching of the Benzophenone Phosphorescence by Ketenimines and DTBN. Phosphorescence lifetimes of 0.10 M benzophenone in benzene at room temperature in the presence of variable concentrations of 1, 2, 3,

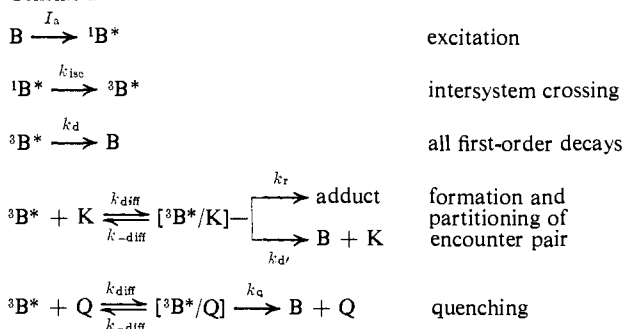
and DTBN were determined by laser flash spectroscopy as described above (Figure 4). From these data the bimolecular rate constant for quenching of the benzophenone triplet by DTBN is calculated to be $k_Q = 4.3 \pm 0.2 \times 10^9 M^{-1} \text{ sec}^{-1}$ which can be compared with a recent value of $3 \times 10^9 M^{-1} \text{ sec}^{-1}$ reported by Caldwell and Schwerzel from a benzophenone-sensitized stilbene isomerization experiment.⁸

Discussion

Benzophenone-Ketenimine Photocycloaddition Reaction. The photokinetic results indicate that the limiting quantum efficiencies for adduct formation for the benzophenone-ketenimine reaction decrease in the order $1 > 2 > 3$, while the phosphorescence quenching experiment shows that **1**, **2**, and **3** all quench the benzophenone phosphorescence almost as efficiently as DTBN ($k_Q = 4.3 \times 10^9 M^{-1} \text{ sec}^{-1}$). Thus, while the rate constants for benzophenone-ketenimine interaction are close to the diffusion limit for all three systems, the fraction of interactions that lead to adduct varies in the order $1 > 2 > 3$. We conclude that a rather efficient energy wasting process involving ketenimine can be competitive with the cycloaddition.

We propose the scheme below as an explanation for these observations. Scheme I kinetically recognizes

Scheme I



the diffusional portion of the bimolecular reactions⁹ and proposes the partitioning of a reversible encounter pair¹⁰ of benzophenone triplet and ketenimine between the competing pathways of adduct formation and deactivation.

Based on Scheme I, the expression for the reciprocal of the quantum yield for adduct formation is (see Appendix)

$$\Phi^{-1} = (1 + k_{d'}/k_r) \{ 1 + (k_d + k_Q[Q]) / (k_{diff}[K]) \} + \{ (k_d + k_Q[Q]) / (k_{diff}[K]) \} (k_{-diff}/k_r) \quad (1)$$

where

$$k_Q = k_{diff} \{ k_q / [k_{-diff} + k_q] \} \quad (2)$$

From the data in Figure 4, we calculate the rate constants for phosphorescence quenching by the ketenimines (k_K) based on the Stern-Volmer expression

$$\tau^{-1} = \tau_L^{-1} + k_K[K] \quad (3)$$

where τ_L is the limiting phosphorescence lifetime under

(8) R. A. Caldwell and R. E. Schwerzel, *J. Amer. Chem. Soc.*, **94**, 1035 (1972).

(9) See A. M. North, *Quart. Rev., Chem. Soc.*, **20**, 421 (1966), for a detailed discussion on diffusion.

(10) We use the term encounter pair, designated as [A/B], to mean the situation resulting after diffusion together of A and B so that they are in proximity suitable for reaction.

the conditions of the experiment in the absence of added ketenimine. According to Scheme I

$$k_K = k_{diff} \{ [k_{d'} + k_r] / [k_{-diff} + k_{d'} + k_r] \} \quad (4)$$

Similarly, the bimolecular rate constant for phosphorescence quenching by DTBN measured in the laser flash spectroscopic experiment, in terms of Scheme I, is given by eq 2.

