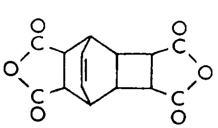
514. *Liquid-phase Photolysis. Part V.*[1] *Mechanism of the Photo-addition of Maleic Anhydride to Benzene.*

By D. Bryce-Smith and J. E. Lodge.

The photo-addition of maleic anhydride to benzene has been shown to involve photo-activation of an intermediate charge-transfer complex rather than individually photo-activated benzene or maleic anhydride molecules. The addition is insensitive to the presence of oxygen, and the activated intermediate is considered to be of singlet character. In contrast, the benzophenone-sensitised addition is inhibited by oxygen and is considered to involve triplet intermediates.

Benzophenone itself inhibits the photo-addition of dimethyl acetylenedicarboxylate to benzene under nitrogen and also appears to inhibit the normal mechanism of unsensitised addition of maleic anhydride. Overall sensitisation of the latter addition by benzophenone is considered to result wholly from the operation of an alternative, more efficient mechanism of intermolecular energy transfer.

It has been shown[1,2] that maleic anhydride reacts with benzene under the influence of ultraviolet radiation to give a 2 : 1 adduct (I) by successive 1,2- and 1,4-additions. The irradiation conditions employed[1] were similar to those under which benzene itself isomerises to fulvene[3] and did not permit a distinction to be made between the three possible primary activation processes, namely, photo-activation of (*a*) benzene, (*b*) maleic anhydride, or (*c*) a benzene–maleic anhydride charge-transfer complex. Possibility (*a*) has been inferred in a recent review.[4] The evidence now to be presented shows that (*c*) is correct.


(I)

Mixtures of benzene and maleic anhydride in chloroform show a pronounced absorption maximum at 278 mμ,[5] not found in the spectra of solutions of the pure components. This

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[1] Part IV, *J.*, 1960, 4791.

[2] Grovenstein, Rao, and Taylor, *J. Amer. Chem. Soc.*, 1961, **83**, 1705.

[3] Angus, Blair, and Bryce-Smith, *J.*, 1960, 2003.

[4] De Mayo, " Advances in Organic Chemistry. Methods and Results. Vol. II," Interscience Publ. Inc., New York, 1960, p. 407.

[5] Barb, *Trans. Faraday Soc.*, 1953, **49**, 143; Andrews and Keefer, *J. Amer. Chem. Soc.*, 1953, **75**, 3776.

has been attributed to a weakly bound 1 : 1 benzene–maleic anhydride charge-transfer complex.[5] It has now been found that the same maximum appears in the spectra of solutions of maleic anhydride in benzene alone. Removal, by a filter, of radiation of wavelength shorter than 280 mμ prevented virtually all photo-activation of individual benzene and maleic anhydride molecules but still permitted a substantial degree of photo-activation of the complex (Fig. 1).* Addition still occurred under these conditions and the yield of the adduct (I) was reduced to an average of 45% of that obtained in the same irradiation period without a filter. This compares with the figure of 43% calculated on the assumption that only absorption of radiation in the 278 mμ band of the charge-transfer complex is effective in leading to the formation of adduct. Mechanism (*a*) would have required a zero yield of adduct, and (*b*) a yield of *ca.* 4%.† These, therefore, do not operate significantly in the addition process. This conclusion was supported by an experiment where the concentration of complex was varied. Andrews and Keefer[5] found ε_{276} 3140 for the charge-transfer complex in benzene–chloroform. The optical density of a solution containing 0·00095 mole l.$^{-1}$ of maleic anhydride in benzene is 0·95 at 276 mμ. With the assumption that the above value of ε_{276} applies also to solutions in pure benzene, application of Beer's law gives the concentration of complex in this solution as 0·0003025 mole l.$^{-1}$. Thus, 32% of the maleic anhydride is present as the charge-transfer complex with benzene. On the other hand, a solution of 0·0375 mole l.$^{-1}$ of maleic anhydride and 0·11 mole l.$^{-1}$ of benzene in cyclohexane contains only 3% of the maleic anhydride as the complex. Irradiation of this solution gave no detectable amount of the adduct (I).

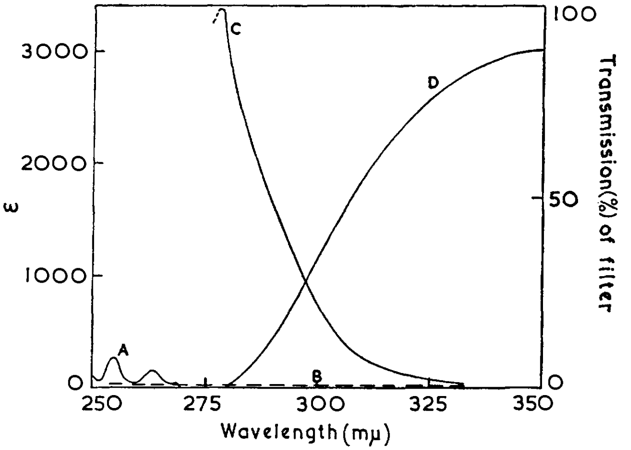

Fig. 1. Absorption curves of (A) benzene, (B) maleic anhydride (in chloroform), and (C) the benzene–maleic anhydride charge-transfer complex. (D) Transmission curve of the filter.

