681. *Chemical Actions of Ionising Radiations on Aqueous Solutions. Part II. The Formation of Free Radicals. The Action of X-Rays on Benzene and Benzoic Acid.*

By Gabriel Stein and Joseph Weiss.

The action of *X*-rays on dilute aqueous solutions of benzene has been investigated qualitatively and quantitatively under various conditions. Phenol and diphenyl have been isolated from solutions irradiated in the absence of oxygen, and the amount of hydrogen evolved has been determined. The reaction has also been studied in the presence of oxygen and in hydrogen. From solutions of benzoic acid (irradiated in the absence of oxygen) *o*- and *p*-hydroxybenzoic acid have been isolated.

The formation of these products, and the detailed quantitative investigation of the reaction (particularly for benzene), have confirmed the theory of indirect action of ionising radiations, involving the formation of hydroxyl radicals and hydrogen atoms, and have led to a partial elucidation of the reaction mechanism.

In Part I (preceding paper) we discussed the view that the primary net process in the action of ionising radiations on water molecules can be represented (Weiss, *Nature*, 1944, **153**, 748; *Trans. Faraday Soc.*, 1947, **43**, 314) as:

$$H_2O \rightsquigarrow H + OH \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

The formation of the free hydroxyl radical and the hydrogen atoms takes place presumably by way of the intermediate formation of H_2O^+ and H_2O^- (Lea, *Brit. J. Radiol.*, 1947, *Suppl.*

1, p. 59; Weiss, *loc. cit.*). It has also been shown that all the known chemical effects of ionising radiations in aqueous solutions, can be interpreted on this basis (Weiss, *loc. cit.*; Allsopp, *Brit. J. Radiol.*, 1947, *Suppl.* 1) which also permits the description of certain biological effects of ionising radiations (Weiss, *loc. cit.*; *Nature*, 1946, **157**, 584).

Recently, Dainton (*Nature*, 1947, **160**, 268) found that acrylonitrile in dilute aqueous solution polymerised on irradiation with X-rays and γ-rays and attributed this to the action of primarily-formed hydroxyl radicals [according to reaction (1)], in view of the fact that these radicals are known to initiate polymerisations (Baxendale, Evans, and Park, *Trans. Faraday Soc.*, 1946, **42**, 668, 675).

We have now attempted to demonstrate the mode of action of ionising radiations, and the intermediate formation of hydroxyl radicals in aqueous solutions, by investigating the products formed on irradiating some simple organic substances, such as benzene and benzoic acid, in dilute aqueous systems in the absence of oxygen.

If hydroxyl radicals are first formed, it should be possible to obtain some of the corresponding substances containing hydroxyl groups, *i.e.*, in these cases, phenols. Hydroxyl radicals are known to be formed by purely chemical means such as by Fenton's reagent, *i.e.*, in the decomposition of hydrogen peroxide by ferrous salts which is now known to occur by way of hydroxyl radicals (Haber and Weiss, *Proc. Roy. Soc.*, 1934, *A*, **147**, 332) and to be capable of hydroxylating benzene at room temperature, with great ease, to phenol and polyphenols (Cross, Bevan, and Heiberg, *Ber.*, 1900, **33**, 2015). In order to obtain definite evidence of the formation of phenol and phenolic compounds by the irradiation with ionising radiations we decided to isolate and characterise them by unambiguous methods. The doses of radiation employed had thus to be large enough to yield the products in amounts that could be isolated, but not so large as to convert any considerable fraction of the benzene present, since in the latter case the phenol (if produced) would itself presumably be further attacked and the qualitative and quantitative results would be obscured by the formation of secondary products. If the irradiation of dilute aqueous solutions of benzene, in the absence of oxygen, should result in the formation of, *e.g.*, phenol, it would show definitely that a hydroxyl group had been introduced into the molecule; and, moreover, this hydroxyl group could have its origin only in the solvent water.

The Action of X-*Rays on Benzene in Aqueous Solutions.*—The irradiations were carried out as described in Part I. The method of degassing the solutions before irradiation, and the analytical methods, are given in the Experimental section. In the qualitative experiments, saturated solutions of benzene in water were employed. 100 Ml. of solution, irradiated in a vacuum with a dose of the order of 10^6 r. (total energy absorption of the order of 10^8 g.-r.) yielded (i) hydrogen (determined by diffusion through a palladium tube; see Experimental section), (ii) phenol, isolated as tribromophenol which was identified by a mixed melting point, (iii) diphenyl, isolated and identified by a mixed melting point and its specific colour reaction (Mulliken, "Identification of Pure Organic Compounds," 1904), and (iv) traces of terphenyl. The presence of the last two compounds was also supported by a re-investigation of the action of Fenton's reagent on benzene (Loebl, Stein, and Weiss, unpublished), in which diphenyl and terphenyl were isolated in addition to phenol and polyphenols. The fact that in our qualitative X-ray experiments no polyphenols were formed in considerable quantities was shown by specific colour reactions.

