Photolysis of Aqueous Solutions of *p*-Benzoquinone: a Spectrophotometric Investigation

By **K. C. Kurien** and **P. A. Robins,*** Department of Chemistry, University College, Nairobi, Kenya

The photolysis of aqueous solutions of *p*-benzoquinone is investigated spectrophotometrically over a wider range of pH, concentration, and the wavelength of irradiation than before. Experimental evidence has been obtained for the formation of benzene-1,2,4-triol as the sole primary photochemical product at all values of pH. Quinol and 2-hydroxy-1,4-benzoquinone are produced in equimolar quantities as secondary products both in acid and alkaline solutions, when the reaction between *p*-benzoquinone and benzene-1,2,4-triol is very fast. 2-Hydroxy-1,4-benzoquinone at higher concentrations polymerizes to the so-called 'humic acid'. Between pH 4 and 6 benzene-1,2,4-triol is the chief photoproduct owing to suppression of the secondary reaction.

BRUCE[1] has reviewed the light-induced reactions of quinones and has pointed out that no solvent so far tried is entirely inert toward quinones, especially under illumination. Leighton and Forbes[2] reported that *p*-benzoquinone (I) in aqueous solutions when irradiated with mercury light was converted into quinol (II) and an unknown product. Later Poupě[3] reinvestigated this system using polarography and confirmed that one of the photoproducts was (II) and that the other was 2-hydroxy-1,4-benzoquinone (III). Poupě suggested a reaction mechanism which assumes that the primary photochemical process is the conversion of (I) into benzene-1,2,4-triol (IV). According to his results, the photolysis was independent of pH in the range 5—8 and of wavelength in the range 3600—4600 Å: at higher pH and at high initial concentrations of (I) the photolysis was more complex. Poupě was unable to investigate the system at lower values of pH because his polarographic technique was not applicable to acid solutions. More recently Joschek and Miller[4] irradiated solutions of (I) with 2537 Å light and, using chromatographic techniques, detected quinol (II) and the triol (IV) as the chief products in the absence of oxygen, while (II) alone was the chief product in the presence of oxygen. The photochemistry of *p*-benzoquinone in aqueous solution is thus not yet fully clarified. Since spectrophotometry not only allows investigation of this system at all pH values but also records the structural changes taking place, it was decided to use this method.

RESULTS AND DISCUSSION

p-Benzoquinone.—*p*-Benzoquinone (I) is somwehat unstable even in very dilute solutions when prepared and kept in subdued daylight: the original colourless solution becomes brown in a few hours. In acid medium there is no such observable colouration, and some authors[5] have incorrectly taken this as a sign of the stability of (I) in acid solution. Lu Valle *et al.*[6] have reported that (I) in acid medium undergoes proton-induced reactions and have claimed that the behaviour in aqueous solution is very complex.

A saturated solution of *p*-benzoquinone in water is *ca.* 0·125M: the solution has three major absorption peaks in the u.v.–visible range both at its natural pH (5·5) and with added acid: $\lambda_{max.}$ 246 (log ε 4·34), 300 (2·51), and 430 nm. (1·34). Although both acid and neutral solutions are somewhat unstable in daylight, they are spectrophotometrically very stable if prepared and kept in the dark. At higher pH, especially above pH 9, solutions of (I) are increasingly unstable both in the absence and the presence of oxygen. The absorption spectrum of a nitrogen-saturated solution of (I) taken immediately after a drop of 0·1N-NaOH is added clearly shows that semiquinone is formed as an intermediate. Investigation of the photolysis of solutions of (I) is not, therefore, possible above pH 9 even in the absence of oxygen.

Quinol.—Quinol (II) is very stable both in acid and in neutral solution even when exposed to daylight. A dilute aqueous solution of (II) has three electronic absorption peaks: $\lambda_{max.}$ 290 (log ε 3·39), 221 (3·62), and < 200 nm. (absorption coefficient decreasing with increase in concentration). Quinol (II) is not oxidized by H_2O_2 in acid or neutral solutions but it is readily oxidized by $KMnO_4$ or ceric ions, the latter giving (I) without further oxidation. Above pH 7, quinol is oxidized by atmospheric oxygen, the rate of oxidation increasing rapidly with pH: the *p*-benzoquinone (I) formed, being unstable under these conditions, reacts further. In strongly alkaline and aerated solutions, both (II) and (I) are oxidized to 2,5-dihydroxy-1,4-benzoquinone (V) and other products.

