

Effects of Ultraviolet Radiation on 3,4-Benzpyrene and Other Polycyclic Aromatic Hydrocarbons

II. The Role of Benzene in the Photoreactions in Solutions Containing It*

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INTRODUCTION

In the preceding paper (3) it was shown that when naphthalene, anthracene, 1,2,5,6-dibenzanthracene, cholanthrene, phenanthrene, or 3,4-benzpyrene was irradiated with radiation of wave length 2,537 A. in the presence of benzene, water-soluble materials were produced that gave rise to very similar absorption spectra. The spectrum of slightly alkaline solutions contained two sharp bands with maxima at 3,600 A. and 2,760 A. respectively and these could be attributed to the presence of two distinct compounds, named for convenience substances *A* and *B*. Comparison with the results obtained when the hydrocarbons were irradiated in solution in pure cyclohexane alone established that (a) the intenser band at 2,760 A. was observed only when benzene was present during the irradiation; and (b) the substance absorbing at 3,600 A. was formed from naphthalene and phenanthrene only when benzene was present. The role of the benzene in producing these results is now discussed.

THE PHOTO-OXIDATION OF LIQUID BENZENE

Under the same conditions of irradiation, benzene, either as pure liquid or when dissolved in cyclohexane at concentrations of over 20 per cent (v/v), also yielded water-soluble products (1, 2) that were much more stable than those of the polycyclic compounds. The absorption spectra of the aqueous solutions, both acid and slightly alkaline, contained a well defined band at 2,760 A., but the spectrum between 3,000 A. and 4,000 A. exhibited strong, unselective absorption, the highest intensity in which was reached at about 3,950 A. (Fig. 1, curve 1). The wave length of this maximum depended only slightly on the pH of the extracting solution and on the concentration of benzene during the irradiation; its intensity diminished a little in the first few hours after the extraction, but then

* Because of the difficulties of international communication the authors have not read proof of this article.

became constant. The band at 2,760 A. showed constant intensity with time, and was not affected by pH up to that of the bicarbonate solutions, but it was destroyed irreversibly in strongly alkaline solution (pH 14).

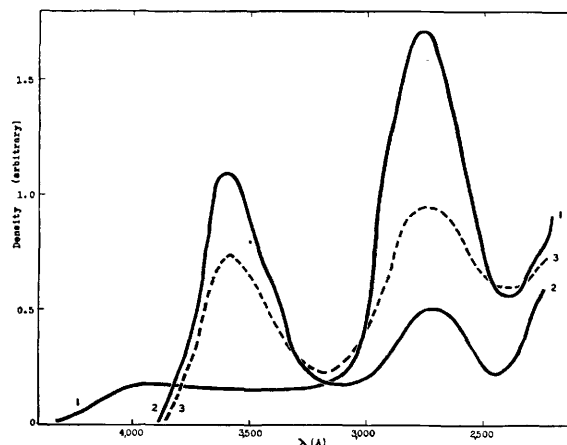


FIG. 1.—Absorption spectra of aqueous extracts from irradiated benzene.

- Curve 1. 20% C_6H_6 in C_6H_{12}
“ 2. 0.01% C_6H_6 in C_6H_{12}
“ 3. The same after standing

(Densities for curve 1 have been divided by 5)

EXISTENCE OF SECONDARY REACTIONS

These results suggested that the band at 2,760 A. in the spectra of the photoderivatives from the polycyclic compounds was due to the benzene only; but this was partly contradicted by the observation that the intensity of the band was much higher when benzene was irradiated alone than when 3,4-benzpyrene was irradiated in it. Reaction between the benzene derivative and the benzpyrene solute was thus probable.

Direct confirmation of such a reaction was obtained in an experiment in which (a) benzpyrene was

irradiated in cyclohexane, and (b) pure benzene was irradiated separately. The unchanged benzene in (b) was dried off, and the residue, taken up in cyclohexane, was added to the irradiated solution from (a). After 4 hours the solvent was again evaporated at room temperature, and the residue was extracted with $N/100$ HCl. The absorption spectra of extracts from solutions (a) and (b) are drawn in curves 1 and 2 respectively of Fig. 2, and that for the final extract in curve 3. It closely resembles that for an extract from 3,4-benzopyrene after irradiation in a solution containing benzene, as shown in Fig. 3 of the preceding paper.