The formation of these products and of diphenyl in particular indicates the operation of a free-radical mechanism involving the intermediate formation of hydrogen atoms and hydroxyl radicals. However, to substantiate this and, if possible, to obtain some information regarding the actual course of the reaction a quantitative investigation was necessary. The relative proportions of the various products were determined and the reaction (i) in the presence and in the absence of air (oxygen) and (ii) in an atmosphere of hydrogen, has been investigated.

Since the presence of the main reaction products had been firmly established by their actual isolation, much smaller doses could be used in the subsequent quantitative experiments—sufficient to give enough phenol for colorimetric determination.

Hydrogen was determined, by the method described below, with an accuracy of about $\pm 1\%$ at yields of the order of 10^{-4} mol. and about $\pm 5\%$ at yields of the order of 10^{-5} mol. The yields are expressed in hydrogen equivalents ($= \frac{1}{2}H_2$). Phenol was determined colorimetrically, using the Folin–Ciocaltau reagent, at concentrations of the order of 10^{-6}—10^{-5} mol./100 ml. with an accuracy of $\pm 3\%$. For the estimation of diphenyl in the presence of a relatively large excess of benzene we found no reliable method. Spectrophotometry (Steyn and Rossellet, *Analyst*, 1949, **74**, 89) cannot be used under these conditions. The only other method, based on the colorimetric method of Mulliken (*loc. cit.*) adapted by Tomkins and Isherwood (*Analyst*, 1945,

70, 330), was found to be qualitative only. Thus we had to restrict the estimation of diphenyl to the weighing of the neutral fraction which is called hereafter "diphenyl." Reproducible results were obtained with quantities of the order of 0·1 millimole, but the product so obtained is not pure diphenyl. Another useful method was the observation of the minimum dose at which, under different conditions, a turbidity, caused by the formation of diphenyl, first became visible in the solution.

The *X*-ray dosage was given in all these experiments at the rate of 3500 r./min. ≈3300 E.U./min. (see Part I, p. 3241).

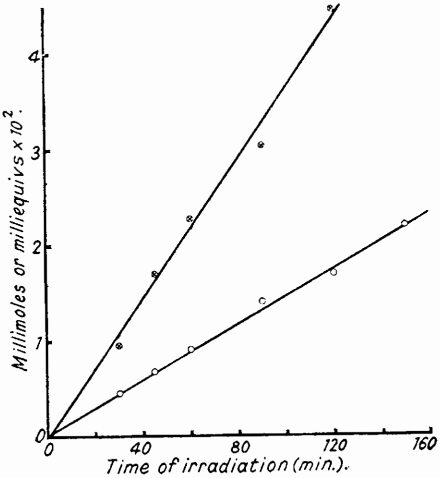
Quantitative results. In a solution initially in a vacuum, the products accumulate slowly as irradiation proceeds. At very large doses, such as those we employed for the qualitative experiments, a certain pressure of hydrogen is built up and the reaction

$$H_2 + OH \longrightarrow H_2O + H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

takes place to some extent. This reaction very likely removes some of the available hydroxyl radicals and results in the decreased yield of phenol which we observed at higher doses. However at the low doses at which the results shown in Fig. 1 were obtained this effect can be neglected. This figure gives the yield of phenol and of hydrogen (= $\frac{1}{2}H_2$) plotted against total dose, the same dose-rate of irradiation being always employed. Both yield–dose curves are linear; the yield of phenol, calculated in terms of an assumed formation of 1 ion pair or one pair of radicals (H, OH) for every 32·5 ev. absorbed (see Part I) is

FIG. 1.

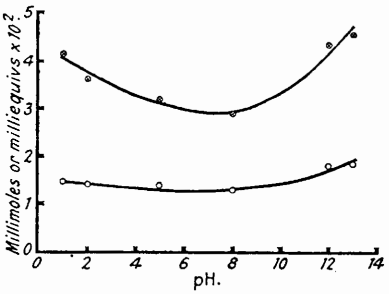
Irradiations of saturated solutions of benzene in water (100 *ml.*) *in a vacuum.*



Yields of phenol (○) *and of hydrogen equivalents* (⊗) *plotted against times of irradiation at a constant dose-rate of approx.* 3500 *r./min.*

FIG. 2.

