Photo-sensitised Decomposition of Anilinium Salts by Acetone

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WE have reported[1] the photo-sensitised decomposition of dimethylaniline hydrochloride by aromatic compounds with high triplet energies, and suggested triplet excitation transfer and electron transfer as possible mechanisms. In this connection, Walsh's report on the direct photolysis of anilinium salts[2] prompts us to report our results on the photo-reaction of trimethylphenylammonium halides, $PhNMe_3{}^+X^-$ (Ia; X = Cl, Ib; X = Br, and Ic; X = I), sensitised by carbonyl compounds.

The salts (Ia) and (Ib) were not appreciably changed by direct photolysis through a Pyrex filter. In the presence of acetone (1 mole/l.), however, (Ia) and (Ib) were rapidly consumed by irradiation,† and 90—94% of benzene was produced at 90% consumption of the salts. After removal of volatile materials, basification of the slight acidic residue with sodium hydroxide gave trimethylamine, which was isolated as its picrate. The yield of benzene and the consumption of the salts were determined by g.l.c. Ethyl

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† Unless otherwise noted, irradiation was carried out through a Pyrex filter by a high pressure mercury arc, with t-butyl alcohol containing 10% (v/v) of water as solvent.

methyl ketone was less effective, and acetophenone and propiophenone did not effect photo-sensitisation.

Triplet intermediacy for the photo-sensitisation by acetone was firmly established by the results of kinetic studies (Figures 1 and 2). The quenching by penta-1,3-diene (Figure 1) provided good evidence for triplet intermediacy.[3]

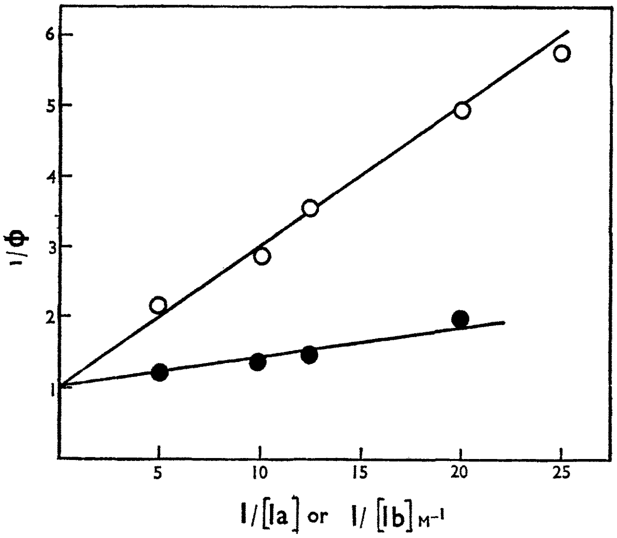

FIGURE 1. *Quantum yields for disappearance of* (Ia) (*open circles*) *and of* (Ib) (*solid circles*) *in irradiation at* 3130 Å *in t-butyl alcohol containing* 10% (*v/v*) *of water when* 1 *mole/l. of acetone was used.*

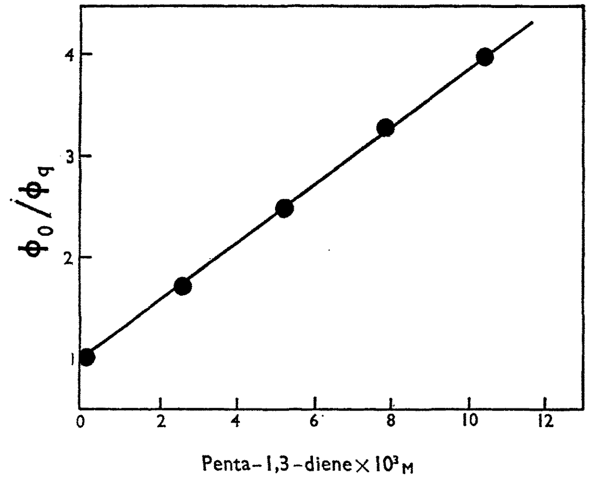

FIGURE 2. *Quenching of disappearance of* (Ia) *by penta-*1,3*-diene in irradiation at* 3130 Å *in t-butyl alcohol containing* 10% *v/v of water when* 1 *mole/l. of acetone and* 0·1 *mole/l. of* (Ia) *were used.*

The results allowed us to suggest the reaction processes (1)—(7), from which the equations (8) and (9) were derived, where A and Q denote acetone and penta-1,3-diene, respectively.

$$A \xrightarrow{h\nu} A^{S} \qquad (1)$$

$$A^{S} \xrightarrow{\phi_{S,t}} A^{t} \qquad (2)$$

$$A^{t} \xrightarrow{k_3} A \qquad (3)$$

$$A^{t} + I \xrightarrow{k_4} A + I^{t} \qquad (4)$$

$$A^{t} + Q \xrightarrow{k_5} A + Q^{t} \qquad (5)$$

$$I^{t} \longrightarrow Ph\cdot + NMe_3 + X\cdot \qquad (6)$$

$$Ph\cdot + \text{Hydrogen donor} \longrightarrow PhH \qquad (7)$$

$$1/\phi = \phi_{S,t}(1 + k_3/k_4\,[I]) \qquad (8)$$

$$\phi_0/\phi_q = 1 + k_5[Q]/(k_4[I] + k_3) \qquad (9)$$

The quantum yield for the intersystem crossing of acetone, $\phi_{S,t}$ has been reported to be unity.[4] On the reasonable assumption that the quenching process (5) is diffusion-controlled ($k_5 = 1{\cdot}3 \times 10^9 M^{-1}$ sec.$^{-1}$), one can obtain the value of k_3 from the slopes of the lines in Figures 1 and 2. The value of k_3, $2{\cdot}5 \times 10^6$ sec.$^{-1}$, is in good agreement with the rate constant for decay of triplet acetone reported previously.[4,5]

The values of k_4 were $2 \times 10^7 M^{-1}$ sec.$^{-1}$ for (Ia) and $4{\cdot}8 \times 10^7 M^{-1}$ sec.$^{-1}$ for (Ib), which were smaller than the rate constant of a diffusion-controlled reaction, but greater than that of a rather endothermic triplet excitation transfer.[6] Since the rate of the triplet excitation transfer with 3 kcal./mole of exothermicity is diffusion-controlled,[7] the values of k_4 may reflect the triplet energies (E_t) of the anilinium salts which are nearly equal to or slightly greater than that of acetone (80 kcal./mole[4]). In these photo-sensitised reactions, the rate of the excitation transfer process (4) may be sensitive to variation in E_t of the anilinium salts. For example, k_4 for (Ib) is greater than that for (Ia); there is some energy difference in E_t between (Ia) and (Ib). This energy difference can be reasonably explained by assuming that a charge-transfer configuration between trimethylphenylammonium cation and halide anion contributes to the reactive triplet state, since the ionisation potential of bromide anion is lower than that of chloride anion. Although this assumption is reminiscent of Walsh's mechanism for the direct photolysis of anilinium salts,[2] our results do not necessarily imply triplet intermediacy to the direct photolysis.

Unfortunately, iodide anion quenches triplet acetone (unlike chloride and bromide anions) and hence (Ic) was not significantly decomposed by the photo-sensitisation.

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