Partition Factors. The partition factors $k_r\tau_{EP}$, $k_{d'}\tau_{EP}$, and $k_{-diff}\tau_{EP}$, where τ_{EP} is the lifetime of the encounter pair ($\tau_{EP}^{-1} = k_r + k_{d'} + k_{-diff}$), can be estimated. From eq 4 we obtain $k_K/k_{diff} = (k_r + k_{d'})\tau_{EP}$. The partition factors $k_r\tau_{EP}$ and $k_{d'}\tau_{EP}$ can be calculated from this expression by using the intercepts in Figure 1 ($\alpha = k_{d'}/k_r + 1$), the experimentally determined k_K 's, and $k_{diff} = 1.55 \times 10^{10} M^{-1} \text{ sec}^{-1}$ as calculated from the modified Debye equation for benzene.^{11a} Since $(k_r + k_{d'} + k_{-diff})\tau_{EP} = 1$, we can determine the last partition factor by difference. These values appear in Table I with the three partition factors being designated as P_r , $P_{d'}$, and P_{-diff} .

Table I. Experimentally Derived Rate Parameters and Estimated Partition Factors

System	Exptl parameters ^a		Partition factors (P) ^b		
	$k_{d'}/k_r^c$	$k_K, M^{-1} \text{ sec}^{-1 d}$	P_r^e	$P_{d'}$	P_{-diff}
Benzophenone-1	~0.0	1.7×10^9	0.11	~0.0	0.89
Benzophenone-2	1.5	2.1×10^9	0.056	0.084	0.86
Benzophenone-3	18.0	2.9×10^9	0.010	0.18	0.81

^a Average experimental error is $\pm 5.6\%$. ^b Maximum error in derived estimates of P_r and $P_{d'}$ is $\pm 14\%$, P_{-diff} determined by difference. ^c Photochemical experiment from $\alpha - 1$ (Figure 1). ^d Laser spectroscopic experiment, slopes (Figure 4).

Because the τ_{EP} 's for the three benzophenone-ketenimine systems may be different depending on the absolute magnitudes of the three rate constants, variations in the P 's down any one row do not necessarily reflect differences in the absolute magnitude of the rate constants for the process represented by those P 's. However, the P 's are useful in assessing the relative importance of the three processes within each benzophenone-ketenimine system.

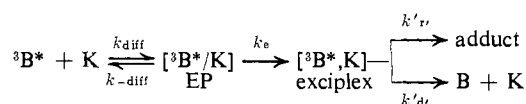
We cannot attach any significance to the apparent trend in P_{-diff} in going from **1** to **3** in Table I since the differences are within our experimental error. A comparison of these P_{-diff} values with others that are available or calculable from literature sources reveals that processes such as cycloaddition, triplet-triplet energy transfer, and quenching appear to have similar limiting P_{-diff} values in benzene.¹² In our own study, $P_{-diff} = 0.72$ for the benzophenone triplet-DTBN encounter pair as determined from eq 2, k_Q , and the calculated k_{diff} .^{11a} Wagner and Kochevar find $P_{-diff} = 0.68$ for exothermic energy transfer from valerophenone triplet to 2,5-dimethyl-2,4-hexadiene in benzene.^{11a} Yang and coworkers report that benzaldehyde triplet cyclo-

(11) Other recent discussions that kinetically separate the diffusional part of bimolecular photochemical processes are: (a) P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968); (b) T. R. Evans, *ibid.*, **93**, 2081 (1971); (c) J. A. Green, II, L. A. Singer, and J. H. Parks, *J. Chem. Phys.*, **58**, 2690 (1973).

(12) The term limiting P_{-diff} means the lower limit that seems to be found which implies an upper limit generally found for the efficiencies of competing processes.

adds to 2,3-dimethyl-2-butene in benzene with $k_r = 1 \times 10^9 M^{-1} \text{sec}^{-1}$ ¹³ from which we estimate $P_{\text{-diff}} = 0.93$ for the benzaldehyde triplet–2,3-dimethyl-2-butene encounter pair within the context of the diffusion model presented above. Thus, in benzene, the inefficiencies observed in encounter pairs involving several different photoprocesses fall in the range $P_{\text{-diff}} = 0.7\text{--}0.9$. Certainly it is possible to find photochemical reactions with inefficiencies approaching 1,¹⁴ but we are not aware of processes where $P_{\text{-diff}} < 0.6$ for [$^3\text{D}^*/\text{A}$] encounter pairs in benzene.