Irradiations of saturated solutions of benzene in water (100 *ml.*) *in a vacuum.*



Influence of pH on the yields of phenol (○) *hydrogen and equivalents* (⊗) *for a constant time of irradiation* (90 *min., corresponding to a constant dose of approx.* 3·15 × 10⁵ *r.*).

$$\frac{\text{number of molecules of phenol formed}}{\text{number of ion (radical) pairs produced}} = \frac{M}{N} = 0{\cdot}15.$$

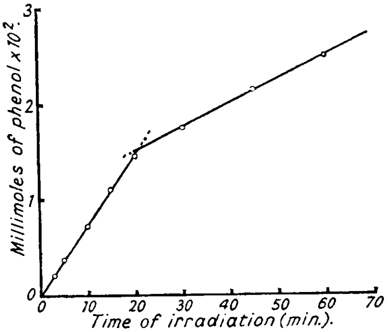
The ratio $\frac{1}{2}H_2$: phenol ≈ 2·45.

Fig. 2 shows the influence of pH on the yield of phenol and hydrogen in a vacuum at a fixed time of irradiation of 90 minutes. The yield of phenol is almost independent of variations in pH within a wide pH range, but rises slightly at very high pH values. The amount of hydrogen is however dependent on the pH, there being a pronounced minimum in the neighbourhood of pH ∼7.

The results shown in both figures were obtained with a saturated solution of benzene in water. Since evacuation was involved in the procedure, it was impossible in this case to investigate the effect of varying concentrations of benzene. This has, however, been done when working in the presence of air. Fig. 3 shows the yield of phenol plotted against dose. A high rate of production is obtained initially, the *M*/*N* value being 0·75 (five times that in a vacuum). This straight line breaks very sharply after about 20-minutes' irradiation (7×10^4 r.), and a straight portion follows, having a slope much lower than that of the initial portion and somewhat higher than that obtained in a vacuum. This second portion remains constant up to the highest doses investigated. These results can be interpreted as caused by exhaustion of the dissolved oxygen initially present and indicate that the oxygen in the solution is only relatively slowly replaced by the oxygen of the air.

FIG. 3.

Irradiations of saturated solutions of benzene in water (100 *ml.*) *in the presence of air.*

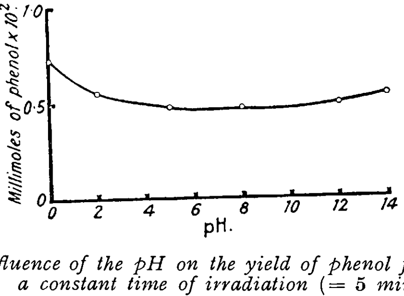


Yield of phenol plotted against times of irradiation at a constant dose rate of approx. 3500 *r./min.*

The initial higher yields are presumably the result of reactions with molecular oxygen. The break in the curve will occur, in general, when the oxygen has been used up to the point where it is just being replenished by diffusion from the air. In general, this point will therefore not be a definite one but will depend on external conditions such as temperature, etc. The same conditions can, of course, influence the slope of the second portion. These results, including the somewhat remarkable sharpness of the break, have been substantiated in experiments by Day and Stein (*Nature*, 1949, **164**, 671) using a different experimental procedure. The initial slope is apparently the same even under somewhat different experimental conditions.

FIG. 4.

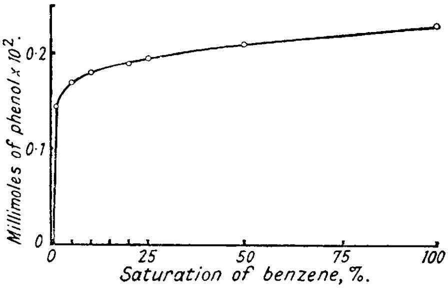
Irradiations of saturated aqueous solutions of benzene (100 *ml.*) *in the presence of air.*



Influence of the pH on the yield of phenol for a constant time of irradiation (= 5 *min., corresponding to a constant dose of approx.* 1·75 × 10⁴ *r.*).

FIG. 5.

Influence of the concentration of benzene (*in water*) *on the yield of phenol at a constant total dose of approx.* 1 × 10⁴ *r.*



The effect of pH on the production of phenol in air is shown in Fig. 4. Again, the yield is independent of the pH within wide limits, rising slightly at both ends of the pH scale.

