Photoreduction of 4-Chlorobiphenyl by Aliphatic Amines

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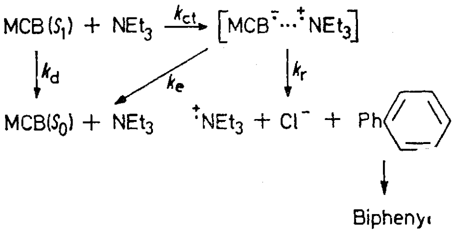
Summary Photoinduced dechlorination of 4-chlorobiphenyl by amines proceeds *via* an excited charge-transfer complex.

Quenchings of the fluorescence of aromatic amines by aromatic halides[1] and of that of aromatic hydrocarbons by aliphatic amines[2] proceed *via* excited charge-transfer complexes. In order to devise a potent tool to decompose polychlorobiphenyl (PCB), a water-polluting substance, we have examined the photoinduced decomposition of 4-chlorobiphenyl (MCB) and have found that charge transfer plays an important role in the photoreduction of MCB by triethylamine (TEA).



Irradiation of a solution of MCB (0·036M) in acetonitrile in the presence of TEA (0·1M) with a low-pressure mercury arc for 70 h gave biphenyl (71%). Quantitative analysis of chloride anion was carried out titrimetrically by the Volhard method and quantum yields were determined by ferrioxalate actinometry. A moderate quantum yield in the photoreduction by TEA (0·15M) in acetonitrile (Φ 0·49) and lower reactivity in t-butyl alcohol (Φ 0·12) and in cyclohexane (Φ 0·083) was shown. n-Butylamine (Φ 0·07) and di-n-propylamine (Φ 0·25) showed lower efficiency than TEA. The photoreduction by TEA in acetonitrile was not quenched by penta-1,3-diene. These effects of solvents and amines are similar to those reported for the photoreduction of benzophenones by amines,[3] suggesting that the reaction proceeds *via* an excited charge-transfer complex.

The results agree with the reaction processes shown in the Scheme, from which the rate equations (i) and (ii) were derived, where k_d is the sum of the rate constants of all of the unimolecular decays of MCB(S_1) involving intersystem crossings and radiative and non-radiative decays.

$$1/\Phi = (1 + k_e/k_r)(1 + k_d/k_{ct}[\mathrm{TEA}]) \qquad \text{(i)}$$

$$\Phi^0{}_f/\Phi_f = 1 + k_{ct}[\mathrm{TEA}]/k_d \qquad \text{(ii)}$$

Stern–Volmer plots of Φ^{-1} *vs.* $[\mathrm{TEA}]^{-1}$ showed the rate constant ratios k_e/k_r and k_{ct}/k_d to be 0·54 and 20·0, respectively; the latter quantity obtained from the fluorescence quenching is 23·1, in fair agreement with that obtained by the quantum yield measurements. This result suggests that the same mechanism is operative both in the photoinduced dechlorination and in the fluorescence quenching. On the basis of these results we conclude that in the photoreduction of MCB by TEA the intermediate is an excited charge-transfer complex.

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