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Radiolysis of Aqueous Benzene Solutions

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Summary

Aerated and deaerated aqueous solutions of benzene have been irradiated with Co^{60} γ-rays. The products of radiolysis in deaerated, unbuffered or acid, solutions were phenol, biphenyl, hydrogen and in acid solutions also hydrogen peroxide with the following yields: G(phenol) = 0.37 (0.37), G(biphenyl) = 1.3 (1.7), $G(H_2)$ = = 0.44 (0.43) and $G(H_2O_2)$ = 0 (0.60), the figures in brackets giving the results for acid solutions. The results are shown to agree with the conclusion that $k(e^-_{aq} + H_2O_2) \gg k(H + H_2O_2)$. Furthermore, the results indicate that a competition takes place between the reactions:

$$2\ C_6H_6OH\cdot \rightarrow \text{dimer} \rightarrow \text{biphenyl}$$

$$C_6H_7\cdot + C_6H_6OH\cdot \rightarrow \text{dimer} \rightarrow \text{biphenyl}$$

The yields in aerated, unbuffered or acid, solutions were: G(phenol) = 2.1 (2.3), G(biphenyl) = 0 (0), and $G(H_2O_2)$ = 2.2 (3.1), the figures in brackets being valid for acid solutions. The ratio $k(H + C_6H_6)/k(H + O_2)$ was $1.4 \cdot 10^{-2}$. The results indicate that peroxides, or more probably hydroperoxides, take part in the reactions.

After the addition of Fe^{2+} or Fe^{3+} to aerated acid solutions G(phenol) was increased to 6.6 and 3.4 respectively. Oxygen was consumed more rapidly in the presence of Fe^{2+}.

Reaction mechanisms are discussed.

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1. Introduction

The radiolysis of aqueous solutions of benzene has been the subject for a great many investigations (1-39). In the reports by Weiss and Stein (1), Burton and Phung (6) and Dorfman et al. (8) the reaction mechanism was thoroughly discussed, and furthermore Burton used the system for a calculation of the primary radiation yields of water. The main products of the radiolysis of aqueous solutions were phenol, biphenyl, hydrogen and hydrogen peroxide. Biphenyl, however, was produced only in deaerated solutions. Manzitti et al. (9) found small amounts of several other compounds such as carboxylic acids and polyphenols. The G-values reported for the phenol formation in aerated solutions ranged from 1. 6 to 3. 1; in deaerated solutions the values ranged from 0. 3 to 0. 41.

In most investigations the system was irradiated with γ- or X-rays. However, Wright (10) used reactor neutrons and Weiss et al. (1) irradiated the system with neutrons as well as with α-particles. When the high LET radiation sources were used, the benzene ring was opened and mucondialdehyde was formed (1-3, 21). Recently Loeff and Stein (11, 12) have found mucondialdehyde when the system was irradiated with 200 kvp X-rays. The addition of various semiconductors in alkaline solutions (12, 13, 19) and of metal salts in acid solutions (15-23) has been studied. It was found (20, 21) that addition of Fe^{2+} increased the G value of phenol formation from 2 to 6, while G(phenol) in the presence of Fe^{3+} increased to 3-4, all in aerated solutions.

Investigations of the system at elevated temperatures and at high oxygen pressures have been reported (21, 25-27, 30). Under these conditions and with utilization of the post-irradiation effect G values as high as 70 have been claimed (26). However, an attempt by Henley et al. (31) to reproduce this value was not successful.

The use of the benzene-system as a dosimeter has been proposed (4, 5). More recently the system has been used as a dosimeter in the presence of dissolved neutron absorbers (32, 33).

Except in the Russian (20-30) and a few other investigations (9, 15, 16) the method used for the determination of phenol has been a measurement of the optical density either directly in the irradiated solution or after the addition of a complexing agent. Goodman and Steigman (39), however, have shown that these methods give too high values.

The potential economic interest in new methods for the phenol production has been a reason for the reexamination of some of the problems involved in the radiation chemistry of the benzene-water system. We have especially aimed at more reliable methods for the determination of phenol. At present the possibility to increase the yield of phenol by adding solids and by increasing the temperature and the pressure is being studied.

The results of the investigation at room temperature are given below.

2. Experimental

2. 1. Materials

Benzene (Merck p. a.) was recrystallized twice. The cooling curve was determined and the melting point found to be 5. 4 °C. The melting point of benzene is 5. 5 °C (46).

Distilled water was further triple distilled: first from alkaline permanganate, then from acid bichromate, and, finally, from pure water. This water was used for all irradiations and in all solutions for the H_2O_2 determination. Phenol, sulfuric acid and sodium carbonate, all of Mercks p. a. quality, biphenyl (Eastman Kodak), n-hexane (Hopkin and Williams spectrosol) and ether (Mallinckrodt p. a.) were used without further purification.

2.2. Irradiation procedure

A saturated aqueous solution of benzene was made up by shaking excess of benzene with water. Saturated solutions were used in all experiments except those described in section 3.2.6.

Two types of pyrex ampoules were used: 1) 60 ml aerated solutions were irradiated in a glass-stoppered pyrex ampoule with a total volume of about 70 ml. 2) 25 ml of benzene-water solution and 0.3 ml benzene in excess were irradiated in the other type of pyrex ampoule with a total volume of about 85 ml. Before irradiation this ampoule was connected to a vacuum system (Fig. 1) and after repeated freezing, pumping and heating, sealed off at a pressure of 10^{-5} mm Hg. The excess benzene was added in order to make up for loss during evacuation.

The ampoules were irradiated with γ-rays in a Gammacell 220 (Manufacturer: Atomic Energy of Canada Ltd.) loaded with 5000 curie ^{60}Co. The dose rate was determined with the Fricke and the ceric sulfate dosimeters using G-values of 15.6 and 2.4 respectively. The dose rate was about 7000 rad/min. (June 1962)

2.3. Analysis

The irradiated samples were analysed for phenol, biphenyl and hydrogen peroxide, and the deaerated samples also for hydrogen.

2.3.1. Hydrogen

The ampoule was connected to a vacuum system and opened (Fig. 1). The gas was extracted from the water and pumped through two liquid nitrogen traps to a Pd-tube, where hydrogen was separated and the amount measured with a McLeod gauge.

The measuring system was calibrated by means of hydrogen, generated in the ampoule opening device from H_2SO_4 and a weighed amount of pure Zn.

2. 3. 2. Biphenyl

Biphenyl was determined by extraction of 10 ml of the sample with 2 x 5 ml n-hexane and subsequent measurement of the optical density of the hexane phase on a Beckman DU spectrophotometer.

The extinction coefficient at 280 mμ was 1090, 557 and ~0 $l \cdot mole^{-1} \cdot cm^{-1}$ for biphenyl, phenol and benzene respectively, so it was necessary to correct for the simultaneously extracted phenol, the amount of which was 11 ± 1 per cent of the total amount of phenol.

We also made a qualitative analysis of the insoluble product formed when 2 l benzene-water solution was irradiated with a dose of 0. 75 Mrad. The product was separated by centrifugation, washed with water and recrystallized from 85 per cent ethanol. The melting point was 68 °C (biphenyl 69-71 °C). The ultraviolet spectrum of the product dissolved in tetrahydrofuran was similar to that of biphenyl and the retention time on a two meter silicone column heated to 200 °C in a Beckman gas chromatograph was the same as for biphenyl. The main content of the "insoluble" product was therefore probably biphenyl.

2. 3. 3. Phenol

After the extraction of biphenyl, the same solution was extracted with 3 x 3 ml ether in order to remove the phenol. The ether phase was brought up to 10 ml and the optical density was measured at 273. 5 mμ in a cell furnished with ground glass stoppers. The results were corrected for the phenol extracted into n-hexane in the first extraction. The method was similar to the one proposed by Baxendale and Magee (40). We found the extinction coefficient to be 2140 l · mole^{-1} · cm^{-1} which may be compared with Baxendale's value 2170 l · mole^{-1} · cm^{-1} at the same wave-length.