Possibility of Exciplex Formation. We note that while the relative importance of adduct formation and energy transfer varies greatly through the benzophenone–ketenimine series, their combined importance relative to dissociation of the encounter pair remains relatively the same (note the similarities of the $P_{\text{-diff}}$'s in Table I). An explanation consistent with this result is that the encounter pair either dissociates, or proceeds on irreversibly to an exciplex (k_e) from where the partitioning between adduct and deactivation actually occurs.¹⁵



With respect to Scheme I, eq 1 and 4, and Table I, the pertinent rate constants are $k_r \equiv k_e \{k'_r / [k'_r + k'_d]\}$ and $k_{d'} \equiv k_e \{k'_d / [k'_r + k'_d]\}$. The intercepts in Figure 1 still provide a measure of the relative rates of adduct formation and deactivation, *i.e.*, $\alpha - 1 = k'_{d'}/k'_r$. The partition factor $P_{\text{-diff}}$ is unchanged; however, the sum of the partition factors for adduct formation and deactivation becomes a measure of the partition factor for exciplex formation, $P_r + P_{d'} = P_e = k_e \tau_{\text{EP}}$. Also note that the process of exciplex formation is the process of phosphorescence quenching so that eq 4 is replaced by

$$k_K = k_{\text{diff}} \{k_e / [k_{\text{-diff}} + k_e]\} \quad (5)$$

Evans^{1b} has presented an analogous scheme for fluorescence quenching. In his scheme, a reversibly formed encounter pair ("proximity pair") proceeds on irreversibly to a complex that has charge-transfer character as indicated by an inverse correlation between quencher efficiency and quencher ionization potential.

Recently, Guttenplan and Cohen¹⁶ showed a similar relationship existed between the donor I.P. and the bimolecular rate constant for donor interaction with benzophenone triplet in benzene. From their data, they conclude that the benzophenone triplet–donor interaction has partial charge-transfer character. Interestingly, the maximum interaction rate constants

(13) N. C. Yang, R. Loesch, and D. Mitchell, *J. Amer. Chem. Soc.*, **89**, 5465 (1967). From Stern–Volmer data reported by these authors on the benzophenone–2,3-dimethyl-2-butene system, we calculate $k_r \approx 1.5 \times 10^9 M^{-1} \text{sec}^{-1}$ which gives $P_{\text{-diff}} \approx 0.90$.

(14) For example, photoreduction of benzophenone by benzhydrol in benzene at room temperature must involve a $P_{\text{-diff}}$ very close to 1 since the observed $k_r \approx 5 \times 10^6 M^{-1} \text{sec}^{-1}$ which is well below the diffusion limit, ref 6.

(15) For example, triplet-state exciplexes have been proposed by (a) A. J. Fry, R. S. H. Liu, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4781 (1966); (b) C. C. Wamser, G. S. Hammond, C. T. Chang, and C. Baylor, Jr., *ibid.*, **92**, 6362 (1970); (c) J. K. Roy and D. G. Whitten, *ibid.*, **93**, 7093 (1971), obtain direct evidence for a triplet exciplex between excited metalloporphyrins and aromatic nitro compounds.

(16) J. B. Guttenplan and S. G. Cohen, *J. Amer. Chem. Soc.*, **94**, 4040 (1972), and references therein.

they observe are for several amines where the k 's $\approx 2\text{--}3 \times 10^9 M^{-1} \text{sec}^{-1}$. These rate constants imply $P_{\text{-diff}}$'s 0.87–0.80 in our scheme above, which are very similar to what we observe in the benzophenone–ketenimine systems (Table I).

In view of the results of Guttenplan and Cohen,¹⁶ and the similar "interaction efficiencies," *i.e.*, $1 - P_{\text{-diff}}$, of amines and ketenimines with benzophenone triplet, we speculate that the proposed benzophenone triplet–ketenimine exciplex has charge-transfer character.

Consistency between the Spectroscopic and Photochemical Data. Previously, we determined the bimolecular rate constant for quenching of the benzophenone phosphorescence by DTBN as $k_Q = 4.3 \pm 0.2 \times 10^9 M^{-1} \text{sec}^{-1}$ from the flash spectroscopic experiment. A value for k_Q can be calculated independently from the benzophenone–ketenimine photochemical data and the ketenimine laser spectroscopic data. According to our modified scheme incorporating an exciplex, the quantum efficiency for adduct formation is

$$\Phi^{-1} = \alpha [1 + \{[k_d + k_Q(Q)] / [k_{\text{diff}}(K)]\} \{1 + k_{\text{-diff}}/k_e\}] \quad (6)$$

The difference between the slopes of the quenched (m_Q) and the unquenched (m) runs (Figure 1), from eq 5 and 6, is

$$m_Q - m = \alpha k_Q [Q] / k_K \quad (7)$$

Thus, for each system, k_Q can be estimated from the intercept and slope values of the photochemical data, and the k_K of the laser spectroscopic data. Taking into account the error limits in each of these experimental values, $k_Q = 5.2 \pm 0.8 \times 10^9 M^{-1} \text{sec}^{-1}$, which is within experimental uncertainty of the value determined directly by the laser experiment.

