Tetrahedron Letters No.26, pp. 2125-2128, 1969. Pergamon Press. Printed in Great Britain.

PHOTOREDUCTION OF FLUORENONE BY AMINES. EFFECTS OF MEDIUM ON INTERSYSTEM CROSSING

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(Received in USA 7 April 1969; received in UK for publication 1 May 1969)

Fluorenone is not photoreduced by 2-propanol or by cyclohexane, and is photoreduced by triethylamine.(1) The quantum yield rises from 0.094 in neat triethylamine to 0.37 in 1 M triethylamine and to 0.92 in 0.2 M triethylamine in cyclohexane.(1) The lower quantum yields at high amine concentrations result from quenching of the excited singlets by the amine. (2,3) Fluorenone is essentially not photoreduced by 1 M triethylamine in 2-propanol and by 0.1 M triethylamine in acetonitrile.(1) We wish to report that less efficient photoreduction in polar media is due to decreased rates of intersystem crossing to triplets.

Solutions were degassed and irradiated in Pyrex under argon on a turntable with a G. E. H-85-A3 lamp. In studies of isomerization of stilbene the light was filtered through Corning 0-52 windows. Analyses for fluorenone were made from the absorbance at 380 nm. Analyses for trans and cis stilbene were made by vpc on a 6 ft 10% carbowax 20 M column. Quantum yields for photoreduction were determined as described previously. (1) Quantum yields of fluorescence were determined on a Farrand Mark I spectrofluorimeter.

Quantum yields were determined for photoreduction of 0.005 M fluorenone by 0.005 M triethylamine in solvents of varied composition, and for fluorescence of fluorenone in the several solvents. The photoreductions were quenched by 0.002 M trans-stilbene and the rates of conversion of trans to cis stilbene were followed. Results are summarized in Table I.

Table I

Effects of Medium on Photoreduction of 0.005 M Fluorenone by 0.005 M Triethylamine.

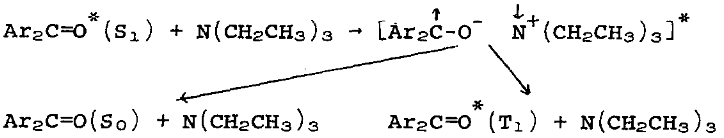
Solvent	Photored.	Stilbene, t→c	Fluorescence[a]	
	φ	M hr^{-1}	$\varphi x10^3$	λ_{max}(nm)
Cyclohexane, C_6H_{12}	0.23	0.011	1.2	460
$C_{16}H_{12}$ + 0.012 M CH_3CN	0.24	0.011	1.4	463
C_6H_{12} + 0.055 M CH_3CN	0.33	0.011	1.6	463
C_6H_{12} + 0.25 M CH_3CN	0.30	0.012	3.4	473
CH_3CN	0.19	0.0060	114.	508
$(CH_3)_2CHOH$	0.028	0.0012	16.	522

[a] Determined in the solvent, column 1, with no triethylamine present.

Since the quantum yield for photoreduction of fluorenone by 0.1-0.2 M triethylamine in cyclohexane is > 0.9, the intersystem crossing yields must also be high in 0.005 M triethylamine in cyclohexane. The observed rate of isomerization of trans-stilbene corresponds to quenching (4) of this high yield of triplet. Low concentrations, 0.012-0.25 M, of acetonitrile do not affect the rate of isomerization of stilbene, and thus do not affect the yields of triplet, while the quantum yields of photoreduction rise from ~ 0.2 to ~ 0.3. The acetonitrile may increase k_r, the rate constant for interaction of the ketone triplet with the amine. This is consistent with the charge-transfer mechanism for photoreduction by amines. (5)

In neat acetonitrile the quantum yield for photoreduction by 0.005 M triethylamine and the rate of isomerization of the stilbene both decrease about 45% from their maximum values, while the fluorescence quantum yield rises 100 fold. This indicates lower rate constant for intersystem crossing, k_{isc}, in this dipolar solvent. In neat 2-propanol the quantum yield for photoreduction by 0.005 M triethylamine (6) and the rate of isomerization of stilbene both fall to about 12% of their values in cyclohexane, indicating that k_{isc} has been decreased to this extent in the alcohol. The excited singlet may form a complex with 2-propanol, (7) and this may increase radiationless decay and lead to the intermediate yield of fluorescence. The excited singlet is (7) π,π^* and thus the lowest triplet is π,π^*; T_2 may be n,π^* and intersystem crossing, $S_1 \rightarrow T_2$, may be very rapid when T_2 lies below S_1.(8) In acetonitrile and 2-propanol the S_1 energies are decreased, as indicated by longer wavelengths for the fluorescence maxima, and in polar solvents, n,π^* triplets are destabilized. (9) The T_2 state may be above S_1 in these media and lead to low k_{isc}.

Isomerization of trans to cis-stilbene is also observed in the quenching of photoreduction of fluorenone in neat triethylamine. The rate of photoreduction of 0.11 M fluorenone by neat triethylamine was decreased from 5.8×10^{-3} M hr^{-1} to 3.7×10^{-3} M hr^{-1} by 0.078 M trans-stilbene. In the process cis-stilbene was formed at a rate of 0.64×10^{-3} M hr^{-1}. This isomerization of stilbene is not due to interaction with excited singlet fluorenone, since quenching of this singlet by triethylamine is diffusion controlled, or nearly so (2,3), and the amine is present in 100 fold excess over the stilbene. The trans-stilbene can compete with the amine for triplet since its quenching of the triplet is diffusion controlled, or nearly so, (4) while the rate constant for interaction of the triplet with the amine is two orders of magnitude less, (1) 1.7×10^7 M^{-1} sec^{-1}. Hence a substantial part of the photoreduction by neat amine, quenched by stilbene, proceeds via the fluorenone triplet. The triplet may be formed in neat triethylamine *via* a singlet fluorenone-triethylamine charge transfer complex, (10) eq. 1.



$$Ar_2C{=}O^*(S_1) + N(CH_2CH_3)_3 \rightarrow [Ar_2\overset{\uparrow}{C}{-}O^- \; \overset{\downarrow}{N}^+(CH_2CH_3)_3]^*$$

$$\swarrow \qquad \searrow$$

$$Ar_2C{=}O(S_0) + N(CH_2CH_3)_3 \qquad Ar_2C{=}O^*(T_1) + N(CH_2CH_3)_3 \qquad (1)$$

Fluorenone triplet may also be formed in 2-propanol by sensitization, by energy transfer from excited benzophenone, and undergo photoreduction (11).

Trialkylamines are efficient photoreducing agents for the so-called unreactive ketones which are not photoreduced by alcohols. (1,5a,c) The amines effect photoreduction *via* a charge-transfer interaction with triplets which leads to partial quenching and efficient reduction, eq. 2.

$$\begin{tikzcd}[column sep=small] Ar_2C{=}O^*(T_1) + N(CH_2CH_3)_3 \arrow[r] & {[Ar_2C{-}O^- \quad N(CH_2CH_3)_3]^*} \arrow[dl] \arrow[d] \\ Ar_2C{=}O(S_0) + N(CH_2CH_3) & Ar_2\dot{C}OH + CH_3\dot{C}HN(CH_2CH_3)_3 \end{tikzcd} \qquad (2)$$

Acknowledgement. This work is supported by the National Science Foundation, GP-9247 and the Atomic Energy Commission, AT(30-1)2499).

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