156. X-*Irradiation of Aqueous Benzene Solutions.*

By J. H. Baxendale and D. Smithies.

The yields (G molecules/100 ev) of phenol, diphenyl, hydrogen peroxide, and hydrogen from X-irradiated aqueous benzene solutions have been measured in various conditions. In de-aerated solutions $G(\mathrm{Ph{\cdot}OH}) = 0{\cdot}34$, $G(\mathrm{Ph_2}) = 0{\cdot}55$, and $G(\mathrm{H_2}) = 0{\cdot}60$, independently of dose and the same in neutral and in 0·1N-sulphuric acid solutions. $G(\mathrm{H_2O_2})$ varies with dose, benzene concentration, and acidity owing to the fact that hydrogen peroxide takes part in secondary reactions. In the presence of oxygen $G(\mathrm{Ph{\cdot}OH})$ and $G(\mathrm{H_2O_2})$ increase substantially and $G(\mathrm{Ph_2})$ falls to zero. Addition of $\mathrm{Cu^{2+}}$ and/or $\mathrm{Fe^{3+}}$ to de-aerated solutions also increases $G(\mathrm{Ph{\cdot}OH})$ and decreases $G(\mathrm{Ph_2})$. There is evidence for unidentified reduction products in the de-aerated solutions, and for other oxidation products in aerated solutions and in solutions containing $\mathrm{Cu^{2+}}$ and $\mathrm{Fe^{3+}}$.

The absorption of ionising radiation by aqueous benzene solution gives mainly phenol and diphenyl in the absence of oxygen, but in air the chief products are phenol and hydrogen peroxide. It has been concluded from previous work [1] that these are formed by the action of H and HO produced from water by the radiation, and investigations using other sources of HO, such as Fenton's reagent [2,3] and ultraviolet-irradiated ferric ion solutions, support this.[4] In the latter study, the reaction of ferric ion with the radicals formed from benzene proved helpful in the elucidation of the reactions involved and it has been used in the work now reported.

Experimental

Materials.—Benzene of A.R. grade was purified by recrystallisation. Solutions of $\mathrm{Cu^{2+}}$ and $\mathrm{Fe^{3+}}$ were made up from A.R. copper sulphate and ferric ammonium sulphate. Reaction

---

[1] Stein and Weiss, *J.*, 1949, 3245.

[2] Merz and Waters, *ibid.*, p. 2427.

[3] Baxendale and Magee, *Discuss. Faraday Soc.*, 1953, **14**, 160.

[4] *Idem, Trans. Faraday Soc.*, 1955, **51**, 205.

mixtures were made up in water distilled once from a glass still. Further purification using alkaline permanganate or by photolysing hydrogen peroxide in the water had no effect. This is not surprising since with the relatively large concentrations of benzene used in the reactions, any effect due to traces of impurities will be negligible.

Irradiation Apparatus.—Solutions, usually 250 c.c. in 750 c.c. flasks, were exposed to the unfiltered radiation from a Siemens constant-potential *X*-ray tube run at 190 kv and 12 mA. In order to calculate the energy absorbed by the solution in the flask, three tubes containing 10^{-3}M-ferrous sulphate in 0·8N-sulphuric acid were exposed at the same time as the flask. The relative doses given to the flask and tubes were obtained by previous calibration experiments in which the flask contained a ferrous sulphate solution containing the same concentration of sulphuric acid as that used in the reaction mixtures. Yields reported previously [5,6] on this system are in error because the absorption by sulphuric acid was not taken into account. For reactions in the absence of acid, the energy absorbed was calculated from a calibration with ferrous sulphate in 0·1N-sulphuric acid. This was corrected (by about 2%) for the extra absorption of sulphuric acid, the results of observations at different acid concentrations being used. All doses were calculated on the basis of 15·6 molecules of Fe^{3+} formed per 100 ev absorbed by ferrous sulphate solution.

Analyses.—The methods used to estimate hydrogen, Fe^{2+}, and hydrogen peroxide have been given elsewhere.[6] Diphenyl was extracted from the reaction mixture by hexane, and phenol by ether, and the amounts of each were obtained by ultraviolet absorption, the methods described previously [4] being used.

