A Study of the Effect of Quenchers upon the Photoreduction of Benzophenone by Amines and Alcohols

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IT has been previously suggested[1] that the first step in the photoreduction of carbonyl compounds by amines is electron donation from the nitrogen atom to the excited carbonyl group. Evidence[2,3] has recently been presented in favour of this mechanism.

We have investigated the effect of physical quenchers upon the photoreduction of benzophenone by amines and alcohols. Values for the ratio k_q/k_r (where k_q = rate of quenching and k_r = rate of hydrogen abstraction) were obtained by measuring the change in quantum yield with change in concentration of the quencher.[4,5]

The reduction of benzophenone by *NN*-dimethylaniline and *N*-methydiphenylamine is remarkably insensitive to the addition of naphthalene ($k_q/k_r < 10$). Ferric acetylacetonate quenched reduction by *NN*-dimethylaniline measurably ($k_q/k_r = 40$) as did ferric dibenzoylmethanate ($k_q/k_r = 330$). Both these ratios are considerably lower than those obtained by Hammond[6] (k_q/k_r 540, 3,400 respectively) for the quenching of the photoreduction of benzophenone by diphenylmethanol. In both the reduction by the amine and alcohol, the relative quenching efficiencies of the chelates are about the same. Naphthalene, a quencher of benzophenone triplets of similar efficiency to ferric acetylacetonate,[5] fails to bring about appreciable quenching, suggesting that the two chelates quench by a similar mechanism, which is different from the mechanism for naphthalene. The lower k_q/k_r values obtained with amine as reductant are not surprising if there is electron transference from the nitrogen atom to the electron-deficient oxygen atom of the excited carbonyl group, since the concentration of "free" excited carbonyl compound will be much lower in this system. As a consequence of this process, amines which do not contain transferable hydrogens, *e.g.* triphenylamine, should act as quenchers. Quenching of the reduction of benzophenone by diphenylmethanol in the presence of triphenylamine and also tri-*p*-tolylamine was studied. In benzene solution the values of k_q/k_r were found to be 44 and 525 respectively. Bäckström and Sandros have previously reported[7] that triphenylamine is an inefficient quencher of biacetyl phosphorescence in benzene solution. The greater quenching ability of tri-*p*-tolylamine is not surprising, if electron transfer occurs, since its radical-cation is more stable than that of triphenylamine.[8] Other examples of amines acting as quenchers for the excited carbonyl group have been previously noted.[9] The quenching efficiency of triphenylamine was found to be dramatically increased by the use of acetonitrile as solvent (k_q/k_r 620). A similar solvent effect has been found[10] by Leonhardt and Weller for the quenching of the fluorescence of perylene by amines. They also showed, by flash spectroscopy, that electron donation from the amine to the excited perylene, leading to the formation of the perylene mono-anion-radical, is favoured by the use of dipolar aprotic solvents.

There appear to be a number of differences between the photoreduction of benzophenone by aliphatic and alkylaryl amines. The reduction by [1-^{2}H]cyclohexylamine shows[3] a small kinetic isotope effect whereas benzylic and methyl C–H bonds of alkylarylamines have about the same reactivity.[2] Naphthalene has been found[3] to quench reduction by 2-butylamine measurably, but not reduction by *NN*-dimethylaniline. It is possible that reduction by amines of high ionisation potential (*e.g.* primary, secondary and perhaps tertiary aliphatic amines), does not involve formation of an intermediate $R_3\overset{+\cdot}{N}\ \overset{-}{O}\text{–}\dot{C}R_2$, but instead, a transition state in which some electron transfer and C–H bond breaking occurs. Amines with lower ionisation potential (*e.g.* alkylarylamines) are more likely to form such an intermediate, but if they do not, their transition state will be different in that much more electron transfer and less C–H bond breaking will occur.

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