Benzene-1,2,4-*triol.*—Benzene-1,2,4-triol (IV) has two electronic absorption maxima: $\lambda_{max.}$ 289 (log ε 3·52) and in the 200—225 nm. region (the wavelength of maximum absorption being dependent upon concentration). Its spectrum is similar to that of quinol (II) especially in the 290 nm. region, but, in contrast, (IV) is not very stable in the presence of oxygen even in strongly acid solutions. It is more reactive in alkaline solution and is readily oxidized by atmospheric oxygen first to 2-hydroxy-1,4-benzoquinone (III) and then to 2,5-dihydroxy-1,4-benzoquinone (V) and other oxidation products. At pH *ca.* 9 oxidation to the quinone (III) is complete in a few minutes, but at this pH (III) is not readily oxidized further and therefore under these conditions the triol

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[1] J. M. Bruce, *Quart. Rev.*, 1967, **21**, 405.

[2] P. A. Leighton and G. S. Forbes, *J. Amer. Chem. Soc.*, 1929, **51**, 3549.

[3] F. Poupě, *Coll. Czech. Chem. Comm.*, 1947, **12**, 225.

[4] H.-I. Joschek and S. I. Miller, *J. Amer. Chem. Soc.*, 1966, **88**, 3273.

[5] M. Eigen and P. Mathies, *Chem. Ber.*, 1961, **94**, 3309.

[6] J. E. Lu Valle, G. M. Goldberg, D. L. Davidson, A. M. M. McNally, J. D. Roches, and M. Neary, Report No. TOI 58—29, 1958, Technical Operations Inc., Burlington, Mass., U.S.A.

(IV) is almost quantitatively converted into the quinone (III) by oxygen. In strongly alkaline solution the oxidation of benzene-1,2,4-triol (IV) is extremely fast and the colourless solution turns pink as soon as traces of oxygen enter. This phenomenon may be used as a sensitive test for oxygen and the purity of the oxygen-free nitrogen used in this work was checked in this manner. The reaction between benzene-1,2,4-triol (IV) and *p*-benzoquinone (I) to form quinol (II) and 2-hydroxy-1,4-benzoquinone (III) is fast in acid and very fast in alkali, but is slow between pH 4 and 6 (Figure 1). The reaction is of the second order ($t_{0\cdot5}$ is inversely proportional to the concentration) and at pH 4·7 (M/15 -KH_2PO_4 solution) the rate constant is 90 l. mole^{-1} sec.$^{-1}$ (31°). Below pH 2 and above pH 7, the rate constant is more than 4000 l. mole^{-1} sec.$^{-1}$.

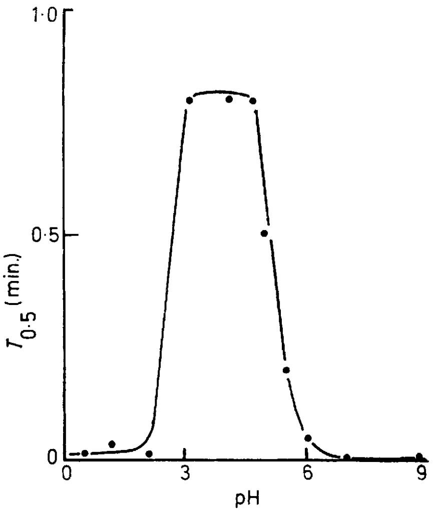

FIGURE 1 $t_{0\cdot5}$ of the reaction between *p*-benzoquinone (I) and benzene-1,2,4-triol (IV) (2×10^{-5}M each) at different pH values

Benzene-1,2,4-triol (IV) in N-H_2SO_4 is more readily oxidized by ceric ions than is quinol (II) so that slow addition of a ceric solution to a mixture of (II) and (IV) oxidizes the latter quantitatively to 2-hydroxy-1,4-benzoquinone (III) before the quinol (II) reacts to form *p*-benzoquinone (I). In Figure 2 the progress of the reaction is followed spectrophotometrically. An increase in the absorbance at 256 nm. is due to the formation of the hydroxy-quinone (III). When all the triol (IV) is oxidized, the quinol (II) begins to oxidize to benzoquinone (I) and the absorption maximum shifts towards 246 nm. About 80% of the quinol (II) is oxidized before further oxidation of the hydroxy-quinone (III) starts. Ceric titration with spectrophotometric control can thus be used to identify and estimate benzene-1,2,4-triol (IV) in the presence of quinol.

