Reaction Mechanism of a Pyrylium Salt-sensitised Photocycloreversion of a Cage Molecule

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The pyrylium salt-sensitised photocycloreversion of a cage molecule (1) was studied in terms of the effects of the concentration of (1), of light intensity, and of a quencher (tetramethoxybenzene), to confirm the mechanism as an electron transfer radical ion chain process.

Recently, we reported the pyrylium salt-sensitised photo-cycloreversion of a cage molecule (1).[1] The reaction was unusually highly efficient having a quantum yield of *ca.* 80. A radical ion chain mechanism was proposed (Scheme 1). Photoinduced radical ion chain processes are known in, for instance, the $S_{RN}1$ reaction[2] which occurs *via* an aromatic radical anion. Relatively little has been reported on radical cation chain processes.[3] Mechanistic investigation of the highly efficient photocycloreversion of (1) should afford a suitable model for the general reaction pathway by the uni-

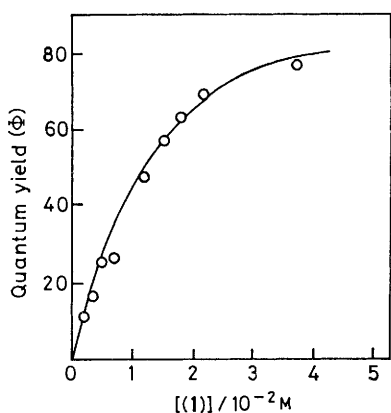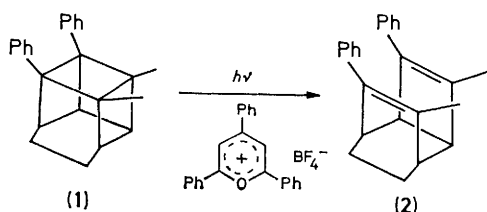**Scheme 1**

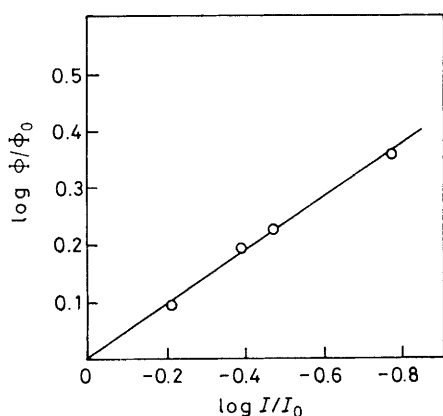**Figure 1.** The dependence of quantum yield on concentration of (1). [sens.] $= 2.52 \times 10^{-4}$ M in acetonitrile.

Figure 2. The effect of light intensity (I) on the quantum yield. [(1)] $= 2.75 \times 10^{-3}$ M; [sens.] $= 2.52 \times 10^{-4}$ M in acetonitrile.

Figure 3. Stern–Volmer plot for the quenching by 1,2,4,5-tetra-methoxybenzene. ▲: [(1)] $= 5.35 \times 10^{-3}$ M; ●: [(1)] $= 2.75 \times 10^{-3}$ M; [sens.] $= 2.52 \times 10^{-4}$ M in acetonitrile.

molecular radical cation chain process. We now report the effects on the reaction caused by changes in concentration of (1) and in light intensity, and a study of the quenching of the reaction using 1,2,4,5-tetramethoxybenzene.

Figure 1 shows the quantum yield as a function of the concentration of (1). In the region 0—1 $\times$ 10^{-2} M the quantum yield increases linearly with concentration. However, at higher concentrations, the quantum yield approaches a plateau in the region $\Phi = ca.$ 80. These results seem to be best explained by the simple reaction scheme given by equations (1) to (7). Assuming the applicability of the steady state approximation[4] for both the excited state and radical ions, and recognising that the solution remains electronically neutral [equation (8)], the quantum yield expression is shown in equation (9). A qualitative explanation for the plateau is the following. When the concentration of (1) increases, the
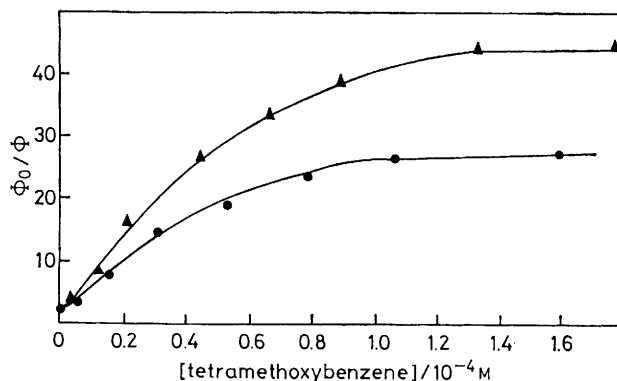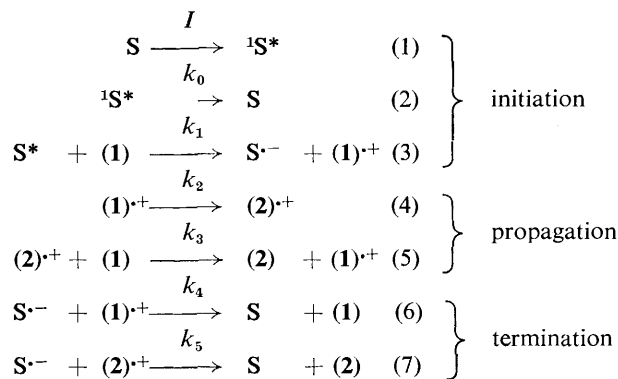
steady state concentration of (1)$^{\cdot+}$ increases via equations (3)— (5). As a result, however, the rate of the electron return process [equation (6)] will also increase.

