489. The Radiation and Photochemistry of Aqueous Solutions of Benzene.

By ISRAEL LOEFF and GABRIEL STEIN.

Saturated aqueous solutions of benzene, when irradiated with *X*-rays in the presence of oxygen, yield as major primary products phenol (*G* 1·8) as well as mucondialdehyde [*G* 1·5 (acid solutions) 0·8 (neutral solutions)]. Another primary product is probably pyrocatechol [$G = 0{\cdot}3$]. It is shown that both phenol and mucondialdehyde may be formed by way of free-radical intermediate. The yields of phenol and of mucondialdehyde depend on the dose rate. A mechanism accounting for the aromatic ring-opening is discussed.

The photochemistry of saturated aqueous solutions of benzene has been investigated in the presence and absence of oxygen. In the presence of oxygen at neutral pH, the main photochemical product is mucondialdehyde, and phenol is not formed in significant amounts. At acid pH values in the presence of oxygen, mucondialdehyde is not formed and acid-catalysed addition of water to benzene appears to prevail. With evacuated solutions the latter process appears to predominate at all pH's.

THE radiolysis of aqueous solutions of benzene has been much investigated.[1-7] In attempts to elucidate the reaction mechanism, attention was paid mainly to phenol and other phenolic products, and relatively little to the reaction in the presence of oxygen, yielding mucondialdehyde, observed by Stein and Weiss.[8,9] These authors assumed this

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[1] (*a*) Stein and Weiss, *J.*, 1949, 3245; (*b*) Loeff and Stein, *Nature*, 1959, **184**, 901.

[2] Sworski, *Radiation Res.*, 1954, **1**, 231.

[3] Baxendale and Smithies, *J. Chem. Phys.*, 1955, **33**, 604.

[4] Baxendale and Smithies, *J.*, 1959, 779.

[5] Proskurnin, Barelko, and Kartasheva, *Doklady Akad. Nauk S.S.S.R.*, 1958, **121**, 671.

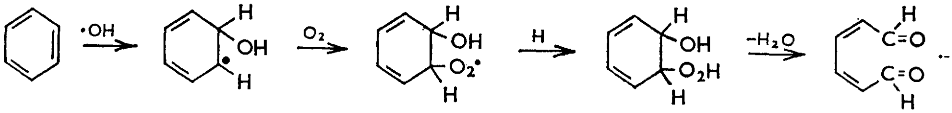
[6] Proskurnin *et al.*, Proc. 2nd Internat. Conference Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. XXIX, 52.

[7] Phung and Burton, *Radiation Res.*, 1957, **7**, 199.

[8] Stein and Weiss, *J.*, 1949, 3254.

[9] Stein and Weiss, *J.*, 1951, 3265.

reaction to be the result of several stages of radiation-induced reaction, involving prior formation of phenol and other products. Daniels, Scholes, and Weiss[10] reinvestigated the reaction and suggested another mechanism (1), involving an unstable hydroxy-hydroperoxide:



(1)

Thus mucondialdehyde would be a "primary" radiation product, albeit according to their determinations a minor one.

Proskurnin *et al*[6] later expressed the opinion that the aldehyde and pyrocatechol (formed as a minor product) are produced by the primary interaction of benzene and oxygen, not however by a free-radical mechanism but by one involving the excited state of one of the reactants.

In the present work we studied quantitatively the formation of the aldehyde and the other products, in attempts to formulate a satisfactory reaction mechanism. The reported *G*(phenol) values differ considerably;[11] dialdehyde formation is completely disregarded by a number of authors;[3,4,7] but the impossibility of achieving a satisfactory material balance has been pointed out.[12]

It was also of particular interest to decide to what extent free-radical intermediates and/or excited molecules are responsible for the formation of the various products, and for ring-opening in particular.

We therefore investigated the photochemistry of aqueous benzene solutions in the presence of oxygen, under conditions where the light was absorbed by the benzene. This system offers some points of general interest in the photochemistry of aqueous solutions, since the interaction of excited aromatic molecules with the aqueous solvent and with oxygen in a dipolar solvent could be examined.

There are two brief records[6,7] indicating that experiments have been performed on this system, but no detailed report. We shall discuss these in the light of our experiments.

EXPERIMENTAL

Materials.—Triply distilled water was used. Low pH values were adjusted with "AnalaR" sulphuric acid, higher values with 0·1M-phosphate buffers prepared from commercial salts (May and Baker's "Suitable for Analysis"). Between pH 2 and 4 experiments were carried out with the pH set by either sulphuric acid or phosphate, with identical results. Benzene was of "AnalaR" grade, with low thiophen and carbon disulphide contents. All aqueous solutions were saturated with benzene and thus contained $\sim$0·15% w/w.