Most of the samples were also analysed for phenol by the extraction method proposed by Proskurnin (27). We extracted 5 ml of the sample with 3 x 3 ml benzene, which was subsequently extracted with 2 x 5 ml of a 1 N sodium carbonate solution. The optical density was measured at 287 mμ where the extinction coefficient was 2470 l · mole^{-1} · cm^{-1}.

We examined two direct methods for the analysis of phenol. In the first method, proposed by Sworski (35), the difference in the optical density in alkaline and unbuffered solutions was measured at 287 mμ, thus eliminating the influence of biphenyl, benzene etc. The reaction of phenol with the Folin reagent (41) was utilized in the other method. Because the samples sometimes turned turbid when the reagent was added, we reduced the amount of reagents to the following values: 10 ml sample + 1 ml Folin reagent + 5 ml of a 20 per cent sodium carbonate solution. The extinction coefficient at 750 mμ was found to be 15,030 l · · mole^{-1} · cm^{-1}.

2.3.4. Comparison of the analytical methods

The methods for the determination of biphenyl and phenol were tested on synthetic mixtures of biphenyl and phenol dissolved in water. The results are given in Table 1.

We also analysed a 1 sample of a benzene-water solution irradiated to 35.000 rad using the same methods. The results are given in Table 1. As was to be expected, all the methods gave approximately correct values in the synthetic mixtures. In the irradiated sample, however, the Folin reagent and the Sworski methods gave results which were 15 per cent higher than the results from the two extraction methods. This discrepancy may be due to a phenol-like substance with absorption maxima at 270 and 345 mμ which is left in the aqueous solution after the extraction (39) and thus interferes only in the direct methods. In the present study therefore, only the two extraction methods were used and this may explain why our results are somewhat lower than those generally reported. (Table 5)

2.3.5. Hydrogen peroxide

H_2O_2 was measured according to the Ghormley method (42): J^- was oxidized by H_2O_2 to J^-_3, the absorption of which was measured at 351 mμ. The extinction coefficient was 24,600 $l \cdot mole^{-1} \cdot cm^{-1}$. In stronger acid solutions we used the titanium method (43), in which titanium sulfate was oxidized by H_2O_2 to form pertitanic acid with an absorption maximum at 412 mμ. The extinction coefficient at this wave-length was 680 $l \cdot mole^{-1} \cdot cm^{-1}$, i. e. 36 times less than for the Ghormley method. Because the hydrogen peroxide was slowly decomposed in the irradiated solution, the determination was always made at a certain time shortly after the irradiation of the sample.

3. Results

The results are given as G-values, calculated from the equation

$$G = \frac{C \cdot 10^{-3} \cdot A \cdot 10^{-6}}{d} \cdot \frac{1.60}{D_F \cdot 10^3 \cdot 10^{12} \cdot e_f} =$$

$$= 0.963 \frac{C}{d \cdot D_F \cdot e_f} ,$$

where

C = concentration in μmole/l,

A = Avogadro's number,

d = density in g/ml,

D_F = dose in krad in a Fricke dosimeter under the same conditions,

e_f = the relation between the electron density of the system and the electron density of the Fricke dosimeter solution.

The ratio C/D_F was obtained from the curves in Fig. 2-11.

The terminology suggested by Allen (44) is used: The primary yield of the product X is denoted G_X and the yield of X measured after possible chemical reactions is denoted G(X).

3. 1. Deaerated solutions

3. 1. 1. Unbuffered solutions

Fig. 2 shows the yields of phenol (Ph), biphenyl (B), hydrogen peroxide and hydrogen as a function of the absorbed dose in the range 0 - 400 krad. The initial part of the curves is linear, while at higher doses the rate of phenol and biphenyl formation decreases. The G-value for phenol (0. 37) is in accordance with the values of Weiss et al. (1), Baxendale et al. (16) and Burton et al. (6). (See Tables 2 and 4). The G-value for biphenyl (1. 3) is in accordance with the values found by Weiss and by Burton, but is higher than that found by Baxendale. We find $G(H_2O_2) = 0.05$, in agreement with Burton's but in disagreement with Baxendale's value. $G(H_2)$ was 0. 44, approximately the primary yield of hydrogen in the radiolysis of water (44, 45). The corresponding values of Weiss and of Baxendale are somewhat higher.

3. 1. 2. Acid solutions

A saturated solution of benzene in 0. 1 N H_2SO_4 was irradiated. Fig. 3 shows the yields of the various products plotted against the dose. G(Ph) is the same and G(B) is somewhat higher as compared with unbuffered solutions. Hydrogen peroxide is formed with a G-value of 0. 60, whereas in unbuffered solutions this product is scarcely formed. G(H_2) was 0. 43, almost the same as in unbuffered solutions. For comparison of our results with those from other investigations, see Tables 2 and 4.

3. 2. Aerated solutions

3. 2. 1. Unbuffered solutions

The yields are constant up to a dose of about 50 krad, where the slope of the curves is changed (Fig. 4). This limit corresponds to the approximate consumption of the oxygen dissolved in the solution. G(Ph) is 2. 1 up to the change of slope[x] (about 6 times the value in deaerated solutions) and 0. 33 after the change (about the same value as in deaerated solutions). The analytical method used gives a value of G(Ph) which is lower than that generally reported (Table 5). However, Baxendale et al. (16), who used the same method, determined G(Ph) as 1. 57. Biphenyl is not formed until the oxygen is consumed. Then it is formed with a G-value of 1. 3, the same value as in deaerated solutions. G(H_2O_2) is 2. 2 and -0. 53 before and after the COS respectively. Our G-value before the COS is lower than Burton´s (2. 88), but equal to Baxendale´s value for a dose of 33 krad (2. 20). Sworski (34) and Burton also observed the decomposition of H_2O_2 after the COS.

3. 2. 2. Influence of pH on the yields

Samples of aqueous solutions of benzene and 0. 1 M Na_2SO_4, the pH of which were varied with H_2SO_4 or NaOH, were given a

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[x] The abbreviation COS will be used below for the term "change of slope".

dose of 40 krad. Fig. 5 shows the influence of pH on the yields of phenol and H_2O_2. The yield of phenol rises at both ends of the pH scale, whereas $G(H_2O_2)$ is largest in acid solutions. Weiss et al. (1) have previously obtained a similar curve for the phenol yield.

3.2.3. 0.8 N H_2SO_4 solutions

Fig. 6 shows the yields as functions of the absorbed doses. G(Ph) is 2.4 and 0.31 before and after the COS, the value 2.4 being a little higher than in unbuffered solutions. Biphenyl is formed with a G-value of 0.88 after the COS. $G(H_2O_2)$ is 3.10 and 0.49 before and after the COS, i. e. hydrogen peroxide is formed in larger amounts as compared with the irradiations in unbuffered solution and it is not decomposed after the COS. The pH of the solutions was 0.5 before and after the irradiation. The results may be compared with the results from other investigations in Table 5.

3.2.4. 0.1 N H_2SO_4 solutions

Fig. 7 shows the yields in 0.1 N acid solutions. The yield of phenol before the COS (2.3) is a little higher than in unbuffered solutions, whereas the yield after the COS (0.36) is about the same as in unbuffered solutions. G(B) is 1.3, i. e. the same as in unbuffered solutions. $G(H_2O_2)$ is 3.1 and 0.51 before and after the COS, respectively. These values are higher than in unbuffered solutions, but the same as in 0.8 N H_2SO_4 solutions. Results from other investigations are shown in Table 5.

3.2.5. Alkaline solutions

Fig. 8 shows the yields in 0.1 N NaOH solutions. Phenol is formed in larger amounts (G(Ph) = 2.7) as compared with irradiations of acid and unbuffered solutions. The same tendency has been found by Weiss et al. (1) and Preve et al. (13). G(B) is 0.95, somewhat lower than in unbuffered solutions. Hydrogen peroxide is formed with G-values of 1.9 and -0.46, before and after the COS respectively, i.e. about the same as in unbuffered solutions.

