Photochemical Study of Energy Transfer from Benzophenone Triplet to Aniline

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Summary The energy-transfer rate constant from benzophenone triplet to aniline has been shown to be independent of the energy gap between the donor and acceptor levels: the favourable geometry of the donor–acceptor pair controls the energy transfer.

THE photoreduction of carbonyl compounds by amines has received a considerable amount of attention.[1,2] During our investigation on the photoreduction of benzophenone we found that aniline did not photoreduce benzophenone, and suppressed the photoreduction of benzophenone by isopropyl alcohol. Further, if oxygen was not excluded, aniline was oxidised mostly to azobenzene.[3] Analysis (g.l.c., t.l.c., and spectra) indicated the formation of benzpinacol and acetone only on irradiation of deaerated solutions: the amount of aniline before and after the reaction remained practically the same. Our studies indicate that the suppression of photoreduction is due to deactivation of benzophenone triplet by triplet energy transfer to aniline. The u.v. absorption spectrum of a mixture of benzophenone and aniline showed no new absorption band and absorbances at various wavelengths amounted to just the sum of the calculated absorbances of aniline and benzophenone in the whole u.v. region. This precludes the formation of a ground-state molecular complex between the ketone and the amine. The triplet–triplet energy transfer rate constant, k_q between benzophenone triplet and aniline has been determined from the suppression of benzpinacol formation by aniline.

$$^3\mathrm{Ph_2CO}^* + \mathrm{Q} \xrightarrow{k_q} \mathrm{Ph_2CO} + {}^3\mathrm{Q}^*$$

Neglecting physical quenching and absorption by quencher, Beckett and Porter[4] gave the following Stern–Volmer expression for the quenching of photoreduction of benzophenone in isopropyl alcohol:

$$\frac{\Phi_0}{\Phi} = 1 + \tau k_q[\mathrm{Q}]$$

where τ is the lifetime of benzophenone triplet in isopropyl alcohol and the data of Backstrom and Sandros[5] indicate τ *ca.* $3{\cdot}7 \times 10^{-8}$ sec at 30°: Φ and Φ_0 refer to the quantum yields of disappearance of benzophenone with and without the quencher respectively. The quantum yield of disappearance of benzophenone is twice that of benzpinacol formation. In the present experiments† quantum yields of benzpinacol formation at 30° ($\lambda = 3650$ Å) for various concentrations of aniline ($1 \times 10^{-3} - 8 \times 10^{-3}$ M) were determined under identical conditions of constant intensity and time of exposure. The amounts of benzpinacol formed were gravimetrically estimated[6] after six hours of irradiation of deaerated solutions. A linear Stern–Volmer plot was obtained. The Stern–Volmer plot yielded a value of $5{\cdot}1 \times 10^9$ M^{-1} sec^{-1} for k_q for aniline when τ value of $3{\cdot}7 \times 10^{-8}$ sec was assumed. For the sake of comparison various other amines such as *p*-toluidine, 2-naphthylamine, and diphenylamine were also used as quenchers and the quenching constants are given in the Table. These amines also did not undergo any photosensitized reactions in deaerated solutions. It can be seen that the k_q values are of the order of 10^9 M^{-1} sec^{-1}, which suggests that the quenching by amines is diffusion controlled even though the triplet levels of amines lie close to that of benzophenone The value of 10^9—10^{10} M^{-1} sec^{-1} for the quenching rate constant is observed only when the acceptor triplet level is at least 2000 cm^{-1} below that of the donor in the case of hydrocarbon quenchers.[7] In the cases where the donor and acceptor (hydrocarbon) triplet levels are close the rate constant is of the order of 10^4—10^6 M^{-1} sec^{-1} only. Deactivation of benzophenone triplet by a chemical reaction even under the best circumstances (*e.g.* ketyl radical formation with isopropyl alcohol.[4]) proceeds with a rate constant not exceeding *ca.* 10^6 M^{-1} sec^{-1}. Further it is known that amines are poor triplet energy transfer reagents.[8] It is significant to note that the phosphorescence measurements[9] on biacetyl in the presence of alcohols as quenchers gave k_q values in the range of 10^2—10^3 M^{-1} sec^{-1} whereas in the case of amine quenchers like aniline and diphenylamine the order was *ca.* 10^9 M^{-1} sec^{-1}. All these facts suggest that when aromatic primary amines act as quenchers, energy transfer is the most probable cause of quenching.