Irradiations.—These were carried out with 200 kvp *X*-rays at 15 mA; 100 ml. of solution were usually used, the dose rate being $\sim$1300 rad min.$^{-1}$ ($\sim 1{\cdot}4 \times 10^{18}$ ev l.$^{-1}$ sec.$^{-1}$). In some experiments a dose rate of 6600 rad min.$^{-1}$ ($\sim 7 \times 10^{18}$ ev l.$^{-1}$ sec.$^{-1}$) was used. The dose was determined by using the Fricke dosimeter and assuming that $G(\mathrm{Fe}^{3+}) = 15{\cdot}5$. If $G\ (\mathrm{Fe}^{3+}) = 14{\cdot}5$, all results in the present paper have to be multiplied by 0·93.

Analyses.—Analytical results reported are the mean values of duplicate experiments.

Phenol was determined by obtaining first the total phenolic equivalent with Folin's reagent at a basic pH.[1] The molar extinction coefficients found were: phenol 5600, pyrocatechol 12,000, and quinol 5600, all at 520 mμ. The dihydric phenols were then determined separately by using Folin's reagent at an acid pH.[9] The molar extinction coefficients, measured at 750 mμ were: phenol 65, pyrocatechol 20,600, and quinol 4200. Thus in the acid Folin test phenol itself may be neglected. As discussed below, it was assumed that the acid Folin test is due to

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[10] Daniels, Scholes, and Weiss, *J.*, 1956, 832.

[11] Goodman and Steigman, *J. Phys. Chem.*, 1958, **62**, 1020.

[12] Kurien, Phung, and Burton, *Radiation Res.*, 1959, **11**, 283.

pyrocatechol, and the appropriate value was subtracted from the results of the basic Folin test to yield the value for phenol alone. The accuracy of the phenol determination was ±3%.

Hydrogen peroxide was determined by the I_3^- mthod [13] at 350 mμ. Control determinations were carried out by the Ti^{4+} method.[14] The more sensitive I_3^- method gives erratic results in acid solutions, where the Ti^{4+} method was used accordingly.

Mucondialdehyde was determined by spectrophotometric measurement at 390 mμ of the di-*p*-nitrophenylhydrazone in aqueous sodium hydroxide, where $\varepsilon = 8240$. The method was essentially similar to Stein and Weiss's qualitative procedure.[8] In order to obtain quantitative results, the following procedure (calibrated with synthetic mucondialdehyde [15]) was used: To the irradiated solution (40 ml.) a solution (20 ml.) of *p*-nitrophenylhydrazine (2·5 g.) in 1·6N-sulphuric acid (1 l.) was added. Condensation was complete in 45 min. at room temperature. The solution was extracted with carbon tetrachloride (50 ml.). A solid always appeared at the interface. The organic phase was separated and washed with 1·6N-sulphuric acid (20 ml.), to remove the excess of reagent. The extracted aqueous phase remaining was filtered through glass wool which retained the precipitate formed at the interface. This solid was dissolved by passing 2N-sodium hydroxide (20 ml.) through the glass wool, and this alkali solution was then used to extract the hydrazone from the carbon tetrachloride. The alkaline extract was kept for 10 min. in a boiling-water bath. The initially bluish, unstable colour became orange-yellow and was then permanent. The accuracy of the determination of mucondialdehyde was ±7%.

The soluble part of the mucondialdehyde derivative, which passed into carbon tetrachloride directly, and the insoluble part gave different initial colours in sodium hydroxide solutions but, when the solution was heated, both changed to the same colour. They may represent different isomeric forms of the derivative. Since the presence or absence of quinones in the solution after irradiation was of interest, we developed methods for the determination of 1,2- and 1,4-benzoquinone when present in aqueous solution simultaneously with the dialdehyde. These gave derivatives with *p*-nitrophenylhydrazine, in the case of *o*-quinone with $\varepsilon = 7000$ at 510 mμ and with a minimum at 400 mμ, and in the case of *p*-quinone with $\varepsilon = 24{,}000$ at 470 mμ. With measurements at these wavelengths it was possible to determine each component of synthetic mixtures.

Photochemical Experiments.—Irradiations were carried out by using, according to the requirements either a medium-pressure 500-w mercury lamp or a low-pressure mercury resonance lamp of spiral form, in the centre of which the reaction vessel was introduced. In order to isolate photochemically active parts of the spectrum, the radiation was in all cases filtered through a sufficient length of 0·1M-sodium chloride, which removed all radiation below 2100 Å. In the low-pressure lamp it was found that 95% of the radiation was in the 2537 Å region. Use of a uranyl oxalate actinometer showed that under our conditions the dose rate was $1{\cdot}3 \times 10^{-3}$ einstein $l.^{-1}$ $min.^{-1}$. 75 ml. of solution were always irradiated.

With the medium-pressure lamp, only the sodium chloride filter was used, so that radiation above 2100 Å reached the solution; using the uranyl oxalate actinometer showed that, after allowance for the difference in absorption between benzene in water and uranyl oxalate over the entire spectrum, and for the relative intensities of the various wavelengths emitted, the dose rate absorbed in our solutions was 5×10^{-3} einstein $l.^{-1}$ $min.^{-1}$. In a number of experiments all radiation below 2900 Å was removed by interposing a copper sulphate filter in order to establish what proportion of the photochemical products obtained is due to light below and above this wavelength.