Fig. 5 shows the dependence of yield of phenol on the concentration of benzene. The various concentrations were obtained by suitable dilution of the saturated solution and are given in terms of percentage saturation. A saturated solution of benzene in water contains approximately 0·15% of benzene. In view of this low solubility, a very low dose of radiation had to be employed to avoid local exhaustion of the acceptor at high dilutions. The results shown by the curve were obtained at a constant time of irradiation of 3 min. (approx. 10,000 r.). The highest dilution used was 100 times the original. It will be seen that at 10-fold dilution the yield drops by only 20%. The curve is of the theoretical shape discussed by Weiss (*loc. cit.*) and supports further the suggested indirect mode of action of the radiation.

The shape is, in general, caused by competition between the recombination of the radicals according to the reaction

$$\mathrm{H + OH \xrightarrow{k_r} H_2O}$$

and the reaction of one of the radicals with an acceptor X, *e.g.*,

$$\mathrm{X + OH \xrightarrow{k_x} reaction\ products}$$

It has been shown previously (Weiss, *loc. cit.*) that for the stationary state [d(OH)/dt = 0] this leads to the following expression for the (differential) yield :

$$\gamma = \frac{K[\mathrm{X}]/[\mathrm{H}]_l}{1 + K[\mathrm{X}]/[\mathrm{H}]_l}$$

where $K = k_x/k_r$ and k_x and k_r are the rate constants of the two reactions (see above) and $[\mathrm{H}]_l$ and [X] represent the local concentrations of the active radical and acceptor, respectively, in the tracks of the fast particles.

As stated above the diphenyl could be determined only at relatively high doses because of the very imperfect method of analysis. The table below gives the results obtained under various conditions.

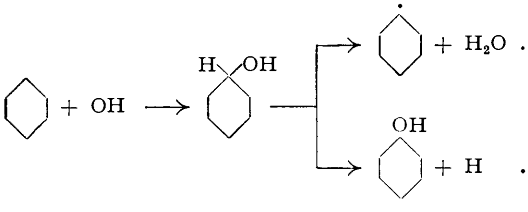
Irradiation of saturated solutions of benzene in water.

	Yield, in millimoles per 10^8 g.-r.		
Conditions.	Phenol.	Hydrogen (equivs.).	" Diphenyl."
Vacuum	0·0372	0·114	0·11
,,	0·0376	0·112	0·12
Air	0·081	...	0·08
,,	0·081	...	0·08
,,	0·082	...	0·09
Hydrogen	0·031	...	0·16
,,	0·031	...	0·18

DISCUSSION.

The qualitative results, showing the formation of phenol, diphenyl, and hydrogen, already make it very likely that one is dealing here with a free-radical mechanism, which involves, as one of its intermediate steps, the formation of phenyl radicals. The fact that in an atmosphere of hydrogen the yield of phenol decreases (see table) lends support to the view that reaction (2), which is well known for the gaseous phase, takes place.

The quantitative results are best explained by assuming that the primary reaction (1), resulting in the formation of hydroxyl radicals and hydrogen atoms, is followed, in the case of the hydroxyl radicals, by an attack on a benzene molecule. This might take place in two possible ways :

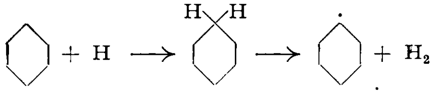


. . . . . . (3a)

. . . . . . (3b)

Reaction (3*a*) would be exothermic by 16 kcals., reaction (3*b*) by 3 kcals. On this ground alone (3*a*) could be favoured. Rice and Teller (*J. Chem. Physics*, 1938, **6**, 489) consider reactions of type (3*a*) to be the most favoured generally in free-radical mechanisms. The assumption that reaction (3*a*) takes place to a large extent, and reaction (3*b*) to a very small extent if at all, is further supported by the quantitative results. Should reaction (3*b*) have taken place with ease, resulting in formation of phenol in the first step of the reaction, the relative ionic yield of phenol in a vacuum would not have been as low as 0·15, and the presence of oxygen should not have resulted in a *five*-fold increase in the yield of phenol. Further, the eventual formation of diphenyl in relatively large quantities in a vacuum, and its very much lower rate of formation in the presence of oxygen (as indicated, for instance, by observing the onset of turbidity in the initial stages of irradiation), are best explained in terms of intermediate formation of free phenyl radicals.

The hydrogen atoms formed initially may undergo similar reactions. A reaction of type (3*b*) would in this case not influence the ultimate yields. The reaction of type (3*a*), *viz.*,


(4)

is, in the case of hydrogen atoms, approximately thermoneutral. Roberts and Skinner (*Trans. Faraday Soc.*, 1949, **45**, 339) give a value of 102 kcals. for fission of the C_6H_5–H bond, which would make reaction (4) slightly endothermic. It is not impossible that in this case the transitionary addition complex C_6H_7 will be rather stable and undergo reactions leading to the partial hydrogenation of the benzene ring, by disproportionation, *e.g.*,

$$2C_6H_7 \longrightarrow C_6H_8 + C_6H_6 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (5)$$

or by its encounter with a hydrogen atom. In any case the production of phenyl radicals by reaction (4) seems less favoured than reaction (3*a*). We have, however, so far not investigated the extent of hydrogenation of the benzene nucleus.