Results.—*De-aerated solutions.* In the absence of oxygen no products other than phenol, diphenyl, hydrogen peroxide, and hydrogen could be detected by the analytical methods used. The 100 ev yields of these at different acidities, doses, and benzene concentrations are given in Tables 1 and 2. Phenol and hydrogen are almost constant throughout, but the diphenyl and hydrogen peroxide yields show some variations. In particular $G(H_2O_2)$ decreases with dose. This suggests that, in neutral (and possibly also in alkaline) solution, reactions occur to remove hydrogen peroxide, and this is confirmed by the effect produced by having hydrogen peroxide present initially. Thus with $1·6 \times 10^{-5}$M-hydrogen peroxide in neutral solution, $G(H_2O_2) = -0·27$ for a total dose of $1·8 \times 10^{21}$ ev/l., *i.e.*, more is removed than formed, while $G(Ph_2)$ and

TABLE 1. *Yields in de-aerated aqueous solutions saturated with benzene.* Dose rate *ca.* 5×10^{19} ev l.$^{-1}$ min.$^{-1}$.

Conditions	Dose (10^{21} ev/l.)	$G(Ph_2)$	G(Ph·OH)	$G(H_2O_2)$	$G(H_2$
Neutral	0·39	—	—	0·34	—
	0·74	0·59	0·33	0·29	0·60
	1·41			0·20	0·60
	1·50	0·57	0·30	0·19	
	2·16		0·16		
	2·83		0·13		
0·01N-H_2SO_4	0·71	0·59	0·35	0·60	—
	1·56	0·56	0·33	0·59	
	2·82	0·53	0·36		0·60
0·1N-H_2SO_4	0·78	0·52	0·32	0·58	0·58
	1·53	0·55	0·35	0·61	
	1·70	0·55	0·32	0·59	
0·8N-H_2SO_4	1·66	0·44	0·30	0·51	0·52
0·1N-NaOH	1·46	0·45	0·35	0·40	0·63

TABLE 2. *Effect of benzene concentration on the yields in de-aerated neutral solution.* Dose rate *ca.* 5×10^{19} ev l.$^{-1}$ min.$^{-1}$. Total dose *ca.* 7×10^{20} ev l.$^{-1}$.

10^3[Benzene]	22 *	4·6	4·5	4·0	3·8
$G(Ph_2)$	0·59	0·55	0·53	0·57	0·56
G(Ph·OH)	0·33	0·30	0·31	0·32	0·34
$G(H_2O_2)$	0·29	0·19	0·19	0·21	0·20

* Means of seven determinations having maximum deviations of $\not> 5$%.

---

[5] Baxendale and Smithies, *J. Chem. Phys.*, 1955, **23**, 604.

[6] *Idem, Z. phys. Chem.* (*Frankfurt*), 1956, **7**, 241.

G(Ph·OH) are increased to 0·64 and 0·31 respectively. In contrast, hydrogen peroxide has no effect on the yields in 0·01N-sulphuric acid.

The values of $G(H_2)$ and G(Ph·OH) agree fairly well with previous work.[1,7,8] Stein and Weiss [1] found about the same value for $G(Ph_2)$ but Phung and Burton [8] report higher values. In acid, $G(H_2O_2)$ agrees with other determinations,[7,8] but in neutral solution $G(H_2O_2) = 0$ has been reported,[7,8] compared with 0·4 obtained by extrapolation of our results to zero dose. There seems little doubt that the earlier value is in error because of the much larger doses used.

Aerated solutions. Previous work showed that G(Ph·OH) increases appreciably in the presence of air. This is evident from Table 3, which also shows a considerable increase in $G(H_2O_2)$ and decrease in $G(Ph_2)$. There is also evidence for other products, since the ether extract of the irradiated solutions absorbs much more at 290 mμ than would be expected if it contained only phenol. The additional absorption is removed by aqueous sodium hydrogen carbonate, and the bicarbonate solution then has a broad absorption band with a peak at *ca.* 265 mμ which increases slightly when the solution is made alkaline and disappears when it is made acid. This behaviour is reversible and indicates the presence of an acidic material which is stable to alkali and oxygen. The contribution of this material to the absorption maximum of phenol at 274 mμ was usually about 15%, so that before measurement at 274 mμ the ether extract was washed with ether-saturated aqueous sodium hydrogen carbonate.

TABLE 3. *Yields in neutral saturated aqueous benzene solutions with oxygen present.* Total dose *ca.* 10^{21} ev/l.

Gas phase	G(Ph·OH)	$G(Ph_2)$	$G(H_2O_2)$
1 atm. O_2	1·56	0·03	2·62
1 atm. air	1·57	0·03	2·50
20 cm. air	1·50	0·07	2·44

In similar conditions, using higher doses, Daniels *et al.*[9] reported the presence of a substance with properties resembling mucondialdehyde and discussed the mechanism of its formation. We found none of these further oxidation products in deærated solutions.