Experiments in the absence of oxygen were carried out by freeing the solution, in the presence of an excess of benzene, of dissolved air by repeated evacuation, until (with all condensable substances trapped by liquid air) the pressure of non-condensable gas in equilibrium with our solution remained below 10^{-3} mm.

Photochemistry of Benzene Solution in the Presence of Hydrogen Peroxide.—The 500-w medium-pressure lamp was used, the light being filtered through 5 cm. of 0·75% copper sulphate solution, which filters out all light below 290 mμ. In the irradiation of solutions of benzene containing hydrogen peroxide, with light of wavelengths which decompose only hydrogen peroxide, it was ascertained that only light below 290 mμ gave photochemical products

[13] Hochanadel, *J. Phys. Chem.*, 1952, **56**, 587.
[14] Eisenberg, *Ind. Eng. Chem.*, 1943, **15**, 327.
[15] Karrer, Eugster, and Perl, *Helv. Chim. Acta*, 1949, **32**, 1013.

directly from benzene. Actinometry was carried out with uranyl oxalate,[16] allowance being made for the differing absorption of uranyl oxalate and hydrogen peroxide. $1{\cdot}55 \times 10^{-5}$ einstein l.$^{-1}$ min.$^{-1}$ was absorbed in the actinometric solution. Account was taken of the significant amount of products obtained in control experiments, without irradiation, particularly at higher hydrogen peroxide concentrations.

RESULTS

Fig. 1 shows the results obtained when air-saturated solutions were irradiated with *X*-rays at pH 7. Curve 1 shows the yield of mucondialdehyde as a function of dose, curve 2 the results obtained by means of the alkaline Folin procedure. The results shown in curve 2 are calculated on the assumption that the product is phenol itself alone, and are thus comparable with those of previous workers. They show that " phenol " is a primary product formed with an intial $G \sim 2{\cdot}5$, in agreement with previous results.

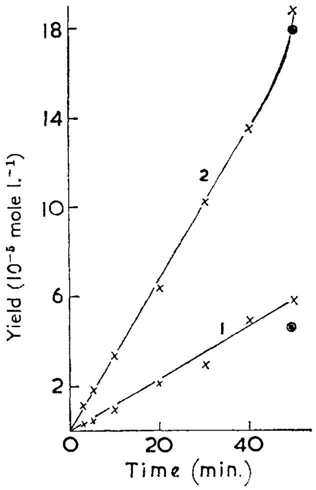

FIG. 1.

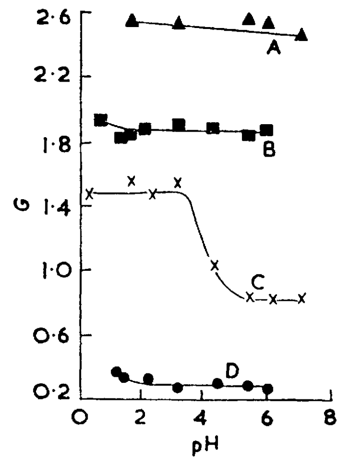

FIG. 2.

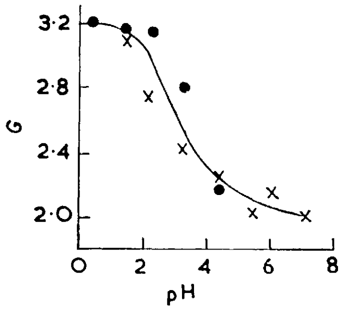

FIG. 3.

FIG. 1. Yields as a function of dose at pH 7·1.

Dose rate, 1378 rad/min. (1) Mucondialdehyde. (2) Phenol, estimated by Folin's reagent at basic pH. The circles show results obtained in presence of initially added phenol (2×10^{-4}M).

FIG. 2. Initial yields as a function of pH.

Dose rate, 1378 rad/min. (A) Phenol, estimated by Folin's reagent in basic conditions. (B) Phenol, corrected for pyrocatechol. (C) Mucondialdehyde. (D) Pyrocatechol, estimated by Folin's reagent in acidic conditions.

FIG. 3. Initial *G* values of H_2O_2 as a function of pH.

● Ti^{4+} method. × I_3^- method.

Baxendale and Smithies [3,4] showed that results obtained in this system by the use of the alkaline Folin procedure are higher than the true yield of phenol. Using a method of analysis [11] which excludes interfering substances and determines phenol only, they found $G \sim 1{\cdot}6$ for the formation of phenol. The alkaline Folin test for phenol is affected by pyrocatechol and quinol, if present. The acid Folin test on the other hand determines mainly these two, but not phenol. Specific colour tests of the irradiated solution indicated the presence of pyrocatechol. The results of the acid Folin test, calculated by assuming that it is due to pyrocatechol alone, gave *G*(catechol) 0·3. Subtracting the optical-density value corresponding to this amount from the results of the alkaline Folin test gives a corrected value of *G* 1·87 for the formation of phenol alone, in fair agreement with the results of the procedure employed by others.[3,4]

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[16] Bowen, " The Chemical Aspects of Light," Oxford Univ. Press, 1946, 2nd edn., p. 283.

