Photochemical Study of Interaction of Excited Anthracene with Amines

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Summary Rate constants for deactivation of the first excited singlet state of anthracene by amines in benzene have been determined from data for the formation of bianthracenyl.

THE lowest excited singlet states of polynuclear hydrocarbons like anthracene ($^1A^*$), pyrene *etc.* have been shown to interact with amines of low ionisation potentials to give transient charge-transfer complexes (exciplexes) which ionise in polar media.[1,2] While *NN*-dialkylanilines quench the hydrocarbon emission and additionally produce new emissions characteristic of the exciplex, aniline[2] and aliphatic primary amines[3] quench hydrocarbon emission without producing any new emission. As part of our general study of the photochemistry of anthracene we have investigated the effect of amines on the photodimerisation of anthracene. According to Bowen's mechanism[4] the bimolecular interaction between $^1A^*$ and A leads to dimer formation. We found that amines suppressed dimer formation owing to quenching of $^1A^*$. From Bowen's mechanism the following Stern–Volmer equation can be written:

$$\theta_0/\theta = 1 + \tau k\ (\mathrm{D})$$

where θ and θ_0 refer to quantum yields of dianthracene formation with and without amines respectively, τ is the lifetime of the excited state of anthracene, and k is the rate constant of deactivation of $^1A^*$ by the added amine (D). We found linear Stern–Volmer plots for anthracene solutions in benzene (0·02M) with amines (0·005—0·02M). Higher amine concentrations caused deviations. Irradiations were done ($\lambda = 3650$ Å) at 30° C under conditions identical to those described earlier.[6] Disappearance of anthracene was followed by measuring the absorbance of the solutions at 3600 Å. k values were obtained using a mean value of $\tau = 4{\cdot}1 \times 10^{-9}$ s (ref. 5) (Table). After irradiation, there was no change in the amine concentrations (v.p.c.), thus precluding chemical reaction involving amines, as shown previously.[7,8] The quenching efficiency was in the order: dimethylaniline $\sim$ diethylaniline $>$ n-butylamine $>$ ethanolamine. Strong exciplex formation is favoured by the low I.P. of the amine and a good overlap between the highest filled amine orbital and lowest vacant orbital of the excited state of the hydrocarbon. The quenching efficiencies suggest that exciplex formation is the significant factor in quenching.

TABLE

Amine	$k \times 10^{-9}$ ($\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$)	I.P. of the amine	% Suppression dimerisation by amine of conc. (0·015M)
NN-Dimethylaniline	6·5	7·14[a]	28·5
NN-Diethylaniline	6·1	6·67[a]	26·5
n-Butylamine	2·5	8·71[b]	13
Ethanolamine	1·2		7

[a] V. I. Vedeneyev, 'Bond Energies, Ionisation Potentials and Electron Affinities', St. Martin's Press, New York, 1966; [b] K. Watanabe and J. R. Mottl, *J. Chem. Phys.*, 1957, **26**, 1773.

Aromatic primary amines behaved differently. Anilines react with excited anthracene under these conditions to give brownish-yellow solutions.[9] Aniline gave a mixture containing a 1:1 adduct between anthracene and aniline. The mixture also contained two coloured isomeric compounds. Since the exciplex does not ionise significantly in benzene (nonpolar) these photoreactions in the case of aniline involve the intermediacy of the exciplex and not the ion pair. The coloured compound results from the removal of two hydrogen atoms from the exciplex. It is somewhat surprising that aromatic primary amines undergo chemical reaction with excited anthracene even in benzene while the dialkylanilines do not. From the fluorescence studies also it is clear that aniline and dialkylanilines are quite different in their interaction with excited hydrocarbons.[2] Differences in behaviour have also been already noted in the photochemical reactions of amines with n,π^* triplet states of carbonyl compounds.[6,10,11] Further work is in progress to elucidate further aspects of this study.

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