The Mechanism of the Ultraviolet Photolysis of Diphenylacetylene in Solution

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ALTHOUGH the photochemical activation of the carbon–carbon double bond has received a great deal of practical and theoretical investigation,[1] the acetylenic bond has received much less attention. Bryce-Smith[2] has reported the formation of adducts between various acetylenes and hydrocarbons by photolysis of mixtures of the two compounds. An adduct formed from diphenylacetylene and *p*-benzoquinone has been investigated concurrently by Bryce-Smith[3] and by Zimmermann.[4] Buchi[5] has studied the photolysis of concentrated solutions of diphenylacetylene in the absence of oxygen but the results did not permit a detailed interpretation of the primary photochemical processes involved. We here present a preliminary account of the photo-oxidation of diphenylacetylene.

Solutions of diphenylacetylene in hexane (5×10^{-5}—5×10^{-6}M) contained in quartz spectrophotometer cells (10 mm. optical path length), were irradiated by light from a medium-pressure mercury arc lamp and a filter system having the transmission spectrum shown in Figure 1. The rate of reaction was measured by following the decrease in optical density at 33,700 cm.$^{-1}$, the longest wavelength absorption band of diphenylacetylene.

When the light intensity and the concentration of dissolved oxygen were kept constant, the initial rate of disappearance of diphenylacetylene was proportional to the diphenylacetylene concentration. Keeping the diphenylacetylene concentration constant and varying the oxygen concentration by preparing systems having known partial pressures of oxygen gave the results shown in Figure 2. The initial rate which was measured for systems to which no oxygen had been added could not be reduced even by rigorous outgassing on a high-vacuum system. The initial rate of the reaction was directly proportional to the intensity of the absorbed light.

The products of the reaction were benzoic acid, benzene, a hexylbenzoate, and a hydroperoxide.

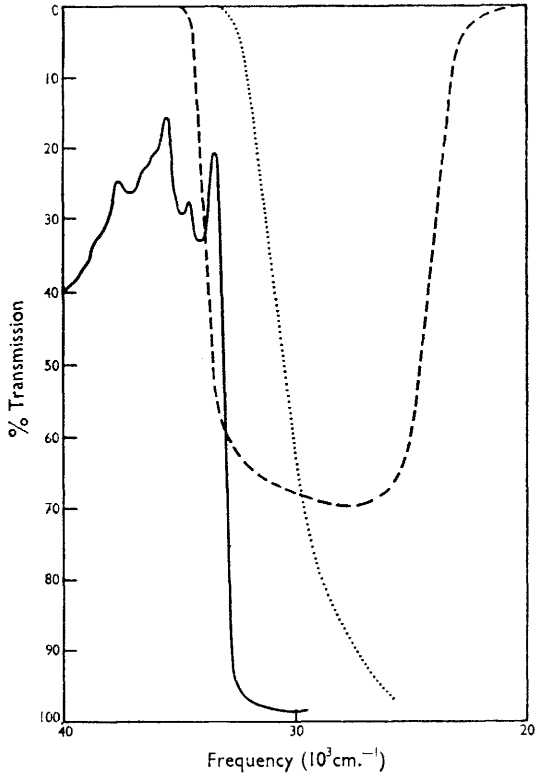

FIG. 1. *Absorption spectra. Full line—diphenylacetylene, broken line—filter system, dotted line—pyrex disc.*

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[1] (*a*) P. De Mayo, *Adv. Org. Chem.*, 1960, **2**, 367. (*b*) O. L. Chapman, *Adv. Photochem.*, 1963, **1**, 323.

[2] D. Bryce-Smith and J. E. Lodge, (*a*) *J. Chem. Soc.*, 1963, 695; (*b*) *J. Chem. Soc.*, 1962, 2675.

[3] D. Bryce-Smith, G. I. Fray, and A. Gilbert, *Tetrahedron Letters*, 1964, 2137.

[4] H. E. Zimmerman and L. Craft, *Tetrahedron Letters*, 1964, 2131.

[5] G. Buchi, C. W. Perry, and E. W. Robb, *J. Org. Chem.*, 1962, **27**, 4106.

In an attempt to decide whether it was the singlet or triplet excited state of diphenylacetylene which resulted in reaction, solutions of diphenylacetylene in hexane were irradiated in the presence of benzophenone and using a Pyrex filter. Under these conditions the diphenylacetylene absorbed none of the incident light and could be excited only by transfer of energy from the benzophenone. Further, the light absorbed by the benzophenone would be of too low a frequency to excite diphenylacetylene to the first excited singlet level and so energy transfer must be by a process of the type:

$$^3B + D \rightarrow B + {}^3D$$

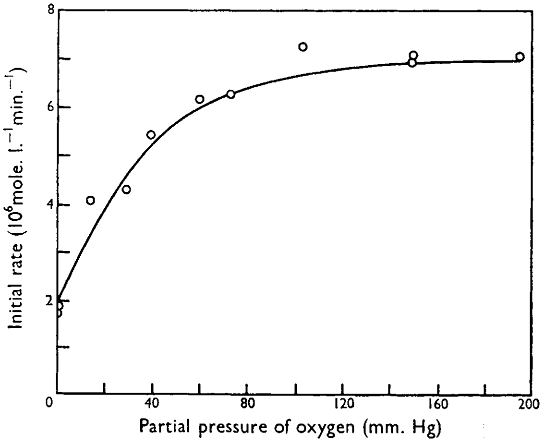

FIG. 2. *Effect of oxygen concentration of the initial rate of reaction [diphenylacetylene] = 5·77 × 10^{-5} M.*

Under these conditions, benzophenone is photoreduced; the reaction proceeds *via* the triplet state of benzophenone.[6] The rate of reaction of benzophenone was markedly affected by the addition of diphenylacetylene (Figure 3) and benzene and benzoic acid were detected as products.