Typical yields in air and oxygen are given in Table 3. Table 4 shows that in acid the hydrogen peroxide yield is higher than in alkali but that both decrease with dose. In all the experiments the doses given are insufficient to exhaust the oxygen in solution. Analysis of the solutions at intervals up to 24 hr. after irradiation did not reveal any post-irradiation changes in phenol and hydrogen peroxide concentrations which have been reported.[10] In comparison with other work [7,8,9,11] our G(Ph·OH) values are much lower, and we suggest that the product mentioned above interferes with the analytical methods used previously—particularly those depending on the absorption of the phenol in the irradiated solution.[7,8] Our $G(H_2O_2)$ values are higher in acid and lower in neutral solution than those of Phung and Burton.[8]

TABLE 4. *Hydrogen peroxide yields in aerated solutions saturated with benzene.*

Dose (10^{20} ev/l.)	6	18	24
$G(H_2O_2)$ in 0·1N-H_2SO_4	3·30	3·14	3·02
$G(H_2O_2)$ in neutral solution	2·50	2·28	2·20

Yields in the presence of metal ions. The effect of metal ions on X-irradiated aqueous benzene is shown in Table 5. Although the phenol increases as Fe^{3+} is added as in the photochemical system, unlike in the latter the diphenyl yield increases at first and then decreases at higher concentration of Fe^{3+}. The yields of phenol, Fe^{2+}, and benzene oxidised, G(PhH), all increase and appear to approach limiting values at high metal-ion concentrations. $G(H_2)$ is almost constant throughout and is of the order usually obtained for the so-called molecular yield.

[7] Sworski, *J. Chem. Phys.*, 1952, **20**, 1817; *Radiation Res.*, 1954, **1**, 231.
[8] Phung and Burton, *Radiation Res.*, 1957, **7**, 199.
[9] Daniels, Scholes, and Weiss, *J.*, 1956, 832.
[10] Wright, *Discuss. Faraday Soc.*, 1952, **12**, 114.
[11] Freeman, Van Cleave, and Spinks, *Canad. J. Chem.*, 1953, **31**, 448.

If diphenyl, phenol, hydrogen, and Fe^{2+} are the only products in these conditions then we should have

$$2G(Ph_2) + 2G(Ph{\cdot}OH) = 2G(H_2) + G(Fe^{2+})$$

The observations in de-aerated solutions without metal ions (Table 1) show a deficiency of reduction products. The results in Table 5 show that this deficiency decreases when metal ions are added and becomes a deficiency in oxidation products amounting to about 10%. This persists even at the highest metal-ion concentration, where it seems likely that all the radicals produced will be caught by either metal ion or benzene. A similar deficiency was observed in the photochemical oxidation, although in the oxidation by Fe^{2+} and hydrogen peroxide good balances were obtained by the same analytical method.[3] It appears that undetected oxidation products are present in the photochemical and *X*-irradiation systems.

TABLE 5. *Irradiations in the presence of* Cu^{2+} *and/or* Fe^{3+}. Dose rate *ca.* 5×10^{19} ev l.$^{-1}$ min.$^{-1}$. Total dose *ca.* $1{\cdot}5 \times 10^{21}$ ev/l. Solutions saturated with benzene and 0·1N in H_2SO_4.

Initial $[Fe^{3+}]$ (10^{-4}M)	$[Cu^{2+}]$ (10^{-4}M)	$G(Fe^{2+})$	$G(Ph_2)$	$G(Ph{\cdot}OH)$	$G(PhH)$	$G(H_2)$
—	—	—	0·55	0·33	1·43	0·58
0·2	—	0·63	1·00	0·36	2·36	—
0·56	—	2·15	1·12	0·43	2·67	—
1·0	—	2·51	1·18	0·52	2·88	0·53
5·0	—	3·20	0·91	0·92	2·74	—
5·0	1·0	4·70	0·41	2·16	2·98	—
5·0	5·0	6·07	0·16	2·98	3·30	—
5·0	10	6·32	0·12	3·10	3·34	—
5·0	20	6·07	0·10	3·20	3·40	0·57