*2-Hydroxy-*1,4-*benzoquinone.*— 2-Hydroxy-1,4-benzoquinone (III) is fairly stable in strongly acid solutions. It has $\lambda_{\text{max.}}$ 256 (log ε 4·14), and 380 nm. (3·08) in acid medium. It polymerizes slowly especially above pH 2. At high concentration the polymeric product precipitates on standing as a dark brown material which has the properties of the so-called humic acid,[7] amorphous, brownish black, soluble in alkali, and insoluble in acid. The product is nonfusible, insoluble in many organic solvents such as chloroform, carbon tetrachloride, light petroleum, benzene, and ether but soluble in alcohol and acetone. The electronic absorption spectrum of an alcohol solution of the polymer has no characteristic maximum.

Photolysis.—pH *Effect.* The absorption coefficient of *p*-benzoquinone is very high at 2537 Å and therefore, when dilute (5×10^{-5}M) solutions of the quinone are exposed inside the helix of the lamp, photolysis is complete in 15 sec. Below pH 4 and above pH 7, the photoproducts are equimolar quantities of quinol (II) and 2-hydroxy-1,4-benzoquinone (III). Between pH 4 and 6, however, the photoproduct consisted chiefly of benzene-1,2,4-triol (IV), with (II) and (III) present as minor products only (Figure 3). On addition of ceric ions to the acidified solution of the photoproduct, the hydroxy-quinone (III) (recognised by its absorption at $\lambda_{\text{max.}}$ 256 nm.) is produced in the case of solutions whose original pH were between 4 and 6. At other pH values, *p*-benzoquinone (I) alone is the ceric oxidation product and $\lambda_{\text{max.}}$ shifts to 246 nm. as ceric solution is added. The absorbance at 256 nm. before addition of ceric ions and the increase in absorbance at 246 nm. after oxidation indicate that the yields of quinol and 2-hydroxy-1,4-benzoquinone during the photolysis are *ca.* 50% each. Dissolved air in the test solution has no effect on the

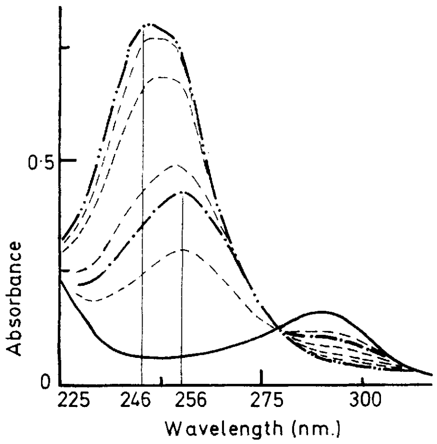

FIGURE 2 The change in the absorption spectrum of an equimolar mixture ($1\cdot25 \times 10^{-5}$M each in 1N-H_2SO_4) of quinol (II) and benzene-1,2,4-triol (IV) as a 0·004M-ceric sulphate solution (in 1N-H_2SO_4) is added in small portions (0·01—0·02 ml.); spectrum before addition of ceric solution (——); after successive additions of ceric (– – – –); corresponding to the complete oxidation of the triol to 2-hydroxy-1,4-benzoquinone (— · — · —); and when maximum absorbance in the 246 nm. region is reached (— · · — · · —) (this corresponds to *ca.* 80% of the quinol oxidized to *p*-benzoquinone; further addition of ceric oxidizes 2-hydroxy-1, 4-benzoquinone also)

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[7] N. M. Atherton, P. A. Cranwell, A. J. Floyd, and R. D. Haworth, *Tetrahedron*, 1967, **23**, 1653.

photolysis except when the photolysis has a long duration and when the pH is more than 7. Under these conditions, quinol is slowly oxidized by atmospheric oxygen to *p*-benzoquinone (I). This secondarily formed product recycles in the photolysis and the final photoproduct consists solely of polymerized (III), humic acid. These results can be explained by the reaction mechanism suggested by Poupě for the photolysis of *p*-benzoquinone solution by 3600—4600 Å light. Our results now offer experimental proof for Poupě's suggestion that the primary photochemical process is the conversion of *p*-benzoquinone (I) into benzene-1,2,4-triol (IV) [reaction (1)].