Quencher	k_q, M^{-1}sec^{-1}	Triplet level of the quencher cm^{-1}
Aniline	$5{\cdot}1 \times 10^9$	24850[a]
Diphenylamine	$4{\cdot}3 \times 10^9$	24150[b]
2-Naphthylamine	$4{\cdot}8 \times 10^9$	—
p-Toluidine	$3{\cdot}2 \times 10^9$	—

(Benzophenone triplet level lies at 24250 cm^{-1})

[a] E. C. Lim and S. K. Chakrabarti, *J. Chem. Phys.*, 1967, **47**, 4726.

[b] V. L. Ermolaev, *Optics and Spectroscopy*, 1964, **16**, 383.

Quenching of the triplet state of benzophenone *via* the formation of a transient charge-transfer complex (exciplex type) as postulated by Weller[10] and Linschitz[11] does not seem significant. Formation of ionisable transient complexes between benzophenone triplet and amines is possible only with amines having low ionisation potentials (aliphatic amines)[2] and alkylarylamines capable of undergoing chemical reaction with the excited ketone.[1,12] From these considerations it is clear that an aromatic primary amine is not likely to form such a complex unless the ionisation potential is lowered by the presence of functional groups. Davidson *et al.*[1] have shown that in the former systems marked effects are noted when a nonpolar solvent like benzene is replaced by a polar solvent like acetonitrile. Further triplet state quenchers like naphthalene do not show any effect. If these can constitute diagnostic tests for exciplex formation our further results on photosensitized oxidation of aniline[3] rule out exciplex formation as a dominant mechanism of quenching. The role of exciplex may be very nominal under the experimental conditions employed.

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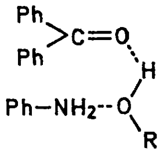
† 500 w High pressure "Hanovia" lamp; 10% $\mathrm{CuSO_4}$ solution filter; potassium ferrioxalate actinometry.

In the presence of oxygen benzophenone triplet sensitized the oxidation of aniline to mostly azobenzene.[3] The rate of sensitized oxidation was low in benzene but was significantly enhanced by the addition of small amounts of hydroxylic solvents like alcohols, acetic acid *etc.* The rates were the same in benzene and acetonitrile. Triplet state quenchers like naphthalene, phenanthrene, and 2-methoxynaphthalene substantially quenched the photosensitized oxidation of aniline and the initial rates of oxidation gave linear Stern–Volmer plots. All these facts suggest the intermediacy of aniline triplet in the sensitized oxidation and that the triplet arises out of an energy-transfer process.

It is necessary to explain the dramatic effect of small amounts of hydroxylic solvents. In the presence of isopropyl alcohol benzophenone forms a hydrogen-bonded complex. This hydrogen-bonded benzophenone might transfer its triplet energy to aniline at a fast rate. Free benzophenone triplet may be ineffective as a triplet transfer agent. Hydrogen bonded benzophenone may also possess an inviting symmetry and structure which would induce the approach of aniline in an orientation most favourable for energy transfer. Emission measurements on similar systems by Richtol and Klappmeir[13] have shown substantial enhancement of sensitized emission on addition of small amounts of alcohols and support this inference. According to Dexter's theory[14] the donor-acceptor pair must approach in one or few specified orientations in order that triplet-triplet energy transfer may occur. Such an energy transfer may be facilitated in the presence of a hydroxylic solvent.



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