3.2.6. Influence of the benzene concentration on the yields

Aqueous solutions of benzene in varying concentrations were given a dose of 30 krad. Fig. 9 shows that the concentration of phenol (C(Ph)) decreases from 64 to 58 μmole/l when the concentration of benzene is changed from a 100 per cent to a 15 per cent saturated solution. At benzene saturations less than 10 per cent C(Ph) decreases more rapidly, being only 42 μmole/l at 2 per cent saturation. Weiss et al. (1) and Burton et al. (6) have found approximately the same trend. The concentration of biphenyl was negligible in all the samples. The concentration of hydrogen peroxide was constant when the benzene concentration was varied from a 100 per cent to a 5 per cent saturated solution but decreased at lower benzene concentrations. These results are in agreement with Burton´s results.

3.3. Irradiation of aerated solutions containing metal ions

Solutions of 0.1 N H_2SO_4 saturated with benzene and containing Fe^{2+} or Fe^{3+} in varying concentrations were irradiated. After irradiation the iron was precipitated and biphenyl was extracted into n-hexane from the alkaline solution in the presence of the precipitate, in order to avoid loss of biphenyl adsorbed on the iron hydroxides.

3.3.1. 10^{-2} N ferrous solutions

Fig. 10 shows the effect of adding Fe^{2+}: The COS appears at a dose of 20 krad compared to normally at 40 - 50 krad. G(Ph) is large (6.7) before the COS, whereas after the COS G(Ph) is only 0.22. G(B) is lower (0.18) than for irradiations in the absence of metal ions. $G(H_2O_2)$ is about 1.1 and 0 before and after the COS, respectively.

3.3.2. 10^{-3} N ferrous solutions

Corresponding results in 10^{-3} N ferrous solutions are shown in Fig. 11. G(Ph) is 6.6 before and 0.40 after the COS. G(B) is considerably higher in the weak Fe^{2+} solutions (0.89 compared to 0.18 in 10^{-2} N ferrous solution). $G(H_2O_2)$ is about the same as in 10^{-2} N ferrous solutions.

3.3.3. 10^{-3} N ferric solutions

Fig. 12 shows the effect of adding Fe^{3+}. It will be noticed that the COS appears at 40 - 50 krad, i. e. at the same dose as for solutions without metal ions. G(Ph) is 3.4 before and 0.61 after the COS. Obviously Fe^{3+} as well as Fe^{2+} increase the yield of phenol, but due to different mechanisms. G(B) is 1.1, or somewhat lower than for irradiations in the absence of metal ions.

4. Discussion

4.1. Primary reactions

When water is irradiated, primary products are formed according to the reaction:

$$H_2O \rightsquigarrow H,\ OH,\ H_2,\ H_2O_2, \qquad (1)$$

where H is the sum of the reducing radicals H and e^-_{aq}. The products are formed with the G values G_H, G_{OH}, G_{H_2} and $G_{H_2O_2}$.

4.2. Burton´s reaction mechanism

The reaction mechanism for the benzene-water system generally accepted until 1962 has been presented by Weiss et al. (1) and Burton et al. (6) and the following is essentially a summary of this mechanism.

4.2.1. Deaerated solutions

The following reactions take place:

$$C_6H_6 + H \rightarrow C_6H_5\cdot + H_2 \qquad (2a)$$

$$C_6H_6 + H \rightarrow C_6H_7\cdot \qquad (2b)$$

reaction (2b) being the more probable.

$$C_6H_6 + OH \rightarrow C_6H_5\cdot + H_2O \qquad (3a)$$

$$C_6H_6 + OH \rightarrow C_6H_5OH + H\ , \qquad (3b)$$

where reaction (3a) is thermodynamically favoured.

$$C_6H_5\cdot + OH \longrightarrow C_6H_5OH \qquad (4)$$

$$C_6H_5\cdot + H \longrightarrow C_6H_6 \qquad (5)$$

$$C_6H_5\cdot + C_6H_5\cdot \longrightarrow (C_6H_5)_2\ , \qquad (6)$$

in which reactions phenol and biphenyl are formed.

Considering the existence of the solvated electrons the decomposition of hydrogen peroxide in unbuffered solutions should be written as

$$H_2O_2 + e^-_{aq} \longrightarrow OH + OH^- \cdot \qquad (7a)$$

The reactions

$$H_2O_2 + H \longrightarrow OH + H_2O \qquad (7b)$$

$$H_2O_2 + H_2^+ \longrightarrow OH + H_3O^+ \qquad (7c)$$

given by Burton take place mainly in acid solutions.

4.2.2. Aerated solutions

In addition to the reactions (1), (2b), (3a) and (7) the following reaction takes place:

$$H + O_2 \longrightarrow HO_2 \ , \qquad (8)$$

which competes with reaction (5) and the reaction between H and OH and therefore the phenol yield is increased. HO_2 is not able to oxidize benzene to phenol, though the oxidation is possible in the presence of Fe^{2+}.

Also the reactions

$$C_6H_5 \cdot + O_2 \longrightarrow C_6H_5O_2 \cdot \qquad (9)$$

$$C_6H_5O_2 \cdot + H_2O \longrightarrow C_6H_5OH + HO_2 \qquad (10)$$

$$C_6H_5O_2 \cdot + C_6H_6 \longrightarrow \text{oxygen containing product} + OH \qquad (11)$$

increase the yield of phenol.

Hydrogen peroxide is formed in the reaction:

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \cdot \qquad (12)$$

4. 3. Dorfman's reaction mechanism

Dorfman studied the benzene-water system using the pulse radiolysis technique, and observed the transient hydroxycyclohexadienyl radical formed in the reaction

$$C_6H_6 + OH \longrightarrow C_6H_6OH \cdot \qquad (13)$$

Thus, reaction (3) should not take place. Reaction (13) had previously been proposed by Russian investigators (21, 28, 29).

In deaerated solutions phenol and biphenyl are formed by the reactions

$$2C_6H_6OH \cdot \longrightarrow C_6H_5OH + C_6H_7OH \qquad (14)$$

$$2C_6H_6OH \cdot \longrightarrow \text{Unstable dimers} \longrightarrow \text{biphenyl} \qquad (15a)$$

$$C_6H_6OH \cdot + C_6H_7 \cdot \longrightarrow \text{Unstable dimers} \longrightarrow \text{biphenyl.} \qquad (15b)$$

In aerated solutions the following reactions take place

$$C_6H_6OH \cdot + O_2 \longrightarrow C_6H_6(OH)O_2 \cdot \qquad (16)$$

$$C_6H_6(OH)O_2 \cdot \longrightarrow C_6H_5OH + HO_2 \qquad (17a)$$

$$2C_6H_6(OH)O_2 \cdot \longrightarrow \text{peroxides} \qquad (17b)$$

$$HO_2 + C_6H_6(OH)O_2 \cdot \longrightarrow \text{hydroperoxides.} \qquad (17c)$$

where reaction (17a) dominates at low radical concentrations. In addition to this reactions (8) and (12) take place.

4.4. Evaluation of the two mechanisms

It would be of interest to examine our data on the basis of the two mechanisms. One should, however, bear in mind the great difference between the dose rate in pulse-radiolysis (10^9 rad/sec in the pulse) and the dose rate in experiments using continuous irradiation (10 rad/sec) resulting in different radical concentrations.

4.4.1. Deaerated solutions

According to Burton's mechanism, the reactions (1), (2b), (3a), (4), (6) and (7) take place in deaerated solutions. When equilibrium conditions are obtained the following relation based on a hydroxyl radical balance is valid:

$$G_{OH} + G_H \cdot \frac{k_7 \cdot (H_2O_2)}{k_7 \cdot (H_2O_2) + k_{2b} \cdot (C_6H_6)} = 2G(Ph) + 2G(B) \qquad (I)$$

where k_7 is the rate constant for the reaction (7) and (H_2O_2) denotes the concentration of H_2O_2.