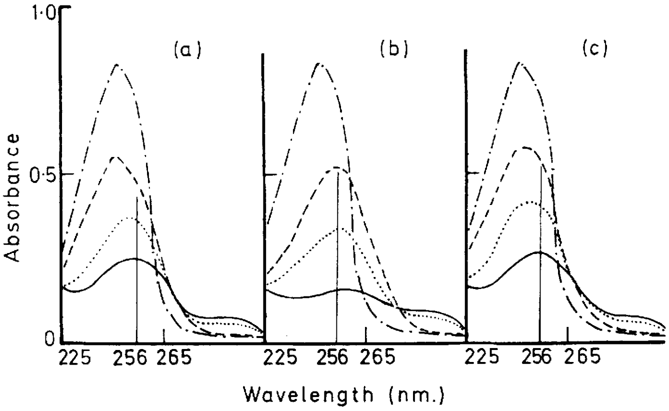
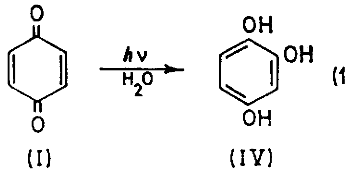
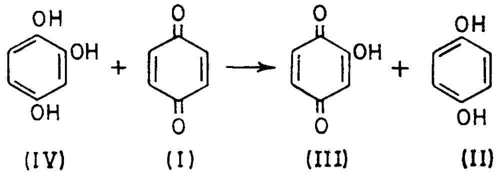


FIGURE 3 The pH effect on the photolysis. Spectra of *p*-benzoquinone (5 ml. of $2{\cdot}3 \times 10^{-5}$M solution in a 2 cm. cell) at pH (a) <3, (b) 4—6, and (c) >7 before irradiation with 2537 Å light (— · — · —); after addition of 6N-H_2SO_4 (1 ml.) to the completely photolysed solution (———); after the addition of 0·01—0·02 ml. portions of 0·004M-ceric solution (· · · ·); and when the maximum absorbance in the 246—255 nm. region is reached (– – – –)



(1)



(2)

In acid or alkaline medium, since reaction (2) is fast, the photoproducts are equimolar quantities of quinol (II) and 2-hydroxy-1,4-benzoquinone (III). Between pH 4 and 6, however, reaction (2) is slow and therefore the photoproduct consists largely of benzene-1,2,4-triol. The quantum efficiencies of the decomposition of *p*-benzoquinone with 2537 Å light at different values of pH are given in Table 1.

Light intensity and concentration effects. Further support for the above reaction mechanism was obtained when the light intensity and concentration effects were investigated. As the intensity of the 2537 Å light used for irradiation was decreased the photolysis took longer to reach completion and correspondingly, in neutral solution, the benzene-1,2,4-triol (IV) yield decreased. At the lowest intensity used more than 4 hr. were required for completion of the photolysis and the photoproducts were equimolar quantities of quinol (II) and 2-hydroxy-1,4-benzoquinone (III) [Figure 4(a)]. Similarly at neutral pH, when the initial *p*-benzoquinone concentration was increased, reaction (2) became dominant, the yield of benzene-1,2,4-triol (IV) decreased to zero [Figure 4(b)], and equimolar quantities of (II) and (III) were the photoproducts with the latter at high concentrations polymerizing to humic acid.