DISCUSSION

The following reactions are generally agreed to occur on the irradiation of de-aerated aqueous benzene:

$$H_2O \longrightarrow H, HO, H_2, H_2O_2$$

$$HO + PhH \longrightarrow Ph{\cdot} + H_2O \qquad (1)$$

$$2Ph{\cdot} \longrightarrow Ph_2 \qquad (2)$$

$$Ph{\cdot} + OH \longrightarrow Ph{\cdot}OH$$

$$PhH + H \longrightarrow C_6H_7$$

The yields of phenol, diphenyl, and hydrogen peroxide are together much bigger than that of hydrogen, which is the only reduction product measured so far. This deficiency is no doubt due to the presence of undetected partially hydrogenated benzenes and possibly diphenyls which, as previously suggested,[1] originate from C_6H_7 by the further addition of hydrogen atoms or by dimerisation. However, even the yields of benzene oxidation products (~0·9 molecule/100 ev) are less than would be expected if all the HO produced (~3 radicals/100 ev) is used in oxidation, and this may be accounted for by the back reaction:

$$Ph{\cdot} + H \longrightarrow PhH \qquad (3)$$

Both these suggestions are supported by the present observations on the effect of Fe^{3+} and Cu^{2+} on the products. By analogy with the photochemical oxidation by $Fe^{3+}OH$, the reactions

$$H_2O + Ph + Fe^{3+} \longrightarrow Ph{\cdot}OH + Fe^{2+} + H^+ \qquad (4)$$

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + OH^- + HO$$

are to be expected, as well as

$$Fe^{3+} + H \longrightarrow Fe^{2+} + H^+ \qquad (5)$$

which has been shown to occur in the *X*-irradiation of other aqueous systems.[6] Reactions (4) and (5) will reduce both the formation of partially hydrogenated compounds and the extent of the back reaction (3), so that G(Ph·OH) and the amount of benzene reacting, G(PhH), are increased as shown in Table 5. The increase in $G(Ph_2)$ at low Fe^{3+} concentrations probably results from the increase in phenyl-radical concentration brought about by the suppression of reaction (3), while the decrease in $G(Ph_2)$ at higher metal-ion concentrations can be attributed to prevention of reaction (2) by reaction (4).

The occurrence of reactions (1)—(5) means that at high Fe^{3+} or Cu^{2+} concentrations the only reactions of H and Ph· will be with the metal ion, so that $G(Ph_2)$ should approach zero, and G(Ph·OH) and $G(Fe^{2+})$ should approach limiting values. In these conditions, phenol and diphenyl being assumed to be the only oxidation products, we should have $G(\mathrm{Ph{\cdot}OH}) = G_w(\mathrm{HO}) + G_w(\mathrm{H_2O_2})$; $G(\mathrm{Fe^{2+}}) = G_w(\mathrm{H}) + G_w(\mathrm{HO})$, where G_w denotes a primary yield.

Table 5 shows that even at the highest metal-ion concentrations a little diphenyl is still formed and G(Ph·OH) is increasing slightly so that the above conditions have not quite been attained. However, as pointed out above, even at low Fe^{3+} concentrations reduction of Fe^{3+} by hydrogen atoms occurs, so that it seems likely that all the latter will be removed by this reaction at the higher concentrations. Assuming this, we have

$$G(\mathrm{Ph{\cdot}OH}) + 2G(\mathrm{Ph_2}) + G_w(\mathrm{HO}) + G_w(\mathrm{H_2O_2}) \quad \text{. . . . . (i)}$$

and

$$G(\mathrm{Fe_2{}^+}) + 2G(\mathrm{Ph_2}) = G_w(\mathrm{H}) + G_w(\mathrm{HO}) \quad \text{. . . . . (ii)}$$

These equations ignore the undetected oxidation products. If these are formed *via* radicals which are oxidised by the metal ion, then equation (ii) will be unchanged but the yield of the product should be included in (i) with those of phenol and diphenyl. This yield will be given by the deficiency of oxidation products in the balance. The yields being taken at the highest metal-ion concentration, the deficiency amounts to 0·35, $G(\mathrm{H_2}) = 0{\cdot}6$, $G(\mathrm{Fe^{2+}}) = 6{\cdot}1$, $G(\mathrm{Ph{\cdot}OH}) = 3{\cdot}2$, and $G(\mathrm{Ph_2}) = 0{\cdot}1$. Hence

$$G_w(\mathrm{HO}) + G_w(\mathrm{H_2O_2}) = 3{\cdot}75$$
$$G_w(\mathrm{H}) + G_w(\mathrm{HO}) = 6{\cdot}3$$

Assuming $G_w(\mathrm{H_2O_2}) = 0{\cdot}6$, which is found in acid solution without metal ions, we have

$$G_w(\mathrm{HO}) = G_w(\mathrm{H}) = 3{\cdot}15; \quad G_w(\mathrm{H_2}) = G_w(\mathrm{H_2O_2}) = 0{\cdot}6$$

which are similar to primary yields previously reported.[12]

THE UNIVERSITY, MANCHESTER.

[*Received, November* 18*th*, 1958.]

---

[12] Hochanadel and Lind, *Ann. Rev. Phys. Chem.*, 1956, **7**, 83.