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RATE CONSTANTS OF INTERACTION OF BENZOPHENONE TRIPLET WITH AMINES

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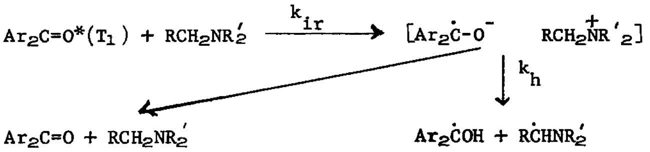
Photoreduction of aromatic ketones by amines may show moderately high quantum yields, $\varphi \sim 0.6\text{-}1.4$, as compared with a theoretical maximum value of $\varphi = 2$, and low sensitivity to diffusion controlled physical quenchers and to concentration of amines.(1,2,3) These properties led us to propose (1,2) a stepwise reaction which proceeds via rapid charge transfer interaction of ketone triplet with amine, with high rate constant k_{ir}, followed either by charge destruction and quenching or by hydrogen transfer and formation of radicals. The relative importance of these two alternatives largely determines the quantum yields, eq. 1



$$\begin{tikzcd} Ar_2C{=}O^*(T_1) + RCH_2NR'_2 \arrow[r, "k_{ir}"] & {[Ar_2\dot{C}\text{-}O^- \quad RCH_2\overset{+}{N}R'_2]} \arrow[d, "k_h"] \arrow[dl] \\ Ar_2C{=}O + RCH_2NR'_2 & Ar_2\dot{C}OH + R\dot{C}HNR'_2 \end{tikzcd} \qquad (1)$$

In photoreduction of benzophenone by amines in benzene we were able to determine k_{ir} for interaction with a primary amine, but not with secondary and tertiary amines, because of formation of light absorbing products.(1) Values of k_{ir} were obtained for photoreduction by the three classes of amines in aqueous media,(3) since the absorbing intermediates were apparently unstable in alkali. There has been a recent report on phosphorescence emission and triplet lifetimes of benzophenone at room temperature.(4) Following those procedures we have obtained and now wish to report values of k_{ir} in benzene for a variety of amines and alcohols.

Degassed solutions of 0.05 <u>M</u> benzophenone and of quencher in spectrograde, redistilled benzene in quartz cells were irradiated at 380 nm and phosphorescence intensity was measured (4) with a Farrand spectrofluorimeter. Least squares values of k_{ir} were calculated from emission intensities and the Stern-Volmer equation, 2.

$$I_0/I = 1 + \tau_0 k_{ir}[Q] \qquad (2)$$

I_0 and I are emission intensities in the absence and presence of quencher at concentration [Q]; τ_0 is the lifetime of benzophenone triplet, determined by flash irradiation with an E. G. & G. "Microflash" in the same solvent, benzene, and temperature, 31°, in the absence of quencher, 6.5×10^{-6} sec.(4) Results are summarized in Table 1. Concentration of primary and secondary aliphatic amines were 10^{-4} - 10^{-3} $\underline{M}$, of the tertiary and aromatic amines, 10^{-5} - 10^{-4} $\underline{M}$, and of the alcohols $\sim 10^{-2}$ $\underline{M}$. Some data from photoreduction studies in benzene and in aqueous media are included for comparison.

Table 1

Rate Constants for Interaction of Quenchers with Benzophenone Triplet

Quencher	k_{ir} [a] $M^{-1}sec^{-1}$	k_{ir} [b] $M^{-1}sec^{-1}$	k_{ir} [c] $M^{-1}sec^{-1}$
2-Butylamine	2.5×10^8	1.9×10^8	6.3×10^7
t-Butylamine	7.0×10^7	-	-
N-Methyl-2-butylamine	1.4×10^9	-	1.6×10^8
Triethylamine	2.3×10^9	-	6.0×10^8
p-Cyanodimethylaniline	2.0×10^9	-	-
Dimethylaniline	2.7×10^9	-	-
p-Methyldimethylaniline	4.3×10^9	-	-
2-Propanol	1.8×10^6	1.7×10^6	1.7×10^6
Benzhydrol	7.5×10^6	1.4×10^7	-

[a] From emission intensities

[b] From quenching by naphthalene of photoreduction, based on $k_q = 6.3 \times 10^9$ $M^{-1}sec^{-1}$, ref. 4; 2-butylamine, ref. 1; 2-propanol, ref. 5; benzhydrol, ref. 6.