The phenyl radicals formed can react with hydroxyl radicals, yielding phenol

$$C_6H_5 + OH \longrightarrow C_6H_5{\cdot}OH \quad . \ . \ . \ . \ . \ . \ . \quad (6)$$

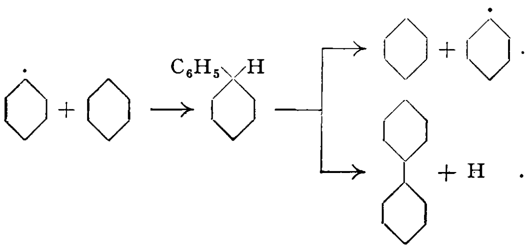
or with hydrogen atoms, re-forming benzene

$$C_6H_5 + H \longrightarrow C_6H_6 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (7)$$

or with other phenyl radicals, giving diphenyl

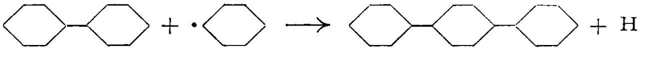
$$2C_6H_5 \longrightarrow C_6H_5{\cdot}C_6H_5 \quad . \ . \ . \ . \ . \ . \ . \ . \quad (8)$$

Perhaps more likely is the reaction with a benzene molecule: here again two reactions, of the type (3*a*) and (3*b*), are possible, *viz.*:

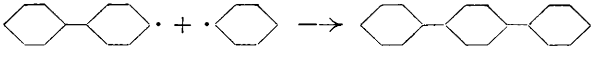

(9*a*)
(9*b*)

In this case, however, reaction (9*a*) is thermoneutral, whilst reaction (9*b*) is exothermic, according to Szwarc (*Nature*, 1948, **161**, 890) who gives a value of 110 kcals. for formation of the central C–C bond in diphenyl, which would make reaction (9*b*) exothermic by about 8 kcals. Roberts and Skinner however (*loc. cit.*) give a lower value of 102·4 kcals. for this C–C bond, which would make this reaction nearly thermoneutral.

Similarly the formation of terphenyl could take place by an attack on diphenyl by a phenyl radical


(10*a*)

or by an attack of OH or H on diphenyl, followed by


(10*b*)

Altogether it seems that the formation of phenol in a vacuum in an ionic yield of 0·15, accompanied by diphenyl in a yield of approx. 0·4 and an ionic yield of hydrogen of 0·45, is best approximated by assuming reaction (3*a*) to be the main reaction leading to phenyl radical formation, followed by reactions (6), (7), (8), and (9*b*). This reaction mechanism would suggest the formation of more hydrogen than has actually been found, pointing to the possibility of hydrogenation of the benzene. The investigations of the reactions of hydrogen atoms with benzene in the gas phase (cf. Steacie, " Atomic and Free Radical Reactions," 1946) indicate that such hydrogenation reactions do take place.

Our mechanism is further supported by the fact that in the presence of oxygen (air), the yield of phenol increases by the unexpectedly high factor of five. This indicates that the low yield of phenol in a vacuum is caused by the fact that its formation is not the first step of the reaction. In a vacuum the concentration of hydroxyl radicals which are necessary for the formation of phenol in reaction (6) is low, since reaction (3*a*) which must precede this consumes hydroxyl radicals. In air, however, the reaction

$$H + O_2 \longrightarrow HO_2 \qquad (11)$$

will remove hydrogen atoms which could react by (7) as well as by the recombination reaction

$$H + OH \longrightarrow H_2O \qquad (12)$$

and, since both reactions (7) and (12) would reduce the yield of phenol, the occurrence of (11) will enhance the formation of this compound. Moreover the HO_2 radical formed in (11) is presumably also capable of reacting thus :

$$C_6H_5 + HO_2 \longrightarrow C_6H_5\text{-O-O-H} \qquad (13)$$

which can result eventually in formation of phenol. In the presence of oxygen (air), there is the possibility also of the reaction

$$C_6H_5 + O_2 \longrightarrow C_6H_5\text{-O-O}\cdot \qquad (14)$$

which can also lead to the eventual formation of phenol.

The energy of the $H{-}O_2H$ bond is often assumed to be about 94 kcals. If this is so, it would be unlikely that the HO_2 radical will be capable of dehydrogenating benzene to phenyl. Much too little is known, however, of the reactions of HO_2 to make a definite statement possible.