The pH-dependence of the yield of phenol, uncorrected and corrected, as well as that of pyrocatechol, is shown in Fig. 2. Between pH 1 and 6 the values remain nearly constant at the dose rate employed.

On the other hand, the G value of formation of mucondialdehyde is seen in Fig. 2 to be strongly pH-dependent. In Fig. 1, curve 1 shows that mucondialdehyde at pH 7 is a primary product, and its formation does not require the preceding production of, *e.g.*, phenol by irradiation. Similar linear dependence on dose is observed at all pH values, but the yield increases from G 0·80 in neutral solution to G 1·5 in acid solutions. In alkaline solution, mucondialdehyde is unstable and could not be determined. We tested for the formation of *o*- and *p*-quinones under all experimental conditions but found none. Were 1,2-benzoquinone formed with G 0·03 or 1,4-benzoquinone with G 0·01 we could have detected them.

Fig. 3 shows the yield of hydrogen peroxide as a function of pH, determined by the I_3^- and the Ti^{4+} method. The former is the more sensitive and could be used at low total doses, so that the initial yield of hydrogen peroxide could be determined. However, it could not be used at low pH values, and at higher doses it gave erratic results, owing to reaction of the reagent with some of the reaction products; this could be shown, *e.g.*, with pyrocatechol. Therefore, the less sensitive Ti^{4+} method was also used for comparison. It is seen that both methods give results in fair agreement and indicate a pH-dependence of the yield of hydrogen peroxide, with G 3·1 at low pH, decreasing above pH 4 to $G \sim 2{\cdot}2$. Our results thus support the findings of Baxendale and Smithies [3,4] who found a pH-dependence, rather than those of Phung and Burton [7] who did not.

To investigate further the possible processes involved in the formation of phenol and mucondialdehyde in X-irradiated solutions, the dose rate was varied. The results obtained at 1225 and at 6570 rad min.$^{-1}$ at different pH values are shown in the Table.

	G (phenol)		G (mucondialdehyde)	
pH	1225 rad/min.	6570 rad/min.	1225 rad/min.	6570 rad/min.
2·2	1·87 ± 0·06	2·15 ± 0·06	1·48 ± 0·1	0·98 ± 0·07
5·4	1·87 ± 0·06	1·97 ± 0·06	0·80 ± 0·06	0·62 ± 0·05

Fig. 4 shows the results obtained when saturated aqueous solutions of benzene containing various concentrations of hydrogen peroxide were irradiated at different pH values with ultraviolet light of wavelengths which are photochemically active in splitting hydrogen peroxide into hydroxyl radicals, but do not affect benzene directly. Fig. 5 shows the ratio of phenol (uncorrected) to mucondialdehyde formed at two pH values, as a function of hydrogen peroxide concentration. Again both mucondialdehyde and phenol are primary products, and their ratio is similar to that in neutral solutions irradiated with X-rays. However, this ratio does not depend on pH in the same manner as in the case of X-rays.

Photochemistry of Benzene Solutions.—In order to establish which part of the absorption spectrum of benzene is photochemically active, and in particular to see whether the singlet–triplet transitions above 3000 Å are photochemically active, saturated aqueous solutions of benzene were irradiated in the presence of air with the light of the medium-pressure lamp, unfiltered except for the sodium chloride filter which removes wavelengths below 2100 Å. The products were quantitatively determined. The irradiations were repeated for identical conditions, but with the copper sulphate filter which transmitted all wavelengths above 3000 Å up to 4000 Å, but removed wavelengths below 2900 Å. Only barely detectable traces of products were obtained. Thus, under our conditions the observed photochemical yield is due to primary absorption in the singlet–singlet bands around 2500—2600 Å.

We investigated the spectra of air-saturated and evacuated aqueous solutions saturated with benzene and found no detectable difference. Thus, at the relatively low partial pressures of oxygen present in our experiments the absorption spectrum between 2100 and 4000 Å is not observably affected by the presence of oxygen.

Result in the Presence of Oxygen.—In view of these results most of the experiments were carried out with the low-pressure mercury resonance lamp, with its main output at 2537 Å. Fig. 6 shows results obtained when air-saturated solutions of benzene in water were irradiated. It shows that at the higher pH, in neutral solutions, mucondialdehyde is formed as a primary product. Its yield is a linear function of the dose. However, at the lower pH, mucondialdehyde is seen not to be formed initially at all.