In unbuffered solutions $G(H_2O_2) \simeq 0$, i. e.

$$G_H \cdot \frac{k_7 \cdot (H_2O_2)}{k_7 \cdot (H_2O_2) + k_{2b} \cdot (C_6H_6)} \simeq G_{H_2O_2}$$

and consequently

$$G_{OH} + G_{H_2O_2} = 2G(Ph) + 2G(B)$$

$$= 2 \cdot 0.37 + 2 \cdot 1.3 = 3.3 \,,$$

which is in good agreement with the known value of $G_{OH} + G_{H_2O_2}$ (3.1 according to Allen (44)).

In acid solutions most of the hydrogen peroxide produced as "the molecular product" remains in the solution. The decomposed amount is $G_{H_2O_2} - G(H_2O_2)$. Equation (I) may therefore be written:

$$G_{OH} + G_{H_2O_2} = G(H_2O_2) + 2G(Ph) + 2G(B)$$

$$= 0.6 + 0.74 + 3.4 = 4.7 ,$$

The value 3.8 for $G_{OH} + G_{H_2O_2}$ given by Allen (44) is not within the limits of the estimated error for the experimental value, indicating that the given reaction mechanism is incomplete.

According to Dorfman's mechanism, phenol is formed in reaction (14) and biphenyl in an obscure way in reaction (15). In addition to these, reactions (1), (2b), (7) and (13) are assumed to take place. The following relation should then be valid provided that all $C_6H_6OH\cdot$ radicals react under the formation of phenol and biphenyl:

$$G_{OH} + G_{H} \cdot \frac{k_7 \cdot (H_2O_2)}{k_7 \cdot (H_2O_2) + k_{2b} \cdot (C_6H_6)} = 2G(Ph) + f \cdot G(B) \qquad (II)$$

The equation which is almost identical with eq. (I) may be reduced to

$$G_{OH} + G_{H_2O_2} = G(H_2O_2) + 2G(Ph) + f \cdot G(B) .$$

The insertion of measured and known values gives $f = 1.8$ in unbuffered solution and $f = 1.4$ in acid solution. Thus in acid solution a greater part of the $C_6H_6OH\cdot$ radicals reacts according to reaction (15b). This is quite reasonable, since reaction (2b) in competition with reaction (7) should be favoured in acid solutions and the concentration of $C_6H_7\cdot$ radicals increased. The $C_6H_7\cdot$ radicals not reacting according to reaction (15b) might be transformed into partly hydrogenated aromatics.

The difference between $G(H_2O_2)$ in acid and in unbuffered solutions (Table 2) may be explained by different rate constants for the reactions (7a), (7b) and (7c). The reaction (7c) is probably much slower than reaction (7a) because H_2^+ may act as an oxidizing as well as a reducing agent (47). If the variation with pH of $G_{e^-_{aq}}$, G_H and $G_{H_2^+}$ is assumed to be that found by Dainton et al. (48) the increase of the reducing radicals when the solution turns acid corresponds to $G(H_2^+)$, i. e. the sum of G(H) and $G(e^-_{aq})$ is nearly constant. Furthermore

$$\frac{k(H+H_2O_2)}{k(H+O_2)} \simeq 10^{-3}; \quad \frac{k(e^-_{aq}+O_2)}{k(e^-_{aq}+H_2O_2)} \simeq 1.5 \ (49),$$

and consequently

$$\frac{k(H+H_2O_2)}{k(e^-_{aq}+H_2O_2)} \cdot \frac{k(e^-_{aq}+O_2)}{k(H+O_2)} \simeq 10^{-3},$$

where $k(H+H_2O_2)$ means the rate constant for the reaction between H and H_2O_2 etc. Since $k(e^-_{aq}+O_2) = 1.0 \cdot 10^{10}\ l \cdot mole^{-1} \cdot sec^{-1}$ (49) and $k(H+O_2)$ is of the same order as $k(e^-_{aq}+O_2)$, it follows that $k(e^-_{aq}+H_2O_2) \gg k(H+H_2O_2)$.

The different yields of H_2O_2 in acid and unbuffered solutions is thus explained by different rate constants for the reactions 7a and 7b.

As H_2 does not enter into any of the reactions, $G_{H_2} = G(H_2) = 0.44$.

4.4.2. Aerated solutions

According to Burton´s mechanism, the reactions (1), (2b), (3a), (7) - (12) take place. In conditions of equilibrium the following equation is valid

$$G(Ph) = G_{OH} + G_H \cdot \frac{k_7 \cdot (H_2O_2)}{k_7 \cdot (H_2O_2) + k_8 \cdot (O_2) + k_2 \cdot (C_6H_6)} \qquad \text{(III)}$$

In acid solutions $k_7/k_8 \simeq 10^{-3}$, thus $G(Ph) = G_{OH} = 2.3$. In unbuffered solution G_{OH} equals the initial value of G(Ph), since $C(H_2O_2)$ is negligible at the beginning of the irradiation, i. e. $G_{OH} = 2.1$. Allen (44) gives the values 2.9 and 2.4 for G_{OH} for acid and unbuffered solutions respectively. At least the value for acid solutions disagrees with Allen´s value.

In addition to (III) the following relation is valid:

$$G(H_2O_2) = G_{H_2O_2} + \frac{1}{2} G_{OH} + \frac{1}{2} G_H \cdot \frac{k_8 \cdot (O_2)}{k_8 \cdot (O_2) + k_7 \cdot (H_2O_2) + k_2 \cdot (C_6H_6)} -$$

$$- \frac{1}{2} G_H \cdot \frac{k_7 \cdot (H_2O_2)}{k_7 \cdot (H_2O_2) + k_8 \cdot (O_2) + k_2 \cdot (C_6H_6)} \qquad \text{(IV)}$$

In acid solutions where $k_7/k_8 \simeq 10^{-3}$ the expression is reduced to

$$G(H_2O_2) = G_{H_2O_2} + \frac{1}{2} G_{OH} + \frac{1}{2} G_H \cdot \frac{1}{1 + \frac{k_2 \cdot (C_6H_6)}{k_8 \cdot (O_2)}}$$

From this equation k_2/k_8 may be calculated by insertion of measured and known values. The concentration of C_6H_6 was 20 mmol/l and the concentration of O_2 was 0.25 mmol/l, i. e.

$$\frac{k(H + C_6H_6)}{k(H + O_2)} = 1.4 \cdot 10^{-2} .$$

According to Dorfman´s mechanism the reactions (1), (8), (12), (13), (16), (17) and probably (2b) take place. Phenol was formed also by the slow post-irradiation decomposition of peroxides, and the higher the intensity, the more post-irradiation phenol was formed. In our experiments we found a 7 per cent increase in the phenol concentration from 1 to 7 h after the irradiation and the concentration was then constant for 8 days. Apparently, the concentration of the hydroxycyclohexadienyl peroxy radical in our experiments is so small that little peroxide is formed. The equilibrium relation

$$G(Ph) + 2G(peroxides) + G(hydroperoxides) =$$

$$= G_{OH} + H \cdot \frac{k_7 \cdot (H_2O_2)}{k_7 \cdot (H_2O_2) + k_8 \cdot (O_2) + k_2 \cdot (C_6H_6)} \qquad (V)$$

may then in acid solutions be simplified to

$$G(Ph) + G(hydroperoxides) = G_{OH} ,$$

which differs from Burton´s expression by the term G(hydroperoxide).

In correspondance with eq. (IV) we have

$$\begin{aligned} G(H_2O_2) = G_{H_2O_2} &+ \left[\frac{1}{2}\, G_{OH} \cdot \frac{k_{17a}}{k_{17a} + k_{17c} \cdot (HO_2)} + \right. \\ &+ \left. \frac{1}{2}\, G_H \cdot \frac{k_8 \cdot (O_2)}{k_8 \cdot (O_2) + k_7 \cdot (H_2O_2) + k_2 \cdot (C_6H_6)} \right] \cdot \\ &\cdot \frac{k_{12} \cdot (HO_2)}{k_{12} \cdot (HO_2) + k_{17c} \cdot (C_6H_6(OH)O_2)} - \\ &- \frac{1}{2}\, G_H \cdot \frac{k_7 \cdot (H_2O_2)}{k_7 \cdot (H_2O_2) + k_8 \cdot (O_2) + k_2 \cdot (C_6H_6)} \end{aligned} \qquad \text{(VI)}$$

This equation contains too many unknown quantities for calculation to be practical. However, the validity of a simplification may be tested: If reaction (2b) and reaction (17c) are neglected, then in acid solutions

$$G(H_2O_2) = G_{H_2O_2} + \frac{1}{2}\, G_H + \frac{1}{2}\, G_{OH} \qquad \text{(VIa)}$$

Through the insertion of known values we find $G(H_2O_2) = 3.8$, whereas the measured value is 3.1 ± 0.2 showing that the reactions (2b) and/or (17c) should not be ignored.