The results obtained when the reaction vessel was filled with hydrogen are in agreement with the above ; the yield of phenol is reduced, a fact which could result from the operation of reaction (2) and would point to the correctness of the assumption of a free-radical mechanism. The demonstration that the yield of phenol, both in a vacuum and in the presence of oxygen (air), is independent of variations in the pH supports the same view and makes it likely that, at least in this particular reaction, a free-radical mechanism predominates.

The slight influence of pH on the yield of phenol at extreme values of pH, as well as the rather marked dependence of hydrogen evolution on pH, may well be caused by intervention of some ionic species. On the basis of our benzene experiments alone not much can be said about this point but we shall return to it later in the discussion of some other reactions.

It will be seen that our results do not give a conclusive answer concerning all the single steps in the reaction mechanism, but the general view that we are dealing in this case with a free-radical mechanism is well supported.

The development of a suitable technique for the quantitative micro-determination of diphenyl, and a further investigation which would show also the extent of partial hydrogenation of benzene, might be helpful in the further elucidation of the mechanism.

The Hydroxylation of Some Monosubstituted Benzene Derivatives.—The results obtained with benzene support the view that the action of ionising radiations on aqueous solutions involves the intermediate formation of hydroxyl radicals. From the chemical point of view one has here a means of producing these radicals in a way which in some respects is advantageous. Thus the quantitative relationships in the reactions of hydroxyl radicals, produced by the catalytic decomposition of hydrogen peroxide in the presence of organic acceptors, were extremely difficult to ascertain. In our experiments, on the other hand, the hydroxyl radicals are formed without the introduction of an external reagent throughout the reaction system according to a definite pattern, and the primary products can be separated with comparative ease. The reactions of monosubstituted benzene derivatives and of higher aromatic hydrocarbons seemed of particular interest. The qualitative and quantitative isolation of the various reaction products might in such cases give additional information on the interesting question concerning the mode of substitution of the aromatic ring—in particular, in this case, about the presence or absence of the directing influence of the substituents.

The general problems of these substitution reactions have been reviewed by Ingold (*Chem. Reviews*, 1934, **15**, 225). Predictions about the way in which free radicals would react in such cases were made on the basis of the theory of resonance by Wheland (*J. Amer. Chem. Soc.*, 1942, **64**, 900).

Benzoic acid in aqueous solution. Qualitative experiments with benzoic acid, described in detail in the Experimental section, resulted in the isolation and identification of *p*-hydroxybenzoic acid and salicylic acid. The formation of *m*-hydroxybenzoic acid has not been completely excluded, but it is unlikely that this acid forms a considerable part of the yield. Small quantities of phenol and diphenyl are formed, presumably by decarboxylation. A very rough estimate of the relative proportions of *para*- to *ortho*-substituted acid gave a value of 2·5. Quantitative experiments on this point are in progress. Other monosubstituted benzene derivatives (nitrobenzene, phenol) have also been investigated qualitatively and quantitatively; the results will be published separately.

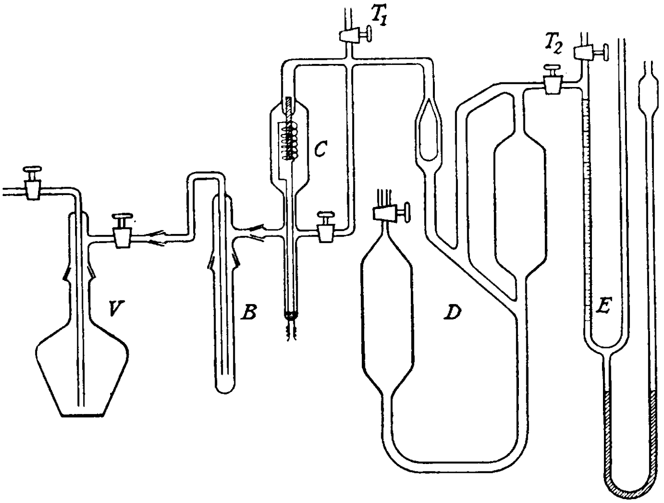
EXPERIMENTAL.

The irradiation vessels and the conditions of irradiation are described in the preceding paper.