In a study of this effect of the pH, the results shown in Fig. 7 were obtained in the acid region. They indicate that in acid solution mucondialdehyde is not formed as a major primary product, whilst as the pH increases its initial yield grows. Thus the pH-dependence of its formation is entirely unlike the situation in *X*-irradiated solutions. (The aldehyde formed in these experiments was isolated as the *p*-nitrophenylhydrazone. Its behaviour on paper chromatography,[17] and its spectrum, were very similar to those of the product of *X*-irradiation. Regarding the relation to synthetic mucondialdehyde we observed the same difference which Daniels, Scholes, and Weiss [10] observed and discussed.)

In order to establish the formation of other products, Folin's test in acid and alkaline media was carried out on solutions irradiated at different pH values. The results are shown in Fig. 8.

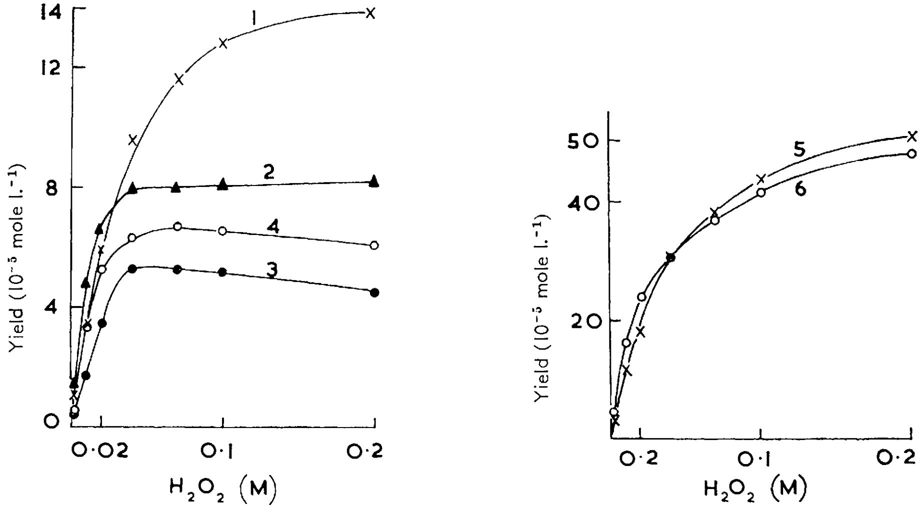

FIG. 4a. FIG. 4b.

FIG. 4a and b. Photodecomposition of hydrogen peroxide in the presence of saturated benzene solutions, as a function of hydrogen peroxide concentration. $\lambda > 290$ mμ The dose absorbed by the same volume of an actinometry solution of uranyl oxalate was $3{\cdot}50 \times 10^{-5}$ einstein.

Yield of (1) mucondialdehyde at pH 1·4, (2) mucondialdehyde at pH 4·3, (3) " pyrocatechol " at pH 1·4 estimated by Folin's reagent at acid pH, (4) " pyrocatechol " at pH 4·3 estimated by Folin's reagent at acid pH, (5) "phenol" at pH 1·4 estimated by Folin's reagent at basic pH, and (6) " phenol " at pH 4·3 estimated by Folin's reagent at basic pH.

It will be seen that in the neutral solution both the acid and the basic Folin test indicate primary formation of a reacting substance whilst at the acid pH the initial yield of the product which reacts with Folin's reagent is greatly decreased.

To see whether the substance giving the Folin test is a phenol or whether the Folin reaction is due to an interfering substance, we investigated the absorption spectrum of the irradiated solutions. The spectrum which is obtained at pH >3 and in the presence of oxygen resembles most closely that of quinol, having $\lambda_{\text{max.}}$ 2940 Å, but is apparently not identical with it. Similarly, when the values of the Folin reagent test are calculated, the results resemble those expected for pyrocatechol, but are not identical with it. The product appears to be more acidic than quinol or pyrocatechol. With diazotised sulphanilic acid it gave a derivative resembling that from pyrocatechol. With 2,6-dichloro-1,4-benzoquinone chloroimide it gave the colour reaction typical of phenols with an unsubstituted *para*-position. We conclude that the product contains phenols, but its main component in the present case is certainly not phenol itself. In an attempt to elucidate the changes occuring as the pH decreases we

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[17] Gasparič and Večera, *Coll. Czech. Chem. Comm.*, 1957, **22**, 1426; Smitt, Moriconi, and O'Connor, *Analyt. Chem.*, 1956, **28**, 249.

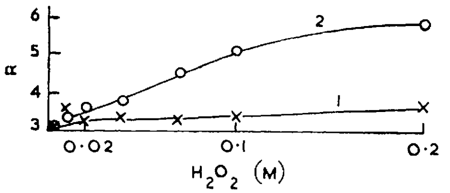

FIG. 5. Photodecomposition of hydrogen peroxide in the presence of saturated benzene solutions as a function of hydrogen peroxide concentration. $\lambda > 290$ mμ. The dose absorbed by the same volume of an actinometry solution of uranyl oxalate was $3{\cdot}50 \times 10^{-5}$ einstein.

R = " phenol "/mucondialdehyde, where " phenol " was estimated by Folin's reagent at basic pH. pH = (1) 1·4, (2) 4·3.