When anthracene (1·16 × 10^{-5}M) was added to a solution of diphenylacetylene (4·82 × 10^{-6}M) the initial rate of disappearance of the diphenylacetylene was reduced by a factor of three, although the anthracene absorbed only 4% of the absorbed light. This suggests that triplet diphenylacetylene was quenched by an energy transfer process of the type:

$$^3D + A \rightarrow D + {}^3A$$

since the transfer of energy from ^3D to ^3A is exothermic. The addition of naphthalene in place of anthracene under the same conditions had no such marked effect on the rate of photolysis since the lowest triplet level of naphthalene lies above that of diphenylacetylene,[7,8] so that the process:

$$^3D + N \rightarrow D + {}^3N$$

would be endothermic.

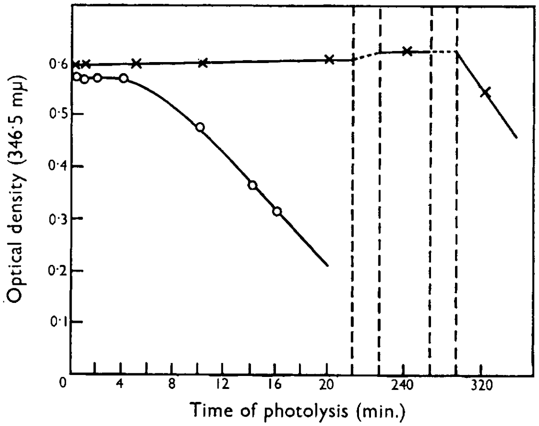

FIG. 3. *The effect of diphenylacetylene on the photolysis of benzophenone in hexane.*

Open circles [benzophenone] = 5·13 × 10^{-3} M.

Crosses [benzophenone] = 5·13 × 10^{-3} M and [diphenylacetylene] = 1·04 × 10^{-2} M.

The results described may be interpreted in terms of a mechanism the essentials only of which are given below.

$$\begin{aligned}
&C_{14}H_{10} + h\nu && \rightarrow {}^1C_{14}H_{10}\\
&{}^1C_{14}H_{10} + {}^3O_2 && \rightarrow {}^3C_{14}H_{10} + {}^1O_2\\
&{}^3C_{14}H_{10} + {}^3O_2 && \rightarrow C_{14}H_{10}O_2\\
&C_{14}H_{10}O_2 + {}^3O_2 && \rightarrow C_{14}H_{10}O_4\\
&C_{14}H_{10}O_4 && \rightarrow 2C_6H_5{\cdot}CO_2^{\bullet}\\
&C_6H_5CO_2^{\bullet} + RH && \rightarrow C_6H_5{\cdot}CO_2H + R^{\bullet}\\
&C_6H_5{\cdot}CO_2^{\bullet} && \rightarrow C_6H_5^{\bullet} + CO_2\\
&C_6H_5^{\bullet} + RH && \rightarrow C_6H_6 + R^{\bullet}
\end{aligned}$$

The superscripts ^{1} and ^{3} refer to singlet and triplet excited states and RH to a molecule of solvent.

Singlet diphenylacetylene formed by absorption of a photon undergoes intersystem crossing to the

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[6] (*a*) G. S. Hammond and P. A. Leermakers, *J. Phys. Chem.*, 1962, **66**, 1148. (*b*) A. Beckett and G. Porter, *Trans. Faraday Soc.*, 1963, **59**, 2038.

[7] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1964, **86**, 4537.

[8] M. Beer, *J. Chem. Phys.*, 1956, **25**, 745.

lowest excited triplet state. This "spin-forbidden" transition may be facilitated by the presence of the paramagnetic oxygen molecule. The triplet diphenylacetylene then adds two molecules of oxygen successively across the carbon atoms of the triple bond. The kinetics of the reaction indicate that the addition of the first molecule is slow and rate-controlling which is in agreement with the work of Schulbach[9] and of Greene.[10] The intermediate so formed breaks down to give two benzoyloxy-radicals which may react in a variety of ways. This intermediate has been isolated from larger scale (10 l) photolyses of diphenylacetylene. It has also been prepared by the oxidation of diphenylacetylene by using the procedure described by Foote[11] in which singlet oxygen is thought to be the oxidising species. The samples obtained by the two methods were small and difficult to obtain in a pure state but they had identical ultraviolet and infrared spectra. The structure of the intermediate is currently being investigated but it is known to be thermally stable and so its decomposition is probably photochemical. Many workers have studied the reactions of benzoyloxy-radicals (formed by the thermal decomposition of dibenzoyl peroxide) and have found the same products as we find in our experiments.

(*Received, May 24th,* 1965.)

[9] H. H. Schlubach and V. Franzen, *Annalen*, 1952, **577**, 60.

[10] F. D. Greene and W. W. Rees, *J. Amer. Chem. Soc.*, 1960, **82**, 893.

[11] C. S. Foote and S. Wexler, *J. Amer. Chem. Soc.*, 1964, **86**, 3879.