4.4.3. Aerated alkaline solutions

The increase in the yield of phenol in alkaline solutions (Table 3) is due to the higher concentration of OH radicals: According to Haissinsky (50) $G_{OH} = 3.15$ in a 0.2 N NaOH solution, which is higher than the value of G_{OH} in both unbuffered and acid solutions (44).

4.5. Influence of metal ions on the yields

The effect of metal ions on the radiolysis of aqueous solutions of benzene has been studied earlier. Yumoto et al. (18) found that G(Ph) of an aerated 0.1 N H_2SO_4 solution increased from 2.17 to 3.67 if the solution was made $5 \cdot 10^{-4}$ N Fe^{3+}. Proskurnin et al. (20-23) irradiated solutions containing Fe^{2+} at high oxygen pressures. Due to the high oxygen pressure they found no change in the slope of the dose-yield curve but G(Ph) was increased from 2 to 6. In the presence of Fe^{3+} the yield of phenol increased to 3 - 4.

In the present investigation G(Ph) increased to 6.6 when acid 10^{-2} - 10^{-3} N ferrous solutions, saturated with benzene, were irradiated. The change of slope occured at about 20 krad compared to normally at 40 - 50 krad, i. e. the oxygen was consumed more rapidly in the presence of Fe^{2+}. The increased phenol yield may be due to an increase in the OH concentration according to reactions well known from the Fricke dosimeter:

$$H^+ + HO_2 + Fe^{2+} \longrightarrow Fe^{3+} + H_2O_2 \qquad (18)$$

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{2+}(OH) + OH \qquad (19)$$

$$OH + Fe^{2+} \longrightarrow Fe^{2+}(OH) . \qquad (20)$$

Reaction (20), however, competes with reaction (3). G(Ph) should then as a maximum be equal to 6.6. The rapid consumption of oxygen may be due to a competition between reaction (18) and (12), thus preventing the reformation of oxygen. After the COS the reactions (19) and (20) continue to take place.

According to Mertz and Waters (51) $k_3/k_{20} = 3.2$ and consequently

$$\frac{k_{20} \cdot (Fe^{2+})}{k_3 \cdot (C_6H_6)} \simeq \frac{1}{3} \cdot \frac{10}{20} = \frac{1}{6}$$

for a 10^{-2} N ferrous solution, i. e. 1/7 of the hydroxyl radicals disappear according to reaction (20). In a 10^{-3} N ferrous solution an insignificant proportion of the hydroxyl radicals disappear in reaction (20). This may explain why after the COS G(Ph) and G(B) are lower in 10^{-2} than in 10^{-3} N ferrous solutions.

The increase of G(Ph) in the presence of Fe^{3+} may be due to the reaction

$$\cdot\, C_6H_6OH + Fe^{3+} \longrightarrow C_6H_5OH + Fe^{2+} + H^+ \,, \qquad (21)$$

which increases the yield of phenol without increasing the rate of oxygen consumption.

5. Conclusion

The experiments presented here show that the reactions (15a) and (15b) and possibly the reaction

$$2\, C_6H_7 \cdot \longrightarrow \text{Unstable dimer} \longrightarrow \text{Biphenyl}$$

compete for the formation of biphenyl in deaerated acid solutions. However, in deaerated unbuffered solutions the agreement between eqs. (I) and (II) is good, the constant f in eq. (II) being equal to 1.8.

The results in aerated solutions suggest that hydroperoxides are formed not only in pulse radiolysis but also under continuous irradiation. The relation between the rate constants for the reactions (2b) and (8) was found to be $1.4 \cdot 10^{-2}$. A pulse radiolysis study of acid solutions of benzene in water might contribute to a further clarification of the complicated reaction mechanism.

When solutions containing Fe^{2+} were irradiated, oxygen was consumed faster and G(Ph) increased from 2.3 to 6.6. When solutions containing Fe^{3+} were irradiated, G(Ph) increased to 3.4. Different mechanisms for the increase in ferrous and in ferric solutions were postulated.

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Appendix

Reactions in the benzene-water system

$$H_2O \xrightarrow{\rightsquigarrow} H,\ OH,\ H_2,\ H_2O_2 \qquad (1)$$

$$C_6H_6 + H \begin{array}{l} \nearrow C_6H_5\cdot + H_2 \qquad (2a) \\ \searrow C_6H_7\cdot \qquad (2b) \end{array}$$

$$C_6H_6 + OH \begin{array}{l} \nearrow C_6H_5\cdot + H_2O \qquad (3a) \\ \searrow C_6H_5OH + H \qquad (3b) \end{array}$$

$$C_6H_5\cdot + OH \longrightarrow C_6H_5OH \qquad (4)$$

$$C_6H_5\cdot + H \longrightarrow C_6H_6 \qquad (5)$$

$$C_6H_5\cdot + C_6H_5\cdot \longrightarrow (C_6H_5)_2 \qquad (6)$$

$$H_2O_2 + e^-{}_{aq} \longrightarrow OH + OH^- \qquad (7a)$$

$$H_2O_2 + H \longrightarrow OH + H_2O \qquad (7b)$$

$$H_2O_2 + H_2^+ \longrightarrow OH + H_3O^+ \qquad (7c)$$

$$H + O_2 \longrightarrow HO_2 \qquad (8)$$

$$C_6H_5\cdot + O_2 \longrightarrow C_6H_5O_2\cdot \qquad (9)$$

$$C_6H_5O_2\cdot + H_2O \longrightarrow C_6H_5OH + HO_2 \qquad (10)$$

$$C_6H_5O_2\cdot + C_6H_6 \longrightarrow \text{oxygen containing product} + OH \qquad (11)$$

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \qquad (12)$$

$$C_6H_6 + OH \longrightarrow C_6H_6OH\cdot \tag{13}$$

$$2\ C_6H_6OH\cdot \longrightarrow C_6H_5OH + C_6H_7OH \tag{14}$$

$$2\ C_6H_6OH\cdot \longrightarrow \text{Unstable dimers} \rightarrow \text{biphenyl} \tag{15a}$$

$$C_6H_6OH\cdot + C_6H_7\cdot \longrightarrow \quad \text{- " -} \quad \rightarrow \quad \text{- " -} \tag{15b}$$

$$C_6H_6OH\cdot + O_2 \longrightarrow C_6H_6(OH)O_2\cdot \tag{16}$$

$$C_6H_6(OH)O_2\cdot \longrightarrow C_6H_5OH + HO_2 \tag{17a}$$

$$2\ C_6H_6(OH)O_2\cdot \longrightarrow \text{peroxides} \tag{17b}$$

$$C_6H_6(OH)O_2\cdot + HO_2 \longrightarrow \text{hydroperoxides} \tag{17c}$$

$$Fe^{2+} + H^+ + HO_2 \longrightarrow Fe^{3+} + H_2O_2 \tag{18}$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{2+}(OH) + OH \tag{19}$$

$$Fe^{2+} + OH \longrightarrow Fe^{2+}(OH) \tag{20}$$

$$C_6H_6OH\cdot + Fe^{3+} \longrightarrow C_6H_5OH + Fe^{2+} + H^+ \tag{21}$$

Table 1

Comparison of analytical methods.