TABLE 1

Quantum efficiency ϕ of the decomposition of *p*-benzoquinone at different pH values by use of 2537 Å light

pH	ϕ
0·4 (1N-H_2SO_4)	0·30
1·1 (0·1N-H_2SO_4)	0·32
2·2 (0·01N-H_2SO_4)	0·28
4·8 (M/15-KH_2PO_4)	0·31
5·5 (Natural)	0·35
6·0 (Phosphate buffer)	0·29
7·0 (Phosphate buffer)	0·31
8·0 (Phosphate buffer)	0·32
Average	0·31 (σ = 0·02)

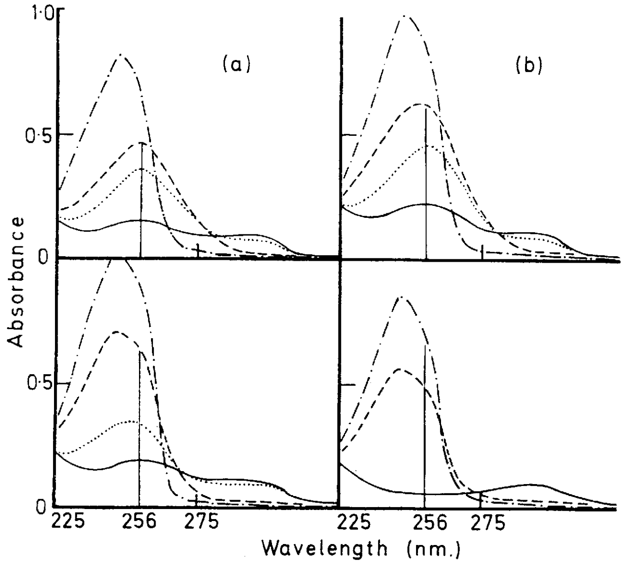


FIGURE 4 Light intensity (a) and the quinone concentration (b) effects on the photolysis with 2537 Å light. Spectra of *p*-benzoquinone (5 ml. of $2{\cdot}3 \times 10^{-5}$M solution in 2 cm. cell) at natural pH before irradiation with 2537 Å light (— · — · —); after addition of 6N-H_2SO_4 (1 ml.) to the completely photolysed solution (———); after the addition of 0·01—0·02 ml. portions of 0·004M-ceric solution (· · · ·); and when the maximum absorbance in the 246—255 nm. region is reached (– – – –). Upper curves $4{\cdot}5 \times 10^{18}$ quanta cm.$^{-2}$ min.$^{-1}$ and initial quinone concentration $2{\cdot}27 \times 10^{-5}$M for (a) and (b) respectively. Lower curves similarly 2×10^{15} quanta cm.$^{-2}$ min.$^{-1}$ and $1{\cdot}25 \times 10^{-2}$M

Wavelength effect. For the study of wavelength effect, $2{\cdot}5 \times 10^{-5}$M *p*-benzoquinone solutions at different values of pH (1N-sulphuric acid, natural, and in a phosphate buffer of pH 7) were employed. When the samples were irradiated 7 cm. from a 125 w u.v. discharge lamp (for 3650 Å light), the photolysis was complete in 2 hr. and when irradiated with a high-pressure mercury lamp (3650, 4046, 4358, 5460, and 5790 Å) the photolysis required 35 min. In both these cases the nature of the photoproducts obtained was similar to the photoproducts obtained when 2537 Å light was used for irradiation. At natural pH some benzene-1,2,4-triol (IV) was formed in addition to quinol (II) and 2-hydroxy-1,4-benzoquinone (III). For 3650 Å light, photolysis took 2 hr. for completion and the yield of (IV) was correspondingly lower. When a 200 w incandescent lamp was used for irradiation the photolysis took 6 hr. for completion and no triol (IV) was detectable even in neutral solution. In the absence of air, the photolysed solution at all pH values contained quinol (II) equivalent to 50% of the *p*-benzoquinone (I) photolysed.

Our results show that the primary photochemical process under all conditions investigated is the conversion of *p*-benzoquinone (I) into benzene-1,2,4-triol (IV). The primary process is independent of pH, the initial quinone concentration, the intensity and wavelength of the light used for irradiation, and the presence or the absence of oxygen. Whatever be the initial excitation process ($n \longrightarrow \pi^*$ or $\pi \longrightarrow \pi^*$) the excited states seem to cross over to the same final reactive state.[1,8]

Chloride and bromide effect. The quantum efficiency of the decomposition of *p*-benzoquinone is greatly diminished by the presence of added chloride or bromide in the test solution. The results are summarized in Table 2.