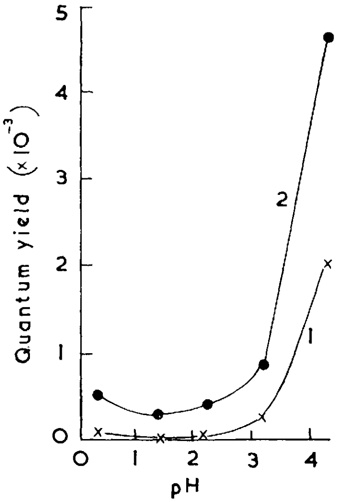

FIG. 7. pH-dependence in the presence of oxygen.

Quantum yield of (1) mucondialdehyde and (2) hydrogen peroxide (Ti^{4+} method) after passage of $6{\cdot}5 \times 10^{-3}$ einstein $l.^{-1}$.

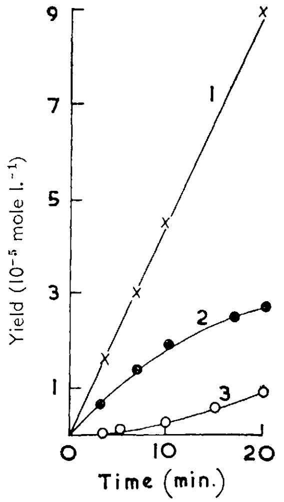

FIG. 6. Yield of products as a function of dose in the presence of oxygen.

Dose rate, $1{\cdot}3 \times 10^{-3}$ einstein $l.^{-1}$ $min.^{-1}$. (1) Mucondialdehyde at pH 7·1; (2) H_2O_2 (Ti^{4+} method) at pH 2·2; and (3) mucondialdehyde at pH 2·2.

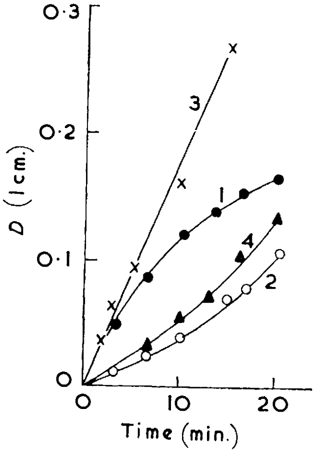

FIG. 8. Yield of products as a function of dose in the presence of oxygen [15 ml. of original solution. Final dilution: (1) and (2) 100 ml.; (3 and 4), 50 ml.]. Dose rate, $1{\cdot}3 \times 10^{-3}$ einstein $l.^{-1}$ $min.^{-1}$.

Absorption in acid Folin test at 750 mμ at (1) pH 7·1, (2) pH 2·2, and in basic Folin test at 520 mμ at (3) pH 7·1, (4) pH 2·2.

investigated the pH-dependence of the formation of the products giving the Folin tests. The results (Fig. 9) show that the behaviour in the basic Folin test has the pH-dependence of the formation of dialdehyde and hydrogen peroxide; they indicate that in acid solution the product giving this test is not formed. In acid solution, however, another product is formed, capable of reacting with the " acid " Folin reagent. When the spectra of the solutions were investigated, no evidence for the formation of a phenolic product could be obtained in solutions irradiated at an acid pH. Diazotisation and the chloroimide tests were also negative.

Fig. 6 shows hydrogen peroxide to be a primary product even in acid solutions. However, its primary yield, as shown in Fig. 7, is strongly dependent on pH, this behaviour paralleling that of the aldehyde; in addition there is a residual yield of hydrogen peroxide even in acid solutions. With increasing dose, hydrogen peroxide is destroyed at all pH values, and thus its rate of formation decreases as the dose increases.

Hydrogen peroxide was determined by the Ti^{4+} and the I_3^- method. Again the Ti^{4+} method gave consistently higher results; this is because some of the iodine liberated is lost by iodination of the products, as could be shown with pure pyrocatechol.

Results in the Absence of Oxygen.—In the presence of oxygen, in acid solution neither the dialdehyde nor the " phenolic compound " is formed, but a new product appears. To investigate the nature of this product, we assumed one possibility, that as the pH decreases, excited benzene molecules may add the elements of water, as was shown for other unsaturated compounds.[18] This addition would compete with the reaction between excited benzene molecules and oxygen, which leads to mucondialdehyde and " phenolic compound." To establish this, we carried out some experiments in evacuated solutions. A product was formed which reacted with great ease in the cold with bromine water, and with Folin's reagent at both acid and alkaline pH.

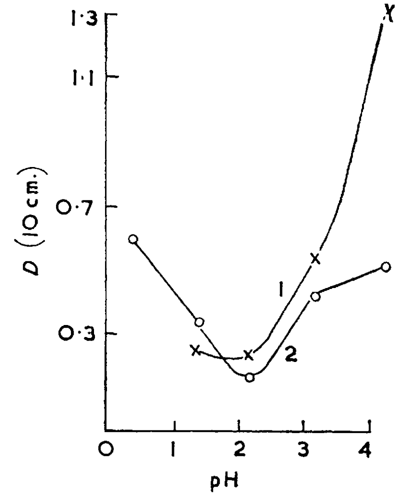

FIG. 9. pH-dependence in the presence of oxygen. Dose: $6{\cdot}5 \times 10^{-3}$ einstein $l.^{-1}$. Absorption in (1) basic Folin test at 520 mμ and (2) acid Folin test at 750 mμ.