Nature of the Benzophenone Triplet–Ketenimine Deactivation Process. It is observed that as phenyl groups replace alkyl groups in the ketenimine structure, $k_{d'}/k'_r$ (or $k_{d'}/k_r$) increases (Table I). We believe that the deactivation process, at least in part, is triplet–triplet energy transfer that assumes increasing importance through the series $1 < 2 < 3$.

This trend is consistent with our rather crude estimate of the relative triplet energies of the ketenimines. The uv–visible absorption spectra shift to the red in the order $1 < 2 < 3$. Although these data reflect only the relative singlet-state energies of the ketenimines, we assume that their relative triplet-state energies parallel the former, if there are not gross differences in the ΔE_{S-T} . Unfortunately, we have observed neither fluorescence nor phosphorescence from the ketenimines so that a direct measurement of their excited-state energies has not been possible. From the $k'_{d'}/k'_r$ values, and by referencing to benzophenone, we conclude that the triplet-state energies of the ketenimines are: **1**, at least several kcal/mole > 69 ; **2**, ~ 69 kcal/mol; **3** < 69 kcal/mol.¹⁷

We cannot exclude the possibility of direct deactivation of the exciplex to ground-state species such that $[\text{B}^*\text{K}] \xrightarrow{\text{heat}} \text{B} + \text{K} + \text{heat}$. The partial charge-transfer character of the exciplex would be expected to increase spin–orbit coupling in benzo-

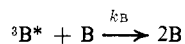
(17) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 120.

phenone and so enhance the transition $T_1 \rightsquigarrow S_0$.¹⁸ However, the trend in relative importance of k'_d through the ketenimine series is less understandable by this mechanism.

Self-Quenching of the Benzophenone Triplet. Pulsed nitrogen laser excitation of benzophenone in benzene at room temperature leads to a rapid (nsec) emission and a slower (μ sec) exponential decay which becomes nonexponential as the benzophenone concentration is increased above 0.15 M . The faster decay has been identified as prompt fluorescence¹⁹ while the slower decay is phosphorescence and E-type delayed fluorescence.^{19,20} The nonexponential behavior for the slower decay at higher benzophenone concentrations results from triplet-triplet annihilation²¹ becoming operative so that the benzophenone triplet decay, under these conditions, is a mixed first-order and second-order process, eq 8.

$$-d(^3B^*)/dt = k_1(^3B^*) + k_a(^3B^*)^2 \quad (8)$$

At the lower benzophenone concentrations, the mean lifetimes of the exponential phosphorescence decays show a dependence on the concentration (Figure 2). Impurity quenching does not seem to be the source of this dependence since these results can be reproduced with either zone-refined (Princeton Organic PAR Grade) or conventionally recrystallized benzophenone. We suggest that self-quenching of the benzophenone triplet²² is occurring such that



Accordingly, the first-order benzophenone triplet decay (k_1) is better represented as unimolecular radiative and nonradiative decays (k_d) plus a pseudo-first-order self-quenching decay (k_B) so that in eq 8, $k_1 = k_d + k_B[B]$.²³

The data in Table II provide a measure of k_B through the Stern-Volmer relationship

$$\tau^{-1} = \tau_L^{-1} + k_B[B] \quad (9)$$

where $\tau_L = (k_d)^{-1}$ is the limiting phosphorescence lifetime at high dilution. A least-squares analysis of the data indicates $\tau_L = 7.7 \pm 0.2 \mu$ sec,²⁴ and $k_B = 4.4 \pm 0.1 \times 10^5 M^{-1} \text{sec}^{-1}$.

These results are supported by the dependence of the

(18) See S. P. McGlynn, T. Azumi, and M. Kimoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969, p 284, for a discussion of the effect of charge-transfer interaction on spin-orbit coupling.

(19) R. E. Brown, L. A. Singer, and J. H. Parks, *Chem. Phys. Lett.*, **14**, 193 (1972).