The probability still remained that part, at least, of the intensity of the band at 2,760 Å. in the spectra of the substances derived from the polycyclic hydrocarbons was due to a derivative of benzene; but this conclusion

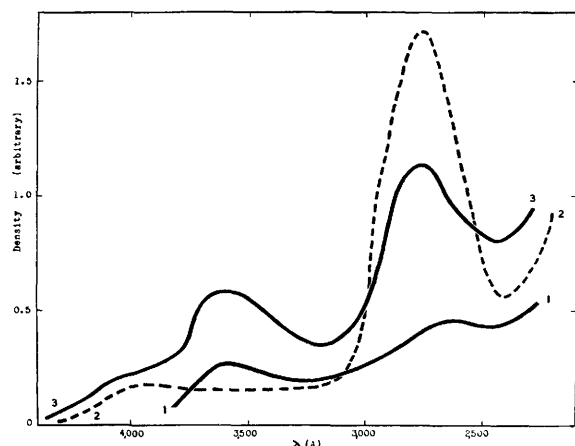


FIG. 2.—Absorption spectra of extracts in $N/100$ NaHCO_3 from

- Curve 1. 3,4-Benzopyrene irradiated in C_6H_{12}
 “ 2. Benzene irradiated in C_6H_{12}
 “ 3. The irradiated solutions after mixing

also needed qualification. When a very dilute solution of benzene in cyclohexane (1.2 mgm. in 10 ml.) was irradiated, the absorption spectrum of the aqueous extracts initially showed only a weaker band at 2,760 Å., but they also contained a well defined and stronger band at 3,600 Å. (Fig. 1, curve 2). When the aqueous solutions were allowed to stand, the band at 3,600 Å. diminished, whereas that at 2,760 Å. increased in intensity (Fig. 1, curve 3). This result might be attributed to a reaction in which substance *B*, absorbing at 2,760 Å., was produced by condensation of substance *A*, absorbing at 3,600 Å., and this would allow of similar reactions between residues from irradiated benzene and from the polycyclic compounds when these were irradiated in solution in it.

Evidence that two different substances absorbing at 2,760 Å. are produced was obtained when the stabilities of the products from benzopyrene in benzene, and

from benzene alone, were compared. In parallel experiments benzene, and a solution of benzopyrene in benzene, were irradiated under the same conditions. The unchanged liquids were evaporated off and the residues, redissolved in cyclohexane, were re-irradiated for 30 minutes. The products were then dried and extracted in the usual way. The extract from the irradiated benzene gave no band at 2,760 Å., whereas that from the benzopyrene exhibited the band at full intensity.

ORIGIN OF THE SUBSTANCE ABSORBING AT 3,600 Å.

Secondary reactions similar to those suggested above could also explain the observation that the presence of benzene was necessary for the formation of a substance absorbing at 3,600 Å. from naphthalene and phenanthrene, and to some extent from 3,4-benzopyrene, but not from the anthracenes or from cholanthrene. If the substance resulted from reaction of a residue from the benzene with one from the polycyclic compound, such residues might be produced simultaneously from some molecules such as anthracene, but not from smaller ones such as naphthalene. In a radical breakdown of this kind, the structures of naphthalene and phenanthrene limit the types of fission possible as compared with molecules of the anthracene type; and in so far as benzopyrene is intermediate in structural type, such an assumption might account for the lower yield obtained from benzopyrene when no benzene is added.

CONCLUSION

It is concluded that although benzene will yield water-soluble products similar to those derived from polycyclic compounds under the same conditions, when these polycyclic hydrocarbons are irradiated in the presence of benzene secondary reactions occur, which lead to the formation of compounds similar to, but not identical with, those derived from benzene alone.

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