The Photoproduct of Benzene in Oxygenated Aqueous Solution

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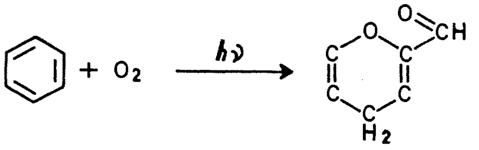
Summary 2-Formyl-4*H*-pyran is confirmed as the only major photoproduct in neutral aqueous solutions of benzene in the presence of oxygen: the mechanism of its formation is indicated.

WE are investigating the kinetics and mechanism of the photochemistry of benzene in polar, particularly aqueous, solutions. In aerated aqueous solutions of benzene illuminated[1] with 2537 Å light, a product was obtained in relatively high yield. This product was similar to, but not identical with, mucondialdehyde, which has been established to be one of the major products of radiation of similar solutions.[2] Wei, Mani, and Pitts[2] reported that irradiation of benzene in nonaqueous media yields mucondialdehyde. However, Farenhorst[4] later showed that the n.m.r. and i.r. spectra of the product in aqueous solution indicate that it is not mucondialdehyde but its isomer, 2-formyl-4*H*-pyran (I).

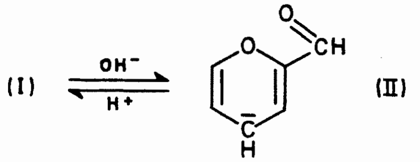
In quantitative investigations, we have established that the photochemistry of aqueous solutions of benzene in the presence of oxygen in the pH range 5—9 with light of 2537 Å initially yields only one photoproduct. This product, when obtained on illumination in neutral solution, shows an absorption maximum at 294 nm. On addition of alkali, the product is quantitatively and reversibly converted into another form, with an absorption maximum at 308 nm. From the spectrophotometric titration curve, the concentration of the product and hence the quantum yield of its formation, were calculated. The results show that the titration involves one acid equivalent per mole of product. The initial quantum yield is about 0·13, ϵ_{294} 9600 and ϵ_{308} 15,600. Irradiation of 10^{-2}M- aerated benzene solution in water with a dose sufficient to give *ca.*



(I)

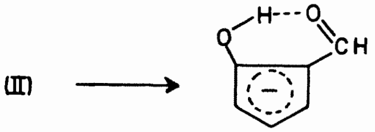
10^{-4}M-product, yielded, on CH_2Cl_2 extraction, a product with an i.r. spectrum in good agreement with the results of Farenhorst,[4] and in agreement with structure (I).

Farenhorst could not obtain any stable derivatives. We obtained a solid derivative using 2,4-dinitrophenylhydrazine which was added to the irradiated solution. After 24 h at room temperature, a solid derivative was precipitated, corresponding to a quantum yield of about 0·10, m.p. 152° (decomp.), uncorrected. Elementary analysis was correct for $C_{12}H_{10}N_4O_5$. The 2,4-dinitrophenylhydrazine derivative indicates the presence of one functional carbonyl group per molecule of product, as in (I). We conclude that the product is 2-formyl-4*H*-pyran which, in aqueous solution, undergoes an acid–base equilibrium [(I) ⇌ (II)], rather than the bivalent change in (II) suggested by Farenhorst, on the basis of products obtained under different conditions.



(II) may be stabilized further by formation of the cyclopentadienyl anion (III). This form may account for the observation[4] that reduction of (I) yields fulvene.

Our kinetic and mechanistic studies including steady-state and flash photochemistry, as well as fluorescence intensity and life-time studies, indicate the following sequence of events: light absorption leads to the formation of the $^1B_{2u}$ singlet excited state of benzene. The different dependence of the quantum yield of fluorescence (τ *ca.* 9 ns) and product formation on the pH shows that it is not the singlet itself but another intermediate formed from it, that reacts with O_2. The O_2 acceptor may either be the triplet excited state of benzene or a labile isomer of benzene. Dependence of product formation on O_2 concentration indicates that this intermediate (τ *ca.* 1 μs) adds oxygen to form a primary unstable peroxide. The primary photoperoxide isomerizes with a half-life of the order of 1s at room temperature and neutral pH into the stable photoproduct described above.



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[4] G. Farenhorst, *Tetrahedron Letters*, 1968, 4835.