Added quantity µM		Determined quantity µM				
Biphenyl	Phenol	Biphenyl	Phenol			
			Folin	Sworski	Baxendale	Proskurnin
	201				200	200
Saturated	339				340	334
"	306	50		306	295	298
"	30	52	30	32	32	30
51	94	40	90	94	90	92
Saturated	115	50	118			
28	500	30				
57	-	60				
56	202	55				
					77.8	
1 l of an aqueous solution of benzene, irradiated to 35000 rad.		2.4	90	93.2	78.1	80
		4.0	92	94.0	83.7	82
		4.8	84	94.8	83.7	80
		4.8	85	94.8	82.4	80
				94.8	81.4	90
				95.6	83.2	78
Mean value		4.0 ± 0.6	88 ± 2	94.5 ± 0.4	81.5 ± 0.9	81 ± 2
Standard deviation		1.2	4	0.9	2	4

Table 2

G-values in deaerated solutions.

Solution	Phenol	Biphenyl	H_2O_2	H_2
Unbuffered	0.37	1.3	0.05	0.44
0.1 n H_2SO_4	0.37	1.7	0.60	0.43

Table 3

G-values in aerated solutions.

Solution	Phenol		Biphenyl		H_2O_2	
	Before the COS	After the COS	Before the COS	After the COS	Before the COS	After the COS
Unbuffered	2.1	0.33	0	1.3	2.2	-0.53
0.8 N H_2SO_4	2.4	0.31	0	0.88	3.1	0.49
0.1 N H_2SO_4	2.3	0.36	0.2	1.3	3.1	0.51
0.1 N NaOH	2.7	0.50	0	0.95	1.9	-0.46
0.1 N H_2SO_4 + 10^{-2} N Fe^{2+}	6.7	0.22	0	0.18	1.1	0
0.1 N H_2SO_4 + 10^{-3} N Fe^{2+}	6.6	0.40	0	0.89	0.8	0
0.1 N H_2SO_4 + 10^{-3} N Fe^{3+}	3.4	0.61	0	1.1	1.4	neg.

Table 4

G-values in deaerated solutions. Literature values.

Reference		Solution	Phenol	Biphenyl	H_2O_2	H_2
Burton	(6)	unbuffered	0.36	1.22	0	0.42
		acid	0.35	0.96	0.57	0.39
Weiss	(1)	unbuffered	0.41	1.2		0.61
Baxendale	(16)	unbuffered	0.3	0.58	0.3	0.60
		acid	0.34	0.55	0.59	0.58
		alkaline	0.35	0.45	0.40	0.63
Sworski	(36)	acid	0.29		0.58	
Manzitti	(9)		0.3			

Table 5

G-values in aerated solutions. Comparison with literature values.

Reference		Solution	Phenol	Biphenyl	H_2O_2	H_2
Burton	(6)	unbuffered	2.64		2.88	0.42
		acid	2.64		2.84	0.39
Weiss	(1)	unbuffered	2.3			
Baxendale	(16)	unbuffered	1.57	0.03	2.20-2.50	
		acid			3.02	
Freeman	(37)	unbuffered	2.74-3.05			
Sworski	(36)		2.6		2.8	
Manzitti	(9)		2.6			
Preve	(13)	alkaline	3.1			
Hotta	(17)	unbuffered	2.63			
		acid	2.63			
Proskurnin	(22)		2			
Johnson	(32)		2.35			
Yumoto	(18)	acid	2.17	0.06	4.29	
		unbuffered	1.98	0.15	2.28	
Dorfman	(8)	unbuffered	1.9			
This investigation		unbuffered	2.1	0	2.2	
		acid	2.3	0.2	3.1	
		alkaline	2.7	0	1.9	

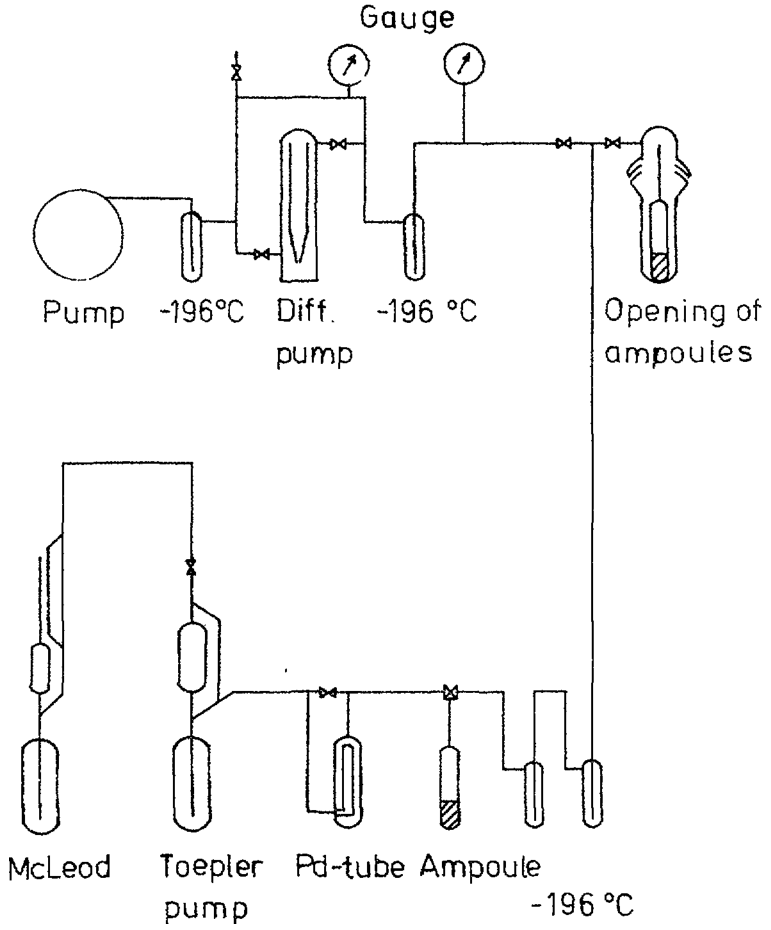

Fig. 1. Vacuum apparatus.