In further experiments it was found that oxygen did not inhibit the addition to a significant degree. Indeed, irradiation under pure oxygen gave the adduct free from the resinous matter normally formed in preparations conducted under oxygen-free nitrogen: so an oxygen atmosphere is recommended for preparative work. Increase in temperature was beneficial, up to a point. Thus in duplicated experiments the yields obtained under nitrogen at 30° were doubled at 40°; but there was no further increase at 50°, and at 80° the yields were zero. The cause of this variation is at present unknown.

The insensitivity of the photo-addition to oxygen indicates that only a singlet excited

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* Since the lamp employed had a strong emission maximum at 300—320 mμ, Fig. 1 overemphasises the reduction of energy absorbed within the charge-transfer band C in the presence of the filter.

† The closeness of agreement between the observed and the calculated value should not be overstressed; as the reproducibility in individual runs was only *ca.* ±15%, this was probably connected with unavoidable variations in the efficiency of the mechanical process by which the cell walls were kept optically clean.

state of the complex is involved (contrast the photosensitised addition below). According to Mulliken's proposals,[6] a complex of the present type has greater polar character in the first excited state than in the ground state. Thus, it may be understood in principle why absorption of a quantum by a weakly bound complex should be able to lead, not to its dissociation (as has been suggested [7]), but to its stabilisation, for the closer approach and greater interaction between donor benzene and acceptor maleic anhydride in the excited state should facilitate the formation of an adduct having more conventional bonding. In this connection it is interesting that there is also evidence for the formation of an intermediate complex during some thermal Diels–Alder 1,4-additions.[8] It is not yet clear why maleic anhydride (cf. free methylenes) should undergo 1,2-addition to benzene when the more conventional 1,4-addition would give a virtually strainless product; but the resistance of benzene to the out-of-plane deformation which might be required to establish a transition state for 1,4-addition could well be an important factor.* The apparent mechanistic similarity between the present photo-addition and the conventional thermal Diels–Alder additions may also imply some specific orientation of donor and acceptor within the charge-transfer complex. Not all photo-additions of maleic anhydride to aromatic systems are of 1,2-type: the photochemical adduct with anthracene, first mentioned by Simons,[7] is identical with the normal thermal adduct.[9]

Schenck and Steinmetz [10] have observed that the photo-addition of maleic anhydride to benzene can be photosensitised by benzophenone. A similar sensitisation by benzophenone or benzil of the corresponding addition to phenanthrene has been reported by Bryce-Smith and Vickery.[11] Oddly enough, benzil has now been found to inhibit the photo-addition of maleic anhydride to benzene, and both benzil and benzophenone inhibit the photo-addition of dimethyl acetylenedicarboxylate to benzene. Thus the use of photosensitisers for this class of aromatic addition is at present largely a matter of trial and error. In the hope of elucidating the factors which may be involved, the benzophenone-photosensitised addition of maleic anhydride to benzene has been studied in some detail.

The ultraviolet spectra of various mixtures of the components were first examined. The ultraviolet spectrum of benzophenone in benzene down to the limit of solvent transparency at *ca.* 280 mμ was almost identical with the spectrum in cyclohexane. The addition of 1% of benzene did not modify the spectrum of benzophenone in cyclohexane over the range 200—280 mμ (the effect of absorption due to benzene was eliminated by compensation in the reference beam). Thus, there is no spectroscopic evidence for interaction between benzene and benzophenone. In a similar way, no indication was found of interaction between maleic anhydride and benzophenone, or between the maleic anhydride–benzene charge-transfer complex and benzophenone.

Investigation of the effect of oxygen on the photosensitised addition showed that the usual reaction was totally inhibited: not even the lower yield of adduct (*ca.* one-third) normally obtained in the unsensitised addition was obtained, although the unsensitised addition is itself indifferent to oxygen. Thus the inhibitory effect of oxygen applies only when benzophenone is present. Various workers [12,13] have shown that photoexcitation of benzophenone produces initially a short-lived singlet excited species which is transformed quantitatively into a triplet. In the absence of oxygen, activation of a benzene–maleic

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* We thank Professor R. C. Cookson for this suggestion.

[6] Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 600; 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801.

[7] Simons, *Trans. Faraday Soc.*, 1960, **56**, 391

[8] Andrews and Keefer, *J. Amer. Chem. Soc.*, 1955, **77**, 6284.