TABLE 2

Dependence of quantum efficiency on the halide concentration

[Halide] (M)	ϕ, in presence of Cl^-	ϕ, in presence of Br^-
0	0·31	0·31
3×10^{-4}	0·27	0·22
1×10^{-3}	0·20	0·17
3×10^{-3}	0·15	0·115
1×10^{-2}	0·068	0·051
3×10^{-2}	0·040	0·030
1×10^{-1}	0·033	0·025

The role of the chloride or bromide in the reaction mechanism is not well understood. These results support the view [4,8] that the excited *p*-benzoquinone molecule abstracts a hydrogen atom from a water molecule forming semiquinone and a hydroxyl radical and that the hydroxyl radical in turn either reacts with the semiquinone radical or another quinone molecule ultimately resulting in the formation of benzene-1,2,4-triol (IV). In the presence of chloride or bromide ions, however, the halide ion could scavenge the hydroxyl radical [9-11] and the resulting halogen atom could oxidize the semiquinone radical back to quinone thus diminishing the rate of the photolysis. Bromide ion is a better scavenger of hydroxyl radicals than chloride ion.[11]

Oxygen effect. An alternative or parallel mechanism, also suggested by Joschek and Miller,[4] namely hydroxyl radical abstraction from water followed by hydrogen atom attack on unexcited quinone, can be ruled out in view of the fact that oxygen showed no effect on the photolysis even at the lowest concentration ($2·3 \times 10^{-5}$M) of the quinone. Although *p*-benzoquinone is 5·7 times more reactive than oxygen towards hydrogen atoms,[12] the relatively high concentration ($1·25 \times 10^{-3}$M) [13] of oxygen in an O_2-saturated $2·3 \times 10^{-5}$M-*p*-benzoquinone solution would have caused some observable effect on the photolysis.

Prolonged irradiation effect. According to Poupě [3] 2-hydroxy-1,4-benzoquinone (III) on prolonged irradiation is reduced to benzene-1,2,4-triol (IV). Our results show that on prolonged irradiation (*a*) both quinols (II) and (III) are degraded more rapidly at lower than at higher values of pH but that no triol (IV) was produced either from (II) or (III) and (*b*) the triol (IV), produced during the photolysis at the natural pH of the solution, was unaffected.

EXPERIMENTAL

p-Benzoquinone (I) was sublimed. Quinol (II) was recrystallized from water and had m.p. 173°.

Benzene-1,2,4-*triol* (IV).—This was prepared by a modification of the method of Healy and Robinson.[14] A drop of concentrated sulphuric acid was added to 20 ml. of methanol and the mixture boiled to remove all dissolved air. Purified 1,2,4-triacetoxybenzene (10 g.) (m.p. 97·5°) was added. The solution was heated under reflux for 3½ hr. and while still hot was evaporated *in vacuo* until a viscous brown liquid was left which solidified to greyish white crystals (m.p. *ca*. 139°). Benzene was used for recrystallization, despite poor solubility, to give white flakes of (IV), m.p. 140—141° (Kofler hot-stage apparatus). Impure material gave a pink melt which did not readily resolidify whereas pure samples gave a colourless melt and recrystallized to square flakes on cooling.

2-*Hydroxy*-1,4-*benzoquinone* (III).—Solutions of known concentrations were prepared by the oxidation of standard solutions of (IV) at pH 8·8 (phosphate buffer) by atmospheric oxygen or by ceric ions in N-H_2SO_4 solution.

All other chemicals used were of AnalaR grade. Water was freshly double distilled. Phosphate buffers were used for solutions of pH 6—8. More alkaline solutions were prepared from sodium hydroxide. Acid solutions were prepared from sulphuric acid. Oxygen-free solutions were prepared by sweeping the solutions with oxygen-free nitrogen.