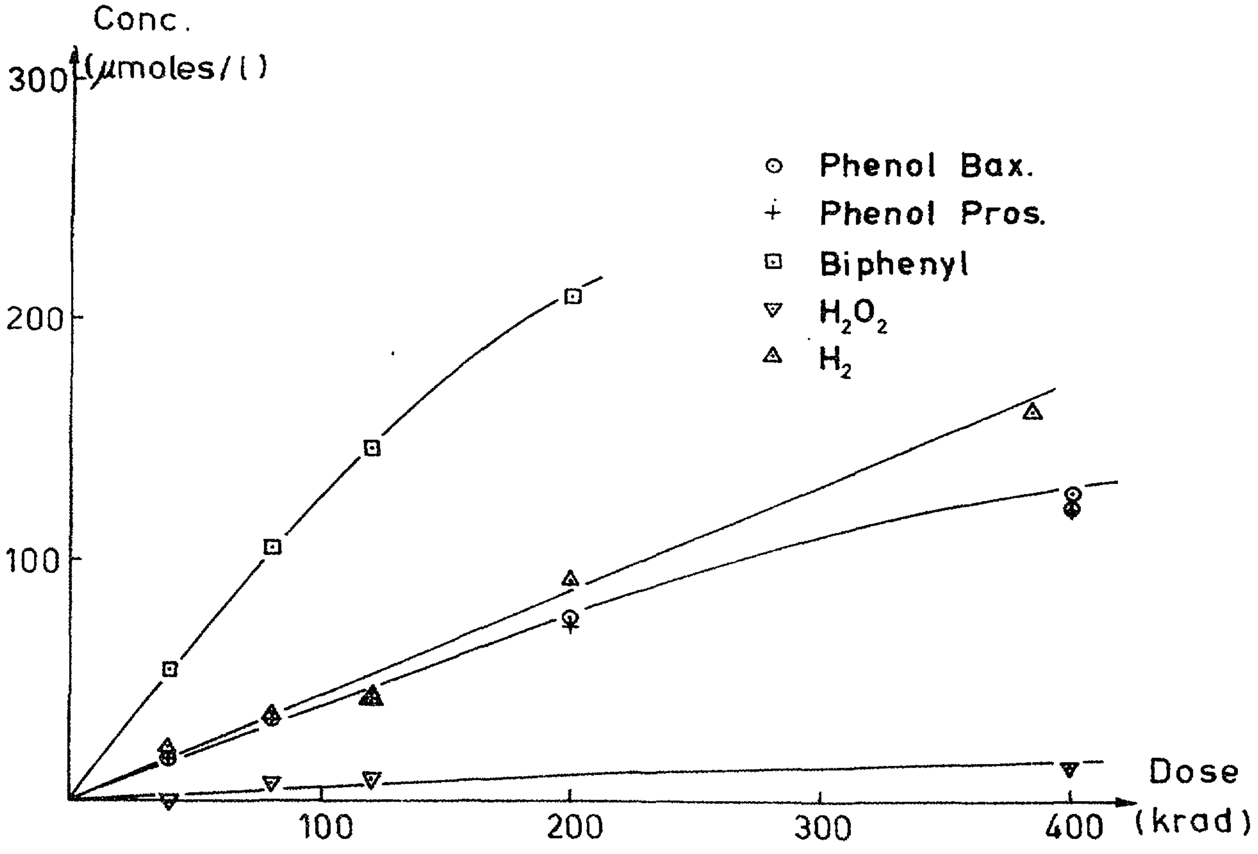

Fig. 2. Yields in deaerated unbuffered solutions.

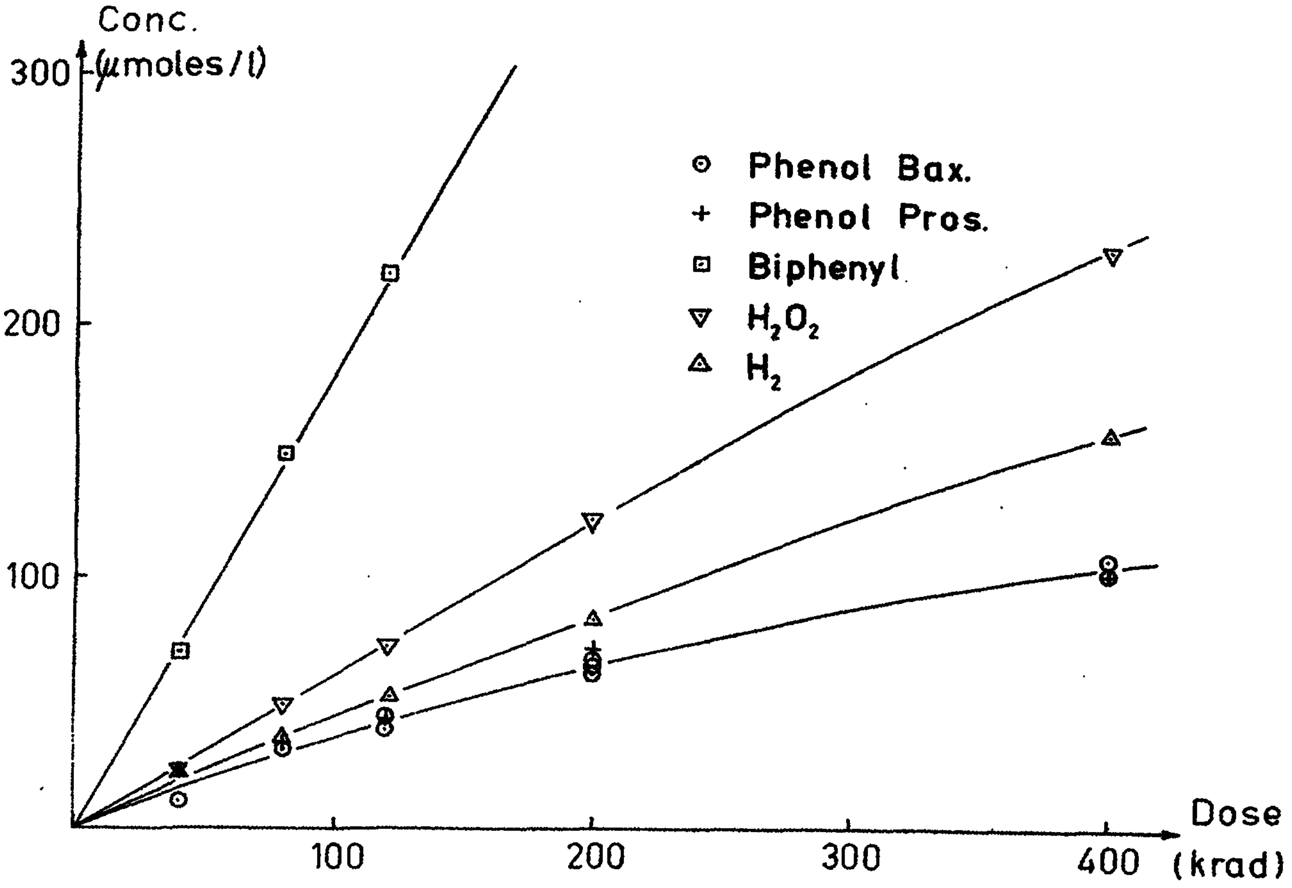

Fig. 3. Yields in deaerated 0.1 N H_2SO_4 solutions.

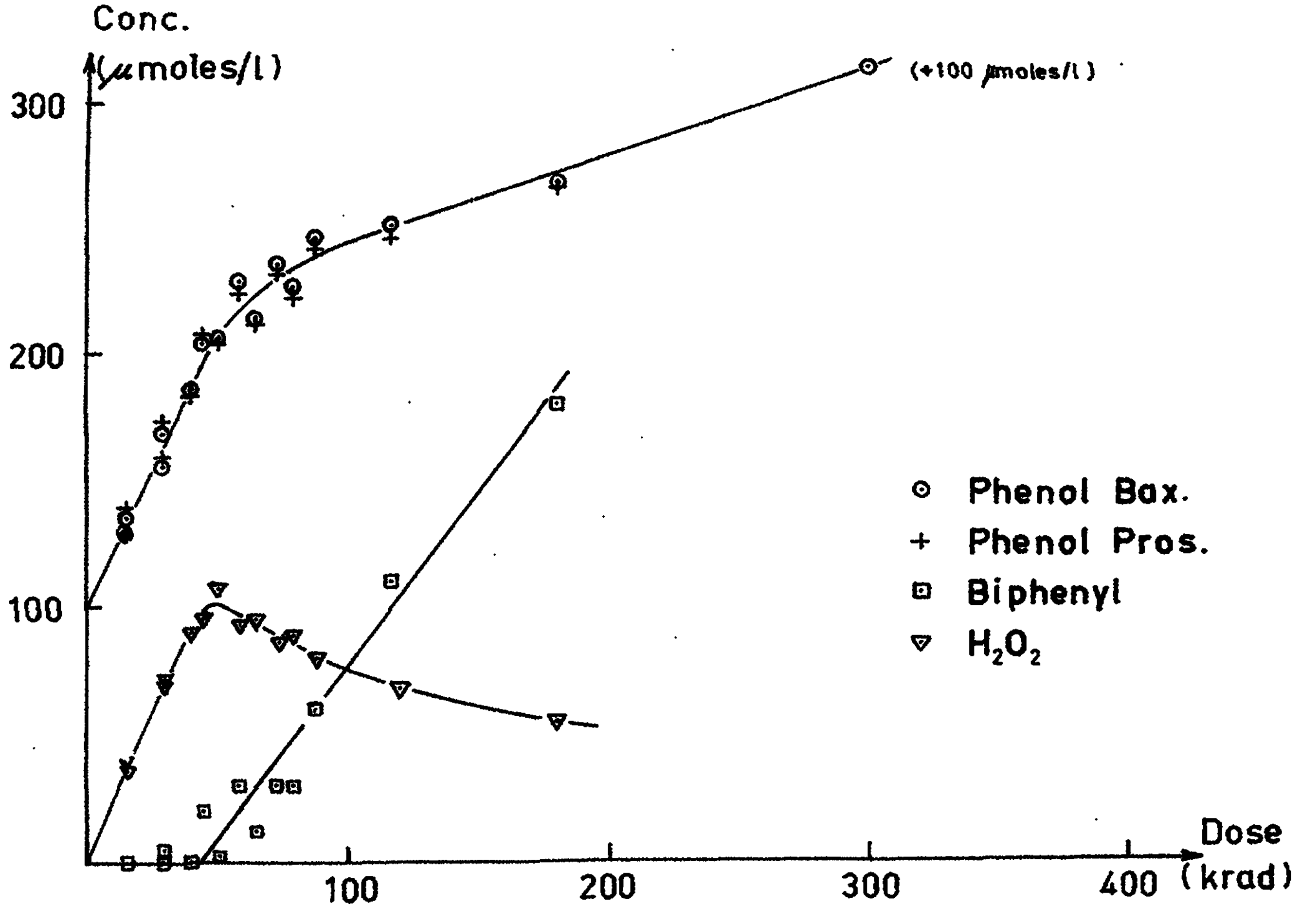

Fig. 4. Yields in aerated unbuffered solutions.

