

PHOTOREDUCTION OF AMINO BENZOPHENONES. EFFECTS OF
SOLVENT ON INTERSYSTEM CROSSING.

by Saul G. Cohen, Martin D. Saltzman and Joseph B. Guttenplan

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154

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p-Aminobenzophenone, PAB, is photoreduced very inefficiently, or not at all, by alcohols (1,2) and primary amines, (2) while it is photoreduced by triethylamine. (2) The efficiency increases when the amine is diluted with cyclohexane, $\phi \sim 0.6$ at 0.1-1.0 M tertiary amine in cyclohexane, but the photoreduction fails when the amine is diluted with a polar solvent, acetonitrile. (2) Fluorenone is also not photoreduced by alcohols, while it is photoreduced by amines, (3) $\phi \sim 0.1$. Photoreduction by triethylamine also becomes much more efficient in dilute, ~ 0.1 M, solution of the amine in cyclohexane, $\phi \sim 0.9$, and less efficient when the amine is diluted with a 2-propanol or with acetonitrile. (3) These results had been attributed to formation of an unreactive charge transfer (CT) or π, π^* triplet from PAB (1,2) and an unreactive π, π^* triplet (4) from fluorenone in the more polar media, (2) and formation of chemically reactive triplets with n, π^* character in the non-polar media. (1,2) Other causes for these effects have since been shown for fluorenone: neat triethylamine may quench the excited singlet (5,6), and the polar solvents, 2-propanol and acetonitrile, lead to decreased intersystem crossing as indicated by increased fluorescence and decreased yields of triplets. (7) We now wish to report that failure of PAB to be photoreduced by or in the polar solvents results from essentially complete absence of intersystem crossing, as indicated by study of isomerization of trans-stilbene.

Solutions of the ketones and stilbene in the several solvents were degassed and irradiated for 4 minutes in Pyrex under argon on a turntable with a G.E. H-85-A3 lamp, filtered through Corning 0-52 windows. Analyses for

trans and cis stilbene were made by glpc on an 8 ft 20% Apiezon L column. Rates of isomerization of stilbene were obtained for simultaneous irradiation of solutions of the aminobenzophenones and of benzophenone in the same solvent, Table 1. Relative rates of isomerization were the same when irradiation was carried out at 366 nm with a monochromator.

Table 1

Effects of solvent on isomerization of trans-stilbene, St, in irradiation of solutions of para-aminobenzophenone, PAB, meta-aminobenzophenone, MAB, ortho-aminobenzophenone, OAB, and benzophenone, B.

| Ketone | Solvent | St. isom., AB ^h M / hr | St. isom., B ^j M/hr |
|---------|--------------------------------|--------------------------------------|-----------------------------------|
| PAB a,b | 2-PROH | < 0.0001 | 0.012 ^k |
| PAB a,b | CH ₃ CN | 0.0006 | 0.010 |
| PAB a,b | C ₆ H ₆ | 0.0045 | 0.011 |
| PAB a,b | C ₆ H ₁₂ | 0.0032 | 0.011 |
| MAB c,d | 2 PrOH | < 0.0001 | 0.012 ^k |
| MAB c,d | CH ₃ CN | 0.0010 | 0.0087 |
| MAB c,d | C ₆ H ₆ | 0.0035 | 0.0093 |
| MAB e,d | C ₆ H ₁₂ | 0.0053 | 0.0093 |
| OAB f,d | 2 PrOH | < 0.0001 | 0.012 ^k |
| OAB c,g | C ₆ H ₆ | < 0.0001 | 0.0093 |

a. 0.002 M ketone. b. 0.005 M trans-stilbene. c. 0.005 M ketone.
 d. 0.002 M trans-stilbene. e. 0.003 M ketone. f. 0.01 M ketone.
 g. 0.05 M trans-stilbene. h. aminobenzophenones. j. 0.05 M benzophenone,
 0.002 M trans-stilbene, irradiation period 2 minutes. k. corrected for
 photoreduction.

The data indicate that irradiation of benzophenone in the several solvents led to essentially the same rate of isomerization of stilbene, 0.011 M hr⁻¹. Under these conditions benzophenone was photoreduced by 2-butylamine at a rate of 0.030 M hr⁻¹, with quantum yield 1.2. This corresponds to a rate of triplet formation of 0.026 M hr⁻¹ and indicates a quantum yield of

isomerization of stilbene ~ 0.4 in agreement with reported data. (8) Trans-stilbene, an efficient quencher of PAB triplet (2) was isomerized during irradiation of PAB in the hydrocarbons at a rate about one third that during irradiation of benzophenones, indicating a substantial but lower yield of triplet from PAB. This corresponds to the substantial efficiency of photo-reduction of PAB by triethylamine in hydrocarbons. In irradiation of PAB in 2-propanol essentially no isomerization of stilbene was found, indicating that intersystem crossing fails, and the absence of photoreduction results not because of a chemically unreactive CT triplet but from absence of triplet, at least of triplet which may isomerize trans-stilbene. It may be that in cyclohexane the n, π^* singlet and triplet are the states of lowest energy, and the CT triplet has intermediate energy, allowing rapid intersystem crossing between unlike states (1). In 2-propanol the CT singlet and triplet levels may be below the n, π^* states and intersystem crossing between the like CT states is slow.

It is conceivable that a triplet is formed and is deactivated, and in effect is quenched by the alcohol. In PAB-acetonitrile an intermediate extent of isomerization is found, about 0.06 that with benzophenone. The quantum yield for reduction of 0.0004 M PAB in 0.04 M triethylamine in acetonitrile is however very low, $\sim 6 \times 10^{-5}$, indicating that the triplet which is formed has exceedingly low reactivity, perhaps due to CT character in the polar solvent. Fluorenone with its π, π^* triplet, shows substantial activity in acetonitrile. (5)

Irradiation of meta-aminobenzophenone, MAB, also led to no isomerization of stilbene, in 2-propanol, to about half that of the benzophenone in the hydrocarbons, and to an intermediate yield in acetonitrile. However this triplet has relatively low reactivity, even with tertiary amine in hydrocarbon. ortho-Aminobenzophenone, OAB, led to no isomerization of stilbene, and to no observed triplet either in 2-propanol or in benzene, because of quenching interactions of the excited carbonyl with the ortho-amino group.

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