(20) (a) J. Saltiel, H. L. Curtis, L. Metts, J. M. Miley, J. Winterle, and M. Wrighton, *J. Amer. Chem. Soc.*, **92**, 410 (1970); (b) P. Jones and A. R. Calloway, *ibid.*, **92**, 4997 (1970); *Chem. Phys. Lett.*, **10**, 438 (1971).

(21) (a) R. E. Brown, L. A. Singer, and J. H. Parks, *J. Amer. Chem. Soc.*, **94**, 8584 (1972); **95**, 3083 (1973); (b) A. Yekta and N. J. Turro, *Mol. Photochem.*, **3**, 307 (1972).

(22) The parameter k_B is an effective rate constant which includes the diffusive processes through the relationship $k_B = K_{EP}k_b$, where $K_{EP} = k_{diff}/k_{-diff}$ and k_b is the actual quenching rate constant for the process at the encounter pair stage.⁹

(23) A preliminary account of these results was presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., Apr 1972, Abstract ORGN-23, and also as a footnote in ref 21a. Similar observations have been reported recently by D. I. Schuster and T. M. Weil, *J. Amer. Chem. Soc.*, **95**, 4091 (1973).

(24) Other recent direct measurements of the benzophenone phosphorescence lifetime in benzene are: (a) W. D. K. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 5413 (1969), $6.5 \pm 0.2 \mu$ sec at 0.01 M ; (b) G. Porter and M. R. Topp, *Proc. Roy. Soc., Ser. A*, **315**, 163 (1970), 2.5μ sec; (c) D. I. Schuster, T. M. Weil, and M. R. Topp, *Chem. Commun.*, 1212 (1971), $10 \pm 1 \mu$ sec at 0.01 M .

Table II. Concentration Dependence of the Benzophenone Phosphorescence Lifetime and Yield in Benzene at Room Temperature

Lifetime expt		Emission yield expt	
[B], M	τ , μ sec	[B], M	$\Phi_p'/\Phi_p^{b,c}$
0.00480	7.7 ± 0.2	0.00480	(1.00)
0.0100	7.6 ± 0.1	0.0160	$1.02 \pm 3.4\%$
0.0210	6.9 ± 0.2	0.0400	$1.14 \pm 14.2\%$
0.0500	6.7 ± 0.1	0.100	$1.35 \pm 2.1\%$
0.100	5.6 ± 0.1	0.150	$1.45 \pm 6.9\%$
0.150	5.1 ± 0.0	0.200	$1.71 \pm 5.8\%$

^a Error limit refers to average of mean lifetimes of duplicate runs. Standard deviation within any individual run was $<1\%$. ^b Excitation at 3660 Å at $I_0 = 3.2 \times 10^{14}$ quanta ($\text{cm}^2 \text{sec}^{-1}$). ^c Error limit refers to average of four orientations of cuvette cells.

phosphorescence quantum yield on benzophenone concentration (Figure 3). The emission yields from benzophenone samples were measured relative to optically matched (*i.e.*, same optical density at wavelength of excitation) quinine sulfate solutions. A linear relationship between the emission yield and benzophenone concentration is observed when the data are handled in the Stern-Volmer manner. In eq 10, Φ_p'/Φ_p is the ratio of the quantum yields at two different concentrations, [B] and [B'], τ' is the lifetime at [B'], and $[B_x]$ is the reduced concentration $\{[B] - [B']\}$.

$$\Phi_p'/\Phi_p = 1 + \tau'k_B[B_x] \quad (10)$$

A least-squares analysis of the data in Figure 3 gives $(\tau'k_B) = 3.25 \pm 0.10 M^{-1}$ with $k_B = 4.23 \pm 0.13 \times 10^5 M^{-1} \text{sec}^{-1}$ by using $\tau' = 7.7 \mu$ sec at $[B'] = 0.0048 M$ (our work).

Our best estimates to date of the three rate constants responsible for the deactivation of benzophenone triplet in benzene solution at room temperature are $k_d = 1.3 \pm 0.04 \times 10^5 \text{sec}^{-1}$, $k_B = 4.3 \pm 0.1 \times 10^5 M^{-1} \text{sec}^{-1}$, and $k_a = 1.1 \pm 0.1 \times 10^{10} M^{-1} \text{sec}^{-1}$.