Experiments in a Vacuum.—Previous workers have shown that the utmost care has to be exercised in ensuring the total absence of oxygen. Solutions after introduction into the vessel *V* (Fig. 6) were first evacuated, through a calcium chloride absorption tower and a liquid-air trap, using a Hyvac oil-pump, and purified nitrogen was then admitted to atmospheric pressure. [Nitrogen from a cylinder was passed through a solution of 10% sodium dithionite (hydrosulphite) in 10% NaOH sodium hydroxide solution containing 1% of sodium anthraquinone-2-sulphonate, then through a calcium chloride and a soda-lime scrubber, and finally through a tube containing copper gauze at approx. 380°. It was frequently tested for absence of oxygen by a Kautsky-gel (Kautsky and Hirsch, *Z. anorg. Chem.*, 1935, **222**, 126). The partial pressure of oxygen was always below 10^{-3} mm.] After being filled with this nitrogen, the reaction vessel was evacuated again, and the admission of nitrogen and evacuation were repeated 3 times. At first we carried out our experiments in an atmosphere of nitrogen. This did not influence the yield of phenol, but resulted in consistently low values for hydrogen. This may be due to a reaction during the process of analysis (see below), the palladium tube acting as a catalyst. Thereafter the solution was evacuated at the oil-pump, and irradiations carried out in a vacuum.

FIG. 6.

Diagrammatic representation of the apparatus for the determination of hydrogen.



The irradiated solution always had a volume of 100 ml. The loss of water during evacuation was of the order of 0·5 ml. No allowance was made for this. All connections were through standard ground joints.

Determination of Hydrogen.—Fig. 6 shows the apparatus employed in the gas analysis. It was designed mainly with the view of determining accurately the amount of hydrogen formed, but can be adapted easily for a total gas analysis. The irradiation vessel is shown at *V*. For the determination of hydrogen a heated palladium tube is used which permits the diffusion of hydrogen. This method has been employed previously with good results by Fleiger (*Ind. Eng. Chem., Anal.*, 1938, **10**, 545). The liquid-air trap at *B* between the irradiation vessel and the palladium tube prevents access of water vapour and other condensable substances to the latter. (The access of any gases not condensed by liquid air has not been prevented.) After irradiation the vessel is attached to the apparatus as shown, and with both taps at T_2 closed, but that at the bottom of *C* open, and the system is evacuated by way of T_1 which leads to the Hyvac pump. During this time the palladium tube in *C* is slowly heated. Evacuation being completed, T_1 is closed and the last traces of gas are pushed into the gas-burette at *E*, using the automatic Toepler mercury pump *D* which is actuated by means of a water pump and a compressor connected through the three-way tap. All taps are then closed including the one at the bottom of *C*, and the tap between *V* and *B* opened momentarily to allow the passage of the gas. This is repeated at intervals. After 10 minutes the accumulated gas in the Toepler pump is passed into the gas-burette and the process repeated. With our arrangement, the pressure was decreased to one-fifth of its original value on each occasion. The process was repeated 5 or more times according to the amount of gas formed, until less than 0·01 ml. of gas diffused through during the last 10—15 minutes. The gas burette could be read easily to 0·01 ml. The accuracy of the analysis depended accordingly on the total amount of hydrogen formed, and was about ±1% for 0·1 milliequivalent of hydrogen. The usual corrections for pressure and temperature were made. To avoid errors due to dead space at the top of the burette, some of the gas from the previous experiment was always retained, and readings were taken, not from zero, but from this small positive value. Calibration was carried out using hydrogen generated in a special vessel (similar to the irradiation vessel) from a weighed amount of pure zinc and sulphuric acid. This specially constructed irradiation vessel, identical in all other respects with the one shown in Fig. 6, carried a small removable glass boat attached to a hooked ground-in stopper. The boat was charged with the weighed amounts of pure zinc, the vessel evacuated and then attached to the apparatus, the zinc dropped into the acid, and the amount of hydrogen formed determined. At a total volume of the order of 2 ml., five determinations gave values of 95, 97, 97, 95, and 98% of the theoretical.

Analysis and Isolation of Reaction Products from the Irradiated Solutions.—Benzene was thiophen-free, cryst. (Macfarlane), redistilled, and kept over sodium. It was added to twice-distilled water which was shaken until saturated. The solubility of benzene in water is approx. 0·15% at room temperature. 100 Ml. of this saturated solution were used for all experiments except those where the influence of dilution was studied.

In experiments carried out in a vacuum, 1 ml. of the pure benzene was added to make up for loss during evacuation.

Evacuation, irradiation, and determination of hydrogen having been carried out as described above, the presence of phenolic substances was shown by colour reactions, with Folin's reagent and with diazotised sulphanilic acid or *p*-nitroaniline. The colours so obtained were identical with those given by solutions of pure phenol. Specific tests for the three isomeric dihydroxybenzenes gave negative results. Pyrocatechol was tested for by an attempted precipitation by lead acetate in buffered solution, resorcinol by the ammoniacal cobalt reagent, and quinol by the following procedure. It was found that quinol alone of the four possible phenolic compounds gave a blue colour with Folin's reagent at pH ~3. This test gave sensitive results with synthetic mixtures. All these tests were negative when applied to the irradiated solutions.

