The Photoreactions of Aromatic Hydrocarbons in the Presence of Amines

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Summary Irradiation of benzene solutions of anthracene and acenaphthylene containing tertiary amines gives photodimers, whereas acetonitrile solutions give photoreduction: these results are interpreted in terms of excited charge transfer complex and radical ion formation.

WELLER[1] and others[2] have shown that a number of aromatic hydrocarbons, in their lowest excited singlet state, react with amines of low ionisation potential in non-polar solvents to give excited charge transfer complexes with consequent quenching of the fluorescence of the hydrocarbon. The use of aprotic polar solvents leads to radical ion formation.[1] Both types of intermediates have been postulated in the photoreactions of carbonyl compounds with amines,[3] sulphides,[4] phosphites,[5] and phosphines.[5] Olefins, such as stilbene, are photoreduced by amines:[6] I describe some similar reactions in which the role of excited charge transfer complexes and radical ions has been determined.

The products obtained by irradiating anthracene† or acenaphthylene in the presence of triethylamine and of *NN*-dimethylaniline in both benzene and acetonitrile solution are shown in the Table. Acenaphthylene is known[7] to produce both *cis* and *trans* photodimers from the singlet and triplet state respectively and therefore some indication of the role of the triplet state in these reactions can be obtained.

Products obtained from the photoreactions of anthracene and acenaphthylene with amines

Hydrocarbon	Amine	Solvent	Products isolated
Anthracene	n-Butylamine	Benzene	Anthracene photodimer
Anthracene	n-Butylamine	Acetonitrile	Anthracene photodimer
Anthracene	*NN*-Dimethylaniline	Benzene	Anthracene photodimer
Anthracene	*NN*-Dimethylaniline	Acetonitrile	9,10-Dihydroanthracene, tetrahydrobianthryl, aminated anthracene
Anthracene	Triethylamine	Benzene	Anthracene photodimer, small amount of tetrahydrobianthryl
Anthracene	Triethylamine	Acetonitrile	9,10-Dihydroanthracene, tetrahydrobianthryl, aminated anthracene
Anthracene	Triethylamine	None	Anthracene photodimer, 9,10-dihydroanthracene, tetrahydrobianthryl
Acenaphthylene	*NN*-Dimethylaniline	Benzene	*cis* and *trans* Acenaphthylene photodimers (yields in the ratio 1 : 1)
Acenaphthylene	*NN*-Dimethylaniline	Acetonitrile	Acenaphthene and *cis* photodimer
Acenaphthylene	Triethylamine	Benzene	*cis* and *trans* Acenaphthylene photodimers (yields in the ratio 1 : 0·72)
Acenaphthylene	Triethylamine	Acetonitrile	Acenaphthene and *cis* photodimer
Acenaphthylene	Triethylamine	Neat	*cis* and *trans* Acenaphthylene photodimers (yields in the ratio 1 : 1·3)

Reactions in benzene: 0·1 M-hydrocarbon and 1 M-amine: in acetonitrile 0·05 M-hydrocarbon and 0·5 M-amine. Reactions in neat triethylamine; 0·1 M-hydrocarbon.

The photodimerisation of anthracene in benzene undoubtedly occurs *via* the singlet state of the hydrocarbon (Figure; Pathway a).[8] Such solutions exhibited fluorescence characteristic of anthracene which indicates that not all the

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† A publication (C. Pac and H. Sakurai, *Tetrahedron Letters*, 1969, 3829) describing the photoreactions of anthracene with *NN*-dimethylaniline has appeared since this publication was submitted.

anthracene singlets are quenched. Benzene solutions of anthracene and triethylamine, in the same molar ratio as was used in the irradiation of anthracene in neat triethylamine, also exhibited fluorescence characteristic of anthracene and formation of the photodimer in this reaction probably occurs *via* Pathway a. The relatively high yield of the *trans*-acenaphthylene photodimer compared with that of the *cis*-photodimer in the reactions of acenaphthylene with the amines in benzene solution and in neat triethylamine indicates that although the singlet state is being partially quenched, there is an enhanced yield of acenaphthylene triplets. Their most logical mode of formation is by dissociation of the excited charge transfer complex (Figure, Pathway b). The photoreduction of anthracene by neat triethylamine, and run in benzene, is taken as occurring *via* the excited charge transfer complex (Figure, Pathway c) since the dielectric constants of the solvents are not high enough to promote radical ion formation and therefore reduction *via* these intermediates is precluded.

The photoreduction of both anthracene and acenaphthylene by the tertiary amines in acetonitrile solution undoubtedly occurs via the radical ions (Figure, pathway d). It has been previously shown that interaction of hydrocarbon such as anthracene in its lowest excited singlet state with amines of low ionisation potential in solvents of high dielectric constant, gives radical ions spontaneously.[1] Formation of reduction products of acenaphthylene via the triplet state is most unlikely since in the reaction in which triplets are known to be formed (*e.g.* in neat triethylamine), reduction did not occur. Furthermore, the non-formation of *trans*-acenaphthylene photodimer in the reactions run in acetonitrile would seem to be good evidence that recombination of the radical ions to give triplet state hydrocarbon does not occur to any appreciable extent.

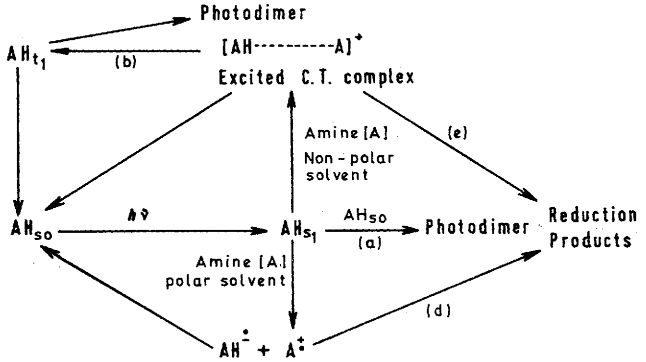

FIGURE. AH = *Aromatic hydrocarbon*: A = *amine which quenches fluorescence of* AH.

The inability of n-butylamine to photoreduce anthracene in acetonitrile solution was shown, by studying its effect upon the fluorescence of anthracene in this solvent, to be due to the fact that it does not interact with anthracene in its singlet state. Furthermore the fact that anthracene did not undergo any photoreduction in either benzene or acetonitrile solutions of n-butylamine indicates that triplet anthracene does not abstract hydrogen.

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