The self-quenching of aldehyde and ketone triplets appears to be a general phenomenon.²⁵ We note that the self-quenching rate constant for benzophenone triplet (n, π^*) is two and three orders of magnitude slower than those reported for π, π^* triplets. The elucidation of the mechanism or mechanisms responsible for self-quenching requires more definitive data than are available at this time.

Summary

(a) The benzophenone triplet-ketenimine photochemical system is described in terms of a general scheme that recognizes diffusion as a separate process. Within the context of this scheme the efficiency or inefficiency of processes originating from the encounter pair can be discussed. (b) The photochemical data reveal that benzophenone triplet-ketenimine encounter leads to competing adduct formation and deactivation. It is proposed that these two processes originate from an exciplex that has some charge-transfer character. The deactivation step is believed to be triplet-triplet energy transfer. (c) In benzene solution two deactivation processes that have been kinetically identified

(25) (a) J. A. Bell and H. Linschitz, *J. Amer. 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. Amer. 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).

for the benzophenone triplet are triplet-triplet annihilation^{21a} and self-quenching.

Experimental Section

Materials. Benzophenone, benzhydrol, and benzene were purified as previously described.^{2b} Zone-refined benzophenone (Princeton Organics PAR Grade) and quinine sulfate dihydrate (Aldrich, mol wt 782.96) were used as received. Di-*tert*-butyl nitroxide was prepared as described and purified by spinning band distillation.

Ketenimines. Ketenimines **1**, **2**, and **3** were prepared by the dehydration of the corresponding amides.^{2b} Ketenimine **3** was identical in all respects with that obtained from the previously reported diphenyldiazomethane-cyclohexyl isocyanide photolysis reaction.^{2b}

Photoadducts. The benzophenone-**1** and -**2** photoadducts were previously described. The benzophenone-**3** photoadduct was prepared as follows. A nitrogen-purged solution of 1.82 g (0.010 mol) of benzophenone and 2.75 g (0.010 mol) of **3** in 150 ml of benzene was irradiated with a 450-W Hanovia Hg lamp through a Pyrex filter at room temperature. The reaction was monitored by infrared spectroscopy by following the decrease at 2006 cm⁻¹ (disappearing **3**) and increase at 1725 cm⁻¹ (adduct). Maximum intensity of the 1725-cm⁻¹ band was observed after 20 hr irradiation. The photolysis was stopped after 27 hr when this band had decreased from its maximum value by 22%. The reaction mixture was concentrated *in vacuo* and chromatographed on a Florisil column. After eluting with 900 ml of petroleum ether, the column yielded 2.46 g (50%) of a white solid in the next 500 ml of petroleum ether, mp 114–115°. Elution of the column with 40:60 ether-petroleum ether gave 0.04 g of an oil showing a band in the ir at 2310 cm⁻¹ (isocyanate): ir (CCl₄) strong band at 1725 cm⁻¹ (>C=N-); nmr (CCl₄) δ 7.1–7.4 (multiplet), 4.0–4.4 (multiplet), 1.4–2.5 (multiplet with relative intensities 20:1:10 and assigned as phenyl H, cyclohexyl α-H, and cyclohexyl H, respectively).

Anal. Calcd for C₃₃H₃₁NO: C, 86.61; H, 6.83; N, 3.06. Found: C, 86.98; H, 6.81; N, 2.73.

It was concluded from pyrolysis and mass spectral data that the benzophenone-**3** photoadduct has the α-iminoacetane structure.^{2c} Pyrolysis at 150° in xylene for 24 hr led to disappearance of the 1725-cm⁻¹ band and appearance of a strong band at 2310 cm⁻¹ (isocyanate). The base peak in the mass spectrum was at *m/e* 332 (tetraphenylethylene).

Photokinetics (Quantum Yield Measurements). Degassed and sealed Pyrex test tubes containing 1.0 M benzophenone in benzene, variable concentrations of ketenimines, and with and without 0.010 M DTBN were irradiated on a rotating photochemical assembly ("merry-go-round") with light from a 450-W Hanovia Hg arc filtered through either Corning 7-39 or 7-51 filters. The progress of the reaction was followed by observing the disappearance of the ketenimine band in the ir at 2022, 2016, and 2006 cm⁻¹ for **1**, **2**, and **3**, respectively. The rates of ketenimine disappearance and photoadduct appearance were the same as determined by monitoring the increasing imine bands of the photoadducts near 1740 cm⁻¹.