Photolysis and Analysis.—The sources of light were a Hanovia helical low-pressure mercury resonance lamp for 2537 Å, an Osram high-pressure mercury discharge lamp (250 w), a Gallenkamp u.v. discharge lamp (125 w) for 3650 Å, and a Mazda Incandescent lamp (200 w). The test solutions were always saturated with pure nitrogen before

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[8] N. K. Bridge and G. Porter, *Proc. Roy. Soc.*, 1958, *A*, **244**, 259, 276.

[9] H. A. Dewhurst, *J. Chem. Phys.*, 1951, **19**, 1329.

[10] K. C. Kurien, P. V. Phung, and M. Burton, *Radiation Res.*, 1959, **11**, 283.

[11] M. Burton and K. C. Kurien, *J. Phys. Chem.*, 1959, **63**, 899.

[12] P. Riesz and E. J. Hart, *J. Phys. Chem.*, 1959, **63**, 858.

[13] E. Douglas, *J. Phys. Chem.*, 1964, **68**, 169.

[14] M. Healy and R. Robinson, *J. Chem. Soc.*, 1934, 1625.

irradiation unless otherwise stated. The samples were irradiated in quartz cells except in the case of white light-irradiation, when Pyrex test-tubes were used. When very high intensity 2537 Å light was required for irradiation, 2 cm. spectrophotometer cells containing the test solution was placed in the centre of the helix. Since the photolysis was complete within seconds, cooling was unnecessary, and the temperature of the solution remained constant at 31°. When lower intensities of light were required for irradiation, the samples were placed further from the lamp. A 10% sodium chloride solution used as a filter for removing any lower wavelengths had no effect on the photolysis. While being irradiated the test solutions were kept cool at *ca.* 33° by a cold air blast, except for white light irradiation when samples were kept at 25° with running water. Checks showed that the products were unchanged when the temperature of the photolysed solution rose to 45°. After irradiation, the solutions were made 1N with respect to sulphuric acid and spectra were taken on a Unicam SP 800 recording spectrophotometer. The pH of solutions was determined with a Radiometer pH meter type PHM 22a.

Determination of Light Intensities and Quantum Efficiencies.—Light intensities were determined by the method of Hatchard and Parker,[15] *i.e.*, by irradiating 0·06M-potassium ferrioxalate solution (in 0·1N-sulphuric acid) in the cells used for irradiation of the *p*-benzoquinone solution. The quantum efficiency of ferrous production was taken as 1·18. Light absorption was almost 100% in all cases except in the case of white light or when the actinometer solution was irradiated inside the helix of the 2537 Å lamp.

In order to determine the quantum efficiency of the *p*-benzoquinone decomposition, the quantity of light absorbed by the test solution was estimated as follows: Four 2 cm. rectangular cells (2 × 1 × 4) were placed in a cardboard box holder whose front and back were open and the two rows of the cells were separated by a piece of cardboard. The holder with the actinometer solutions in all cells was placed in a reproducible position in front of the 2537 Å lamp. The solution in the front cells absorbed all the light. Filling the front cells 1 and 3 with water and the rear cells with the actinometer solution, light intensities in the positions 2 and 4 were also determined and found to be identical. The ratio, *k*, of light intensities in positions 2 and 3 was established by placing actinometer solution in cells 2 and 3 and water in cell 1 before irradiation. Finally, cell 3 was filled with *p*-benzoquinone solution ($3{\cdot}4 \times 10^{-5}$M), cell 1 with water, and the other cells with the actinometer solution. After irradiation for 30 sec., the amount of quinone decomposed and the ferrous ions produced in the respective cells were determined spectrophotometrically. The quantity of light absorbed was determined from equation (3), where $I_{4,\mathrm{w}}$ is the quantity of light absorbed by the actinometer solution in cell 4 with water in cell 3

$$\text{Quantity of light absorbed by the quinone solution in cell } 3 = k(I_{4,\mathrm{w}} - I_{4,\mathrm{b}}) \qquad (3)$$

(this is equal to $I_{2,\mathrm{w}}$, *i.e.*, the quantity of light absorbed by the actinometer solution in cell 2 with water in cell 1), and $I_{4,\mathrm{b}}$ is the quantity of light absorbed by the actinometer solution in cell 4 with the *p*-benzoquinone solution in cell 3.

[9/1810 *Received, October 24th*, 1969]

[15] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, *A*, **235**, 518.