[9] Bryce-Smith and Vickery, unpublished work.

[10] Schenck and Steinmetz, *Tetrahedron Letters*, 1960, No. 21, 1.

[11] Bryce-Smith and Vickery, *Chem. and Ind.*, 1961, 429.

[12] Hammond and Moore, *J. Amer. Chem. Soc.*, 1959, **81**, 6334; Hammond, Leermakers, and Turro, *ibid.*, 1961, **83**, 2395; Moore, Hammond, and Foss, *J. Chem. Phys.*, 1960, **32**, 1594; Backstrom and Sandros, *ibid.*, 1955, **23**, 2197.

[13] Hammond, Moore, and Foss, *J. Amer. Chem. Soc.*, 1961, **83**, 2789; Becker, *J. Mol. Spectroscopy*, 1951, **3**, 1.

anhydride charge-transfer complex can be pictured as occurring by collisional energy-transfer from triplet-excited benzophenone.* If, as seems likely, the benzophenone reverts to the ground state in this process, spin conservation requires that the activated complex must initially be of triplet character, and thus different from that formed directly in the absence of the photosensitiser. Quenching of triplet states by oxygen is a familiar process (see, *e.g.*, ref. 13) and is doubtless responsible for the inhibitory effect of oxygen on the sensitised photo-addition. It further seems that singlet-excited benzophenone does not effectively participate in the energy transfer.

The effect of varying the wavelength range of the activating radiation was next examined. Irradiation through a filter (transmission curve shown in Fig. 1) of a mixture of benzophenone, maleic anhydride, and benzene under nitrogen produced no adduct: removal of the filter led to a normal yield. Evidently, photosensitisation requires the absorption by benzophenone of radiation having a wavelength shorter than 280 mμ. In particular, absorption in the 340 mμ region, which corresponds to a $n \longrightarrow \pi$ transition in the carbonyl group, is ineffective.[13] † Since in the absence of benzophenone, addition occurred when the filter was used (see above), it appears that the normal mode of addition by direct photoactivation of the benzene–maleic anhydride charge-transfer complex does not occur in the presence of benzophenone. Absorption by benzophenone at the concentrations employed is calculated to reduce the energy available for photoactivation of the complex by only 30% (Fig. 2), so the effect of benzophenone must arise largely from some cause other than competition for the activating radiation. Thus it is concluded, from the effect of both oxygen and the filter, that benzophenone *inhibits* photo-addition of maleic anhydride to benzene by the normal direct photoactivation route, and that the observed photosensitisation results from the operation of an alternative more efficient energy-transfer mechanism.

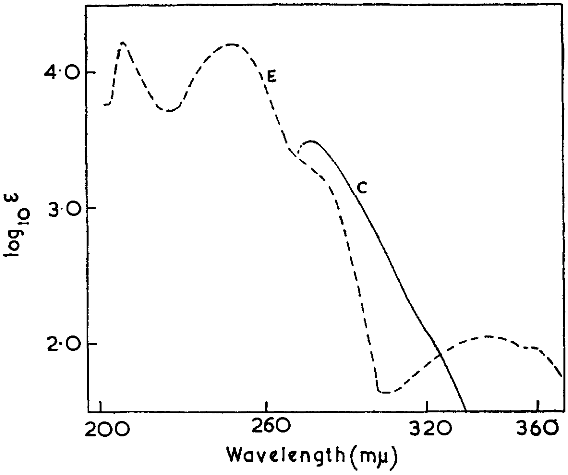

FIG. 2. Absorption curves of (C) the benzene–maleic anhydride charge-transfer complex in benzene, and (E) benzophenone in cyclohexane. (Above 280 mμ, the absorption curve for benzophenone in benzene is almost identical with E.)

As the spectroscopic evidence indicates little or no interaction between benzophenone and the unactivated charge-transfer complex, it appears most probable that benzophenone deactivates the excited complex before its transformation into a 1 : 1 adduct, presumably by collisional quenching.

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* Energy transfer to uncomplexed benzene or maleic anhydride would be possible in principle, but seems less likely to result in chemical reaction.

† Porter and Wilkinson [13a] have recently provided evidence for the production of triplet benzophenone following the absorption of radiation of λ *ca.* 330 mμ. This suggests that the triplet benzophenone involved in the present energy-transfer is an excited species.

[13a] Porter and Wilkinson, *Trans. Faraday Soc.*, 1961, **57**, 1686.

In view of the evidence that inhibition of the type now proposed is in fact more general, the question of overall sensitisation may depend on the fortuitous existence of an alternative pathway for energy transfer, as in the present case. This may make the uncertain behaviour of potential sensitisers in related systems easier to understand, if not to predict.