A series of actinometer samples was simultaneously irradiated and periodically removed during each run. Benzophenone-benzhydrol actinometry⁶ was used in the benzophenone-**1** and -**2** systems and ferrioxalate actinometry⁷ was used in the benzophenone-**3** system. Several spot checks on the benzophenone-**1** and -**2** systems with ferrioxalate actinometry gave the same results as with the other actinometer method. Each quantum yield in Figure 1 represents an average of at least four measurements made over the range of 0–25% conversion of ketenimine to photoadduct with a resulting average error of ±7.5%.

Phosphorescence Quantum Yield Measurements. Relative phosphorescence quantum yields from variable benzophenone in benzene solutions were determined by measuring the emission yields relative to the emission from quinine sulfate-0.1 N sulfuric acid solutions having the same optical density at the wavelength of excitation

(3660 Å). The emission spectra were recorded on an American Instrument Co., Model 4-8212 spectrophotofluorimeter with a 250-W Hg-Xe source, and IP 21 photomultiplier. The benzophenone samples, in 1-cm square Pyrex cuvettes, were degassed to 5 μ with 6–8 freeze-pump-thaw cycles and sealed. The total phosphorescence spectra were recorded and the relative emission yields determined by mechanical integration of the area under the spectra and comparison with the similarly determined emission yields from quinine sulfate samples. The intensity of the excitation source at 3660 Å was 3.2 × 10¹⁴ quanta/(cm² sec)⁻¹ by ferrioxalate actinometry.⁷

Direct Phosphorescence Lifetime Measurements. Degassed and sealed 1-cm square Pyrex cuvettes containing variable concentrations of benzophenone with and without variable concentrations of **1**, **2**, **3**, or DTBN were irradiated with a 50-kW nitrogen laser (3371 Å, ≈6 nsec pulse width, 8 × 10¹³ quanta/pulse). The emission from the sample was monitored at 4500 Å by passing it at right angles through a 0.5-m Bausch and Lomb monochromator onto either an RCA 931 or IP 21 photomultiplier tube. The output from the latter was terminated with 50 ohms impedance in either a Tektronix 546 (50 MHz) or Hewlett-Packard 183 (250 MHz) oscilloscope and the displayed decay traces were photographically recorded. The data from these photographs were used for log *I* vs. time plots for determining the mean lifetimes of the emissions. Exponential decays were observed out to several half-lives with average errors in the mean lifetimes of ±5.6%.

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Appendix

The quantum yield for adduct formation according to Scheme I is

$$\Phi = k_r[{}^3B^*/K]/I_a \quad (A-1)$$

where *I_a* is the einsteins of light absorbed by benzophenone. Solving the steady-state equations for [¹B*], [³B*], and [³B*/K] gives

$$d[{}^1B^*]/dt = I_a - k_{isc}[{}^1B^*] = 0 \quad (A-2)$$

$$d[{}^3B^*]/dt = I_a + k_{-diff}[{}^3B^*/K] - (k_d + k_{diff}[K] + k_Q[Q])[{}^3B^*] = 0 \quad (A-3)$$

$$d[{}^3B^*/K]dt = k_{diff}[{}^3B^*][K] - \tau^{-1}_{EP}[{}^3B^*/K] = 0 \quad (A-4)$$

where $\tau^{-1}_{EP} = k_d' + k_r + k_{-diff}$.

From eq A-3 and A-4, the steady-state concentration of [³B*/K] is

$$[{}^3B^*/K] = (\tau_{EP}k_{diff}[K]I_a)/(k_d + k_{diff}[K] + k_Q[Q] - \tau_{EP}k_{-diff}k_{diff}[K]) \quad (A-5)$$

The quantum yield for adduct formation from eq A-1 and A-5 is

$$\Phi = (\tau_{EP}k_r k_{diff}[K])/(k_d + k_{diff}[K] + k_Q[Q] - \tau_{EP}k_{-diff}k_{diff}[K]) \quad (A-6)$$

so that, after substituting for $\tau_{EP} = (k_d' + k_r + k_{-diff})^{-1}$

$$\Phi^{-1} = (1 + k_d'/k_r)\{1 + (k_d + k_Q[Q])/k_{diff}[K]\} + \{(k_d + k_Q[Q])/k_{diff}[K]\}(k_{-diff}/k_r) \quad (A-7)$$

(26) J. A. Green and L. A. Singer, *Tetrahedron Lett.*, 5093 (1969).