[c] Rate constants for interaction with triplet of 4-benzoylbenzoate in an aqueous medium, ref. 3.

2-Butylamine shows a value of k_{ir}, from its effect as a quencher of the phosphorescence emission intensity of benzophenone triplet, which is high, 2.5×10^8 $\underline{M}^{-1}sec^{-1}$, and is similar to that found previously, $k_{ir} = 1.9 \times 10^8$ $\underline{M}^{-1}sec^{-1}$, by an entirely different method, from the effect of naphthalene as a diffusion controlled quencher of photoreduction of benzophenone by 2-butylamine.(1) The alcohols, 2-propanol and benzhydrol show much lower rate constants for quenching of emission, which are similar to those obtained from naphthalene quenching of photoreduction by these alcohols.(5,6) These results support the method and its application to the amines which we have not been able to study by photoreduction in benzene.

t-Butylamine, which is a very inefficient photoreducing agent,(7) $\varphi \sim 0.15$, is an efficient quencher of emission, with k_{ir} substantially greater than those of the alcohols, which are of course efficient photoreducing agents. Interaction of triplet ketone with the N-electrons of t-butylamine, eq. 1, is somewhat less rapid than with 2-butylamine, perhaps for steric reasons, but, because of absence of α-hydrogen, charge destruction and quenching follow, k_e. Abstraction of hydrogen from the methyl groups may not be assisted by a heteroatom and presumably would have the low rate constant of a direct abstraction.

The secondary and tertiary aliphatic amines, N-methyl-2-butylamine and triethylamine, show higher rate constants for quenching of emission. The increasing order of reactivity lies in the order of decreasing ionization potentials,(8) consistent with the charge transfer mechanism, eq. 1. The rate constant for interaction of the tertiary amine with the triplet of benzophenone is 0.4 that of a diffusion controlled process and about two orders of magnitude greater than that for interaction with the less reactive triplets of fluorenone (9) and p-aminobenzophenone.(2) Dimethylaniline and the two p-substituted derivatives also show very high rates of interaction with the triplets consistent with their low ionization potentials and with the low sensitivity of photoreduction by such compounds to quenching by naphthalene.(10) The electron withdrawing cyano group leads to lower k_{ir}, while the electron donating methyl group increases k_{ir}, effects consistent with the charge transfer mechanism, eq. 1. The rate constant for p-methyldimethylaniline is ~ 0.7 that of a diffusion controlled process.

The rate constants for the aliphatic amines and alcohols may be compared with those obtained for interaction of these compounds with the triplet of 4-benzoylbenzoate ion in aqueous media(3), $k_{ir}{}^{c}$. The value of k_{ir} for the triplet of 4-benzoylbenzoate with 2-propanol in the aqueous medium was essentially the same as that for interaction of benzophenone triplet with 2-propanol in that medium, indicating that the two ketone triplets have similar reactivity.(3) It is also the same as that for interaction of benzophenone triplet with 2-propanol in benzene, $k_{ir}{}^{a}$ and $k_{ir}{}^{b}$, Table 1, indicating that 2-propanol has similar reactivity towards the triplets in benzene and in the aqueous medium. However the amines had higher rate constants for interaction with triplets in benzene than in aqueous medium by factors varying from 4 to 9. While this effect may appear small, one might have anticipated that it would be in the reverse direction, since the interactions develop charge. It may be that hydrogen bonding in solvation of the amines by water renders more difficult attack of the ketone triplet on the N-electrons.

While quenching of emission due to interaction of benzophenone triplet with the other amines is accompanied by efficient photoreduction, the interaction with t-butylamine merely quenches, and t-butylamine may act as a retarder of photoreduction. Photoreduction of 4-benzoybenzoate by 2-propanol in aqueous alkali was retarded by presence of small concentrations of t-butylamine. From the effect of concentration of the amine on rate of photoreduction the ratio $k_{ir}(t\text{-BuNH}_2)/k_{ir}(2\text{-PrOH})$ was obtained, ~ 11. This corresponds to $k_{ir}(t\text{-BuNH}_2) \sim 1.9 \times 10^7$, about one-fourth that in benzene, consistent with the other data in Table 1.

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