EXPERIMENTAL

The irradiation apparatus was the water-cooled form of that described in Part I.[14] Quartz wool was used in place of the glass wool previously employed as its cleaning action proved to be superior. Sulphur-free benzene was dried and refractionated. Maleic anhydride (recrystallised from chloroform) was dissolved in benzene and *ca.* one-third of the benzene was distilled under nitrogen from the filtered solution immediately before each experiment. Where benzophenone was employed, this was added before the distillation stage. Benzophenone was recrystallised twice from methanol.

Nitrogen (B.O.C. " White Spot ") was purified by passage through chromous chloride in a " Nilox " apparatus (Southern Analytical Ltd.), followed by drying through concentrated sulphuric acid, phosphorus pentoxide, and magnesium perchlorate. From data provided by the manufacturers, this treatment reduced the oxygen content to $<0{\cdot}1$ p.p.m. Where appropriate, any last traces of dissolved oxygen were removed from solutions by passage of a stream of purified nitrogen for several hours before irradiation.

The filter (see Fig. 1) was a cylinder of Pyrex glass having a wall thickness of 1·0 mm. which completely shielded the quartz section of the cell. Calculations which required a knowledge of the variation of lamp emission intensity with wavelength were based on data kindly provided by the manufacturers (Messrs. Engelhard Industries Ltd.)

Each of the experiments described below was repeated three or four times. The reproducibility in yields of adduct was within $\pm 15\%$ of the values given (usually much better than this).

Unsensitised Addition.—(*a*) Maleic anhydride (5·0 g.) in benzene (100 g.) was irradiated at 50° for 8 hr. under nitrogen. Working up as in Part IV[1] gave the adduct (0·70 g.), m. p. 350° (decomp.).

(*b*) Repetition of (*a*) with use of the filter gave 0·34 g. of adduct.

(*c*) Repetition of (*a*) with the passage of a stream of oxygen through the irradiated solution gave 0·63 g. of adduct. Much less resin was formed in this experiment.

(*d*) Repetition of (*c*) with the use of the filter gave 0·30 g. of adduct.

(*e*) Irradiation of a solution of maleic anhydride (1·1 g.) in a 1% solution of benzene in cyclohexane (150 ml.) for 4 hr. at 52° under nitrogen gave no adduct. Before irradiation the solution had ε_{278} mμ 116 based on the concentration of free and complexed maleic anhydride.

Sensitised Addition.—(*f*) A solution of maleic anhydride (5·0 g., 0·051 mole) and benzophenone (2·5 g., 0·0137 mole) in benzene (100 g.) was irradiated under nitrogen at 62° for 4 hr., giving 1·0 g. of adduct, m. p. 350°, identical with that obtained in unsensitised additions (mixed m. p., infrared spectrum).

(*g*) Irradiation of a similar solution for 8 hr. at 50° gave 2·0 g. of adduct [cf. experiment (*a*)].

(*h*) Repetition of (*f*) with passage of oxygen through the irradiated solution gave no trace of adduct. A control experiment showed that as little as 0·005 g. would have been detected.

(*i*) Repetition of (*f*) with use of the filter gave no trace of adduct. Removal of the filter led to visible precipitation of the very sparingly soluble adduct within 15 min.

(*j*) Repetition of (*g*) with the use of benzil (2·5 g.) in place of benzophenone gave no adduct. The starting materials were recovered. Longer periods of irradiation led to a similar result (cf. ref. 11).

(*k*) Irradiation of a solution of dimethyl acetylenedicarboxylate (2·0 g.) and benzophenone (1·0 g.) under nitrogen for 12 hr. at 50° gave no detectable amount of the dimethyl cyclooctatetraene-1,2-dicarboxylate which is formed in the absence of benzophenone.[15] A similar result was obtained when benzil (1·0 g.) was used in place of benzophenone

Ultraviolet Spectrum of the Benzene–Maleic Anhydride Adduct.—The figures given previously [1]

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[14] Blair, Bryce-Smith, and Pengilly, *J.*, 1959, 3174.

[15] Grovenstein and Rao, *Tetrahedron Letters*, 1961, 148; Bryce-Smith and Lodge, *Proc. Chem. Soc.*, 1961 333.

for the derived free acid in aqueous solution were obtained with an instrument of limited range and should be replaced by the following (cf. ref. 2): $\lambda_{max.}$ 194 mμ, ε 2924; $\lambda_{min.}$(shoulder) 197 mμ, ε 2741; $\lambda_{max.}$(shoulder) 201·5 mμ, ε 2193; $\lambda_{max.}$(shoulder) 206 mμ, ε 1718. Above 206 mμ, absorption tailed off smoothly to 300 mμ, at which $\varepsilon \approx 0$. These extinction coefficients are unusually high for an unconjugated carboxylic acid but are consistent with the previous proposal[1] of transannular interaction between C:C and CO_2H.

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