In these experiments in the absence of oxygen, careful search for hydrogen was made by gasometric micro-methods. None is evolved in the reaction leading to the photochemical product. Numerous attempts to isolate and identify the product or its derivatives failed, also no solid bromo-derivative could be isolated. At no pH value could the formation of dialdehyde or " phenolic compound " be shown by their specific reactions. When solutions prepared by irradiation at acid pH in the presence or absence of oxygen are irradiated and then heated at 90—100° in the presence of oxygen and 0·8N-sulphuric acid they yield mucondialdehyde with simultaneous decrease in the Folin value.

DISCUSSION

Irradiations with X-Rays.—The experimental results lead to conclusions regarding some hitherto controversial points, but for some others suffice only to indicate likely possibilites.

Phenol and mucondialdehyde are both " primary " radiation products in the sense that their formation does not involve any of the stable reaction products as intermediates. Their formation is initiated by the free radicals derived from the decomposition of water

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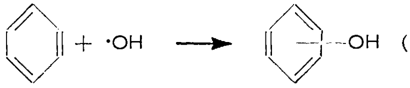
[18] Sinsheimer and Hastings, *Science*, 1949, **110**, 525; Wang, *Nature*, 1959, **184**, 184; BA 59.

by the ionising radiation. That free-radical intermediates may lead to simultaneous formation of phenol and mucondialdehyde at the various pH values, and in approximately the proportion observed in the radiolysis, is shown by the photochemical decomposition of hydrogen peroxide in the presence of benzene. Here the primary photochemical process results in the formation of hydroxyl radicals. There will be competition for these radicals between the benzene present and hydrogen peroxide, the latter yielding hydroperoxy-radicals ($\cdot OH + H_2O_2 \longrightarrow H_2O + HO_2\cdot$). Thus $\cdot OH$ and $HO_2\cdot$ radicals will be present. These will be also the reactive intermediates produced by the ionising radiations, since the primary overall radiolysis, which may be represented as (HOH) $\longrightarrow$ H, OH, H_2, H_2O_2, will yield molecular hydrogen, hydrogen peroxide, hydroxyl radicals, and hydrogen atoms, which in the presence of oxygen form hydroperoxy-radicals ($H + O_2 \longrightarrow HO_2\cdot$). In the photochemical decomposition of hydrogen peroxide the ratio $\cdot OH : HO_2\cdot$ will depend on the concentration of hydrogen peroxide employed. In the pH range used in the present work, of the intermediates considered here only the hydroperoxy-radical will be affected by changes in pH. Its p*K* value being [19] ~4, the equilibrium, $HO_2\cdot \rightleftharpoons H^+_{aq.} + O_2{}^-{}_{aq.}$, has to be taken into account. For radiolysis in neutral solution the primary intermediate, e_{aq}, may be directly captured by oxygen before it is transformed into hydrogen atoms by reaction with $H^+_{aq.}$ or with water, and so in these solutions $O_2{}^-{}_{aq.}$ will be the primary form, entering the last equilibrium as formulated.

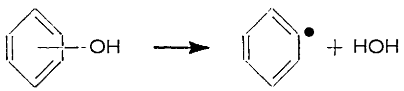
Qualitative comparison of the radiolytic experiments and the photolytic decomposition of hydrogen peroxide in the presence of benzene shows that radical reactions can lead to the observed products. A more quantitative comparison is difficult because of the different $\cdot OH : HO_2\cdot$ ratio, because of possible reaction between an intermediate R· and hydrogen peroxide at higher concentrations leading to one of the final products, and because of the different dose rates employed.

Regarding the mechanism of formation of the various products, the results in the Table confirm the observations of Proskurnin and his co-workers [20] that an increase in dose rate increases the yield of phenol and that its pH-dependence also changes slightly with dose rate. Our results show also that increased formation of phenol with increased dose rate is accompanied in both acid and neutral solution by decreased dialdehyde formation. A possible explanation, which agrees with the experimental results, is the following: Hydroxyl radicals add to benzene molecules:

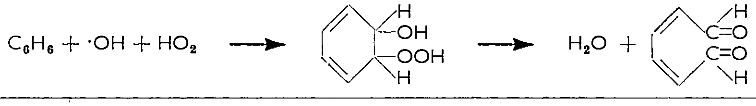


(1)

the formula on the right indicates the possibility of addition to any one of the six carbon atoms of the benzene ring. The addition radical (I) may lose water in an exoergic process:



and the resulting phenyl radical reacts with oxygen or a hydroperoxy-radical, to yield eventually phenol and hydrogen peroxide. If, however, the addition radical (I) during its existence adds oxygen or a hydroperoxy-radical then by the mechanism envisaged by Daniels, Scholes, and Weiss [10] it may form a hydroxy-hydroperoxide which on dehydration gives mucondialdehyde:



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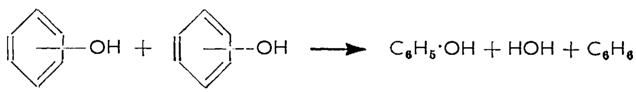
[19] Czapski, personal communication.