The above expression suggests that the quantum yield should increase when irradiated with low intensity light. This proved to be the case. Figure 2 shows the log–log plot of quantum yield against light intensity. The experimental slope (-0.45) is in good agreement with that (-0.5) predicted from equation (9).
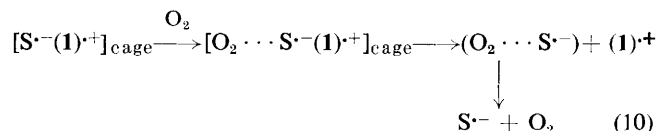
$$
\begin{array}{ll}
\quad\quad I \\
S \xrightarrow{} {}^1S^* & (1) \\
\quad\quad k_0 \\
{}^1S^* \xrightarrow{} S & (2) \\
\quad\quad k_1 \\
S^* + (1) \xrightarrow{} S^{\cdot-} + (1)^{\cdot+} & (3) \\
\quad\quad k_2 \\
(1)^{\cdot+} \xrightarrow{} (2)^{\cdot+} & (4) \\
\quad\quad k_3 \\
(2)^{\cdot+} + (1) \xrightarrow{} (2) + (1)^{\cdot+} & (5) \\
\quad\quad k_4 \\
S^{\cdot-} + (1)^{\cdot+} \xrightarrow{} S + (1) & (6) \\
\quad\quad k_5 \\
S^{\cdot-} + (2)^{\cdot+} \xrightarrow{} S + (2) & (7)
\end{array}
\right\}
$$

initiation

propagation

termination

$$[S^{\cdot-}] = [(1)^{\cdot+}] + [(2)^{\cdot+}] \tag{8}$$

$$\Phi = k_2 k_3 [(1)] \times$$

$$\sqrt{\frac{k_1[(1)]}{\{k_0 + k_1[(1)]\}\{k_2 + k_3[(1)]\}\{k_2 k_5 + k_3 k_4[(1)]\}\, I}} \tag{9}$$

Stern–Volmer quenching of the sensitised reaction by tetramethoxybenzene provided another insight into the mechanism. The plot obtained (Figure 3) is not a straight line. The quantum yield sharply dropped in the concentration region 0—1 $\times$ 10^{-4} M and then approached a constant value { 0.3 for [(1)] $= 2.75 \times 10^{-3}$ M and 0.6 for [(1)] $= 5.35 \times 10^{-3}$ M }. In the concentration region used, however, tetramethoxy-benzene hardly quenched the fluorescence of the sensitiser ($k_q \tau = 157$ dm^3 mol^{-1}). The sharp drop in the quantum yield is due to the curtailment of the propagation cycle. The fact that the quantum yield was 0.3 for [(1)] $= 2.75 \times 10^{-3}$ M or 0.6 for [(1)] $= 5.35 \times 10^{-3}$ M at high concentration of quencher, suggests that the cycloreversion of (1)$^{\cdot+}$ to (2)$^{\cdot+}$ [equation (4)], is very rapid and cannot be impeded by exother-mic diffusional quenching.

Thus, the scheme presented sketches a rough picture of the reaction mechanism. Nevertheless, the true mechanism must be more complicated than indicated in the scheme. Under degassed conditions, the quantum yield is much lower $\{\Phi = 8.5$ aerated, 3.7 degassed at $[(1)] = 2.78 \times 10^{-3}$ M$\}$ than under aerated conditions.† Decolourisation of the sensitiser did not occur and no oxidation product was detected under the experimental conditions. Apparently oxygen has a catalytic function. One possibility is that molecular oxygen assists the charge separation in the initially formed radical ion pair $[S\cdot^-(1)\cdot^+]$ in the solvent cage making available a new and competive channel to the free radical cation $(1)\cdot^+$ [equation (10)]. A series of similar observations are observed in the iodine-sensitised photocycloreversion of (1).[5]

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† A similar oxygen effect has been observed in ref. 3. A ground state complex of (1) with oxygen was not detected spectrophotometrically. All experiments were done under aerated conditions.

$$[S\cdot^-(1)\cdot^+]_{cage} \xrightarrow{O_2} [O_2 \cdots S\cdot^-(1)\cdot^+]_{cage} \longrightarrow (O_2 \cdots S\cdot^-) + (1)\cdot^+$$
$$\downarrow$$
$$S\cdot^- + O_2 \qquad (10)$$

References

1 K. Okada, K. Hisamitsu, and T. Mukai, *Tetrahedron Lett.*, 1981, 1251.
2 J. F. Bunnett, *Acc. Chem. Res.*, 1978, **11**, 413.
3 A. Ledwith, 'Exciplex,' eds. M. Gordon and W. R. Ware, Academic Press, New York, 1975, p. 220; T. Majima, C. Pac, J. Kubo, and H. Sakurai, *Tetrahedron Lett.*, 1980, 377; T. Majima, C. Pac, and H. Sakurai, *J. Am. Chem. Soc.*, 1980, **102**, 5265.
4 S. Hoz and J. F. Bunnett, *J. Am. Chem. Soc.*, 1977, **99**, 4690.
5 K. Okada, K. Hisamitsu, and T. Mukai, unpublished results.