The irradiated solution was then acidified with dilute sulphuric acid and extracted continuously with ether, and the extract was shaken in turn with solutions of sodium hydrogen carbonate, sodium carbonate, and sodium hydroxide. The first two of these did not yield any products. The sodium hydroxide extract was run immediately into excess of acid and treated with bromine water; the precipitate, treated according to Mulliken (*loc. cit.*), had m. p. 93°, not depressed by admixture with authentic 2 : 4 : 6-tribromophenol.

The original ethereal extract, after treatment with the alkaline solutions and washing with water, was dried (Na_2SO_4) and evaporated. The waxy residue sublimed, leaving very little residue. The sublimate melted at 64°, not depressed by admixture with an authentic sample of diphenyl, and gave the specific color reaction of diphenyl (Mulliken, *loc. cit.*). The residue from the sublimation melted at 198°, but there was insufficient to enable the material to be identified definitely as terphenyl (m. p. 205°); amounts of terphenyl sufficient for identification accompanied the formation of phenol and diphenyl in the re-investigation of the action of Fenton's reagent on benzene (Loebl, Stein, and Weiss, unpublished).

Quantitative Determination of Phenol.—Phenol was determined colorimetrically by the Folin–Ciocaltau reagent (Snell, " Colorimetric Methods of Analysis," Vol. 2, 1937). A suitable aliquot of the irradiated solution in a 100-ml. graduated flask was diluted to approx. 50 ml. and neutralised. 2 Ml. of reagent solution and 10 ml. of 18% sodium carbonate solution ("AnalaR") were added, and the whole diluted after 15 minutes. The extinction was measured with a Spekker colorimeter and an Ilford No. 607 filter. " Absolute " phenol was used as the standard for calibration. Determinations and standardisation were reproducible within ±3%.

Solutions of definite acid pH values were made up containing either sulphuric or phosphoric acid. No specific influence was observed in experiments at the same pH with the two different anions. Intermediate values were maintained with phosphate buffers, alkaline values with sodium hydroxide.

Qualitative Analysis of Irradiated Benzoic Acid Solutions.—A saturated solution of benzoic acid (" AnalaR ") in water (0·25%) was used. After the determination of hydrogen, the irradiated solution (dose given approx. 10^8 g.-r.) was further acidified with dilute sulphuric acid and extracted continuously with ether for 12 hours. The ethereal extract was shaken in turn with solutions of sodium hydrogen carbonate, sodium carbonate, and sodium hydroxide, all three solutions being run into excess of acid immediately. Nothing was isolated from the sodium carbonate solution. The sodium hydroxide solution gave a Folin reaction, suggesting the formation of some phenol. The acidified hydrogen carbonate solution was extracted with ether, the extract washed, dried (Na_2SO_4), and evaporated, and the residue treated with chloroform. This residue melted at 207—208°, not depressed by admixture with authentic *p*-hydroxybenzoic acid.

The chloroform extract gave positive colour tests with reagents specific for salicylic acid (ferric chloride, Jorissen's reagent). Attempted isolation by bromination did not yield a pure product. The chloroform extract was evaporated, the residue dissolved in alkali and coupled with diazotised *p*-nitroaniline, and the solution neutralised and precipitated with 5% aqueous aluminium chloride. The precipitate (alizarin-yellow R) was filtered off, washed, redissolved in alkali, and acidified. The m. p. of the precipitate (recrystallised from alcohol) was 234°, not depressed by admixture with a sample obtained from salicylic acid by the same procedure. The dry substance is explosive.

The original ethereal extract of the irradiated solution, after treatment with the alkaline solutions, was washed, dried, and evaporated. The residue contained some diphenyl, identified by its colour reaction (see above).

No attempt has been made to isolate any diphenyldicarboxylic acids, which might have been formed in the reaction.

A very rough estimate of the relative proportions of *para*- to *ortho*-substitution was made by weighing the precipitates obtained finally in the qualitative separation described. This gave a *p* : *o* ratio of ~2·5.

The irradiations were carried out in the Radium Department of the Royal Victoria Infirmary, Newcastle-on-Tyne. We are indebted to Mr. J. Thurgar, Dr. F. T. Farmer, and Mr. M. J. Day for their co-operation. Our work was supported by grants from the Northern Council of the British Empire Cancer Campaign to whom our grateful thanks are due.

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[*Received, August 3rd*, 1949.]