[20] Proskurnin, Orekhov, Barelko, and Chernova, Proc. 1st All-Union Conference Radiation Chemistry, Moscow, April 1957, p. 117.

At high dose rates, however, two addition radicals (I) may encounter each other, reacting as follows:



In this process one molecule of phenol is formed for the loss of two radicals which might have yielded mucondialdehyde. There are a number of possible variations on this sequence, *e.g.*, addition of oxygen instead of a hydroperoxy-radical. We have insufficient evidence to elucidate the mechanism in greater detail.

Dorfman *et al.*[21] recently investigated the aqueous benzene system with the help of pulse radiolysis, finding that hydroxyl addition to the benzene ring is indeed the initiating step. Owing to very high intensities used by these workers, the dose-rate-dependence of G(phenol) observed by them cannot be extrapolated to the dose rates employed in the present work. With regard to the monomolecular decomposition of the primary radical (C_6H_6OH), which certainly takes place in the absence of oxygen, to yield biphenyl, its rate constant remains to be measured before its importance in the presence of oxygen can be estimated.

Two further points deserve mention. The increase in the yield of mucondialdehyde and hydrogen peroxide as the pH decreases is very nearly equivalent, while the yield of phenol remains constant. We cannot account for this. Secondly, a minor primary product, which may be pyrocatechol, is formed with G 0·3. In neutral, but not in acid, solutions the rate of its initial formation shows it to be a " primary " product. The photochemical experiments offer some indication of its mode of formation. Pyrocatechol is an isomer of mucondialdehyde: experiments will have to be carried out to decide whether their photochemical interconverion is possible. The results of Scholes and Weiss[22] appear to provide indirect support of the conclusion that the mechanism involves hydroxyperoxide intermediates, and of the present conclusion that in the case of benzene these yield mucondialdehyde as the preferred product.

Photochemical Results.—Comparing our photochemical results with those of *X*-irradiation, we conclude that the mechanisms are entirely different in the two cases with regard to the major products. In solutions irradiated with ultraviolet light which is absorbed by benzene and leads to a singlet–singlet transition, mucondialdehyde is formed in neutral solutions in a reaction involving oxygen. This reaction is in competition with (probably) the addition of the elements of water to benzene. In acid solutions the latter reaction prevails, even in the presence of oxygen. We have no evidence whether the benzene species actually reacting is the excited singlet state first obtained or another species derived therefrom. Nor have we proved that the product in acid oxygen-containing solutions is identical with that formed in the absence of oxygen at all pH values.

In addition to mucondialdehyde, a phenolic product, which is not phenol but may contain quinol and/or pyrocatechol, is produced in the presence of oxygen at neutral pH. On the other hand, in *X*-irradiated solutions phenol itself is the major product, with mucondialdehyde, both being formed apparently from free-radical intermediates. We cannot exclude the possibility that in *X*-irradiated solutions of benzene a minor part of the products (mucondialdehyde and " phenolic compound ") is derived from excited molecules, but there is no evidence for this. On the contrary, *X*-irradiated solutions at acid pH give higher yields of dialdehyde. When kept at 100° such *X*-irradiated solutions give no evidence for prior formation of a benzene–water addition product or products.

The acid-catalysis observed may be due to the proton affinity of the excited state of benzene, which may be higher than that of the ground state.

The evidence shows that mucondialdehyde is indeed formed in the presence of oxygen

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[21] Dorfman, Taub, and Bühler, *J. Chem. Phys.*, 1962, **36**, 3051.

[22] Scholes and Weiss, *Radiation Res.*, 1959, Suppl. 1, 177.

in the photochemistry of aqueous solutions of benzene at neutral pH, but contrary to the report by Proskurnin *et al.*[6] the mechanism of its formation is different from that in radiation chemistry.

Phung and Burton's[7] statement, that the quantum yield of oxygen consumption is below 0·01, agrees with the result that the quantum yields of all the products are not higher than $\sim 10^{-3}$.

A recent brief report[23] indicates that addition of the elements of water to an unsaturated molecule may occur, not only under ultraviolet irradiation,[18] but also as a result of X-irradiation. The present work excludes this in the case of benzene, in dilute solutions. However, in more concentrated solutions of other compounds, where a large portion of the absorbed radiation energy may be dissipated in direct excitation of the solute even in the case of ionising radiations, photochemical processes may appear.

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[23] Scholes, Ward, and Weiss, *Science*, 1961, **133**, 2016.