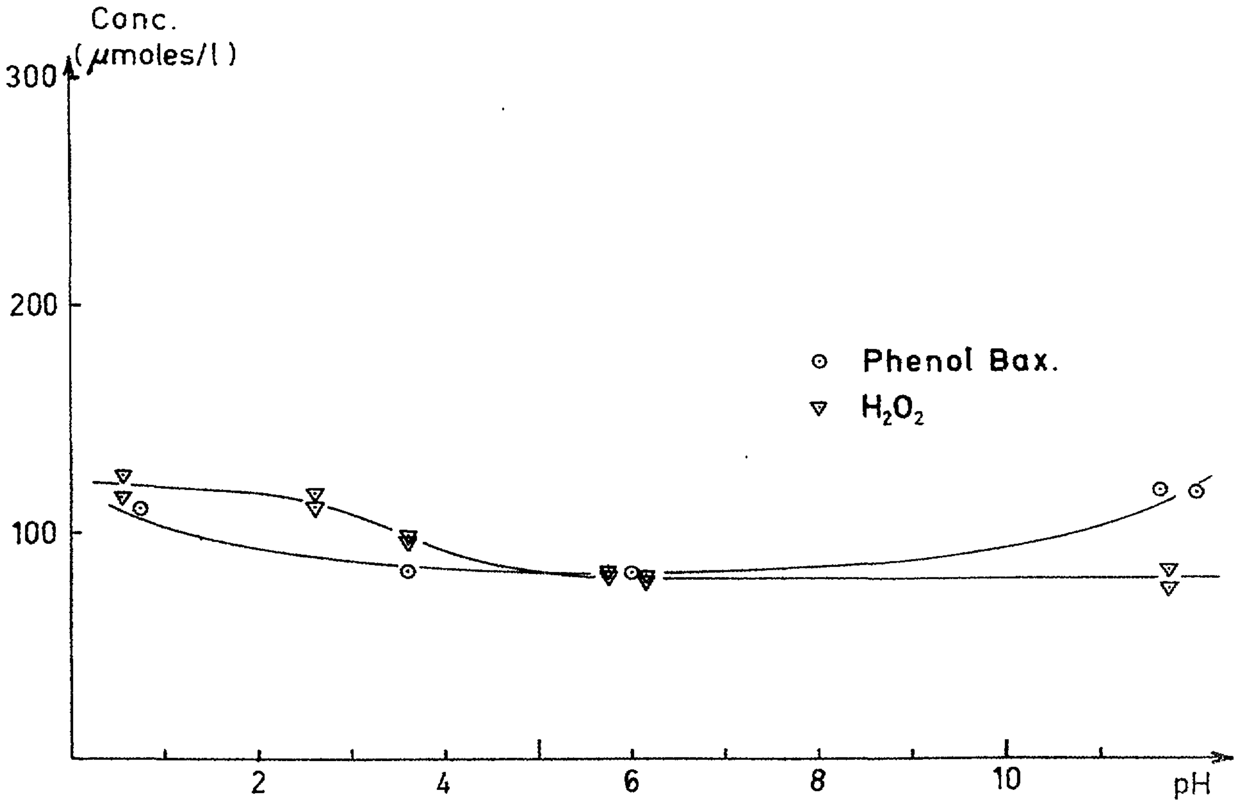

Fig. 5. Yields in aerated solutions. Dependence on pH.

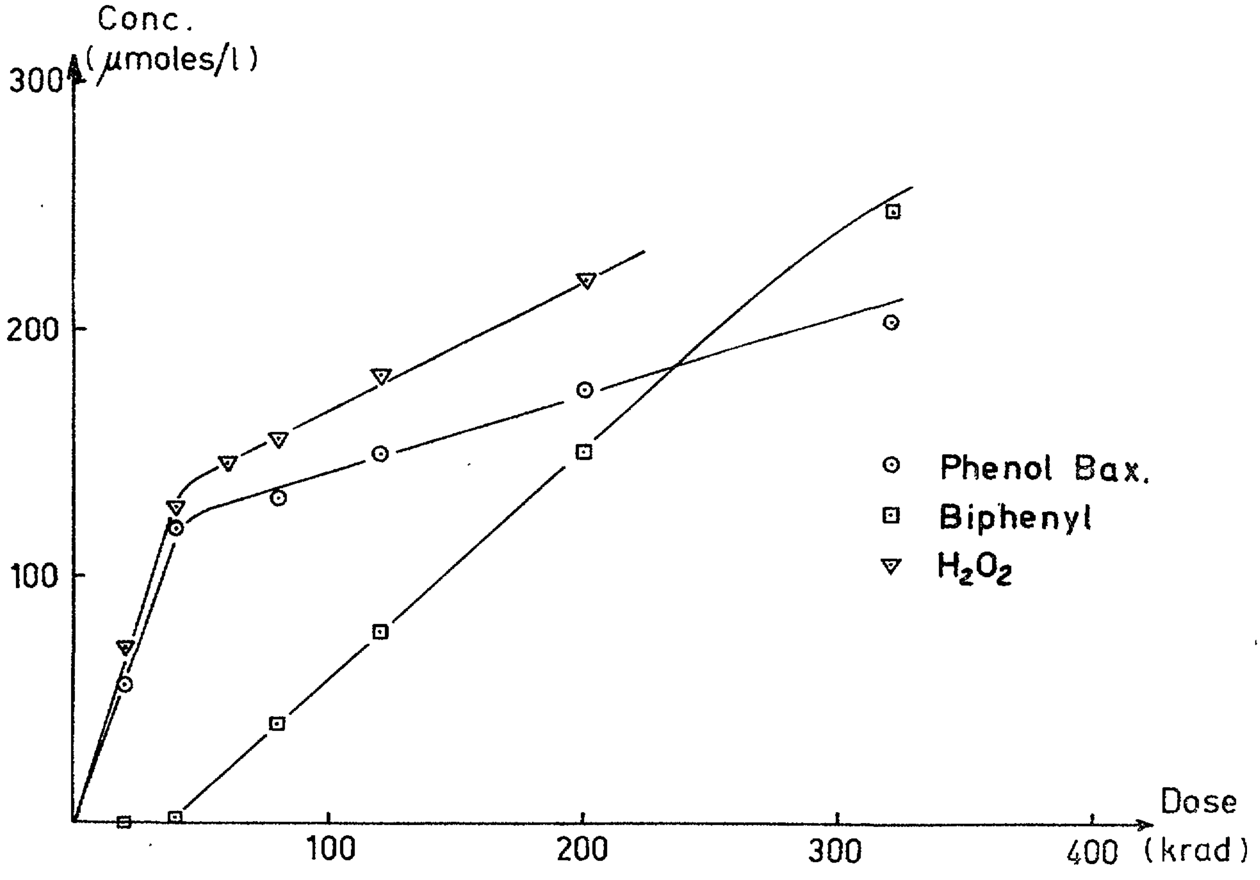

Fig. 6. Yields in aerated 0.8 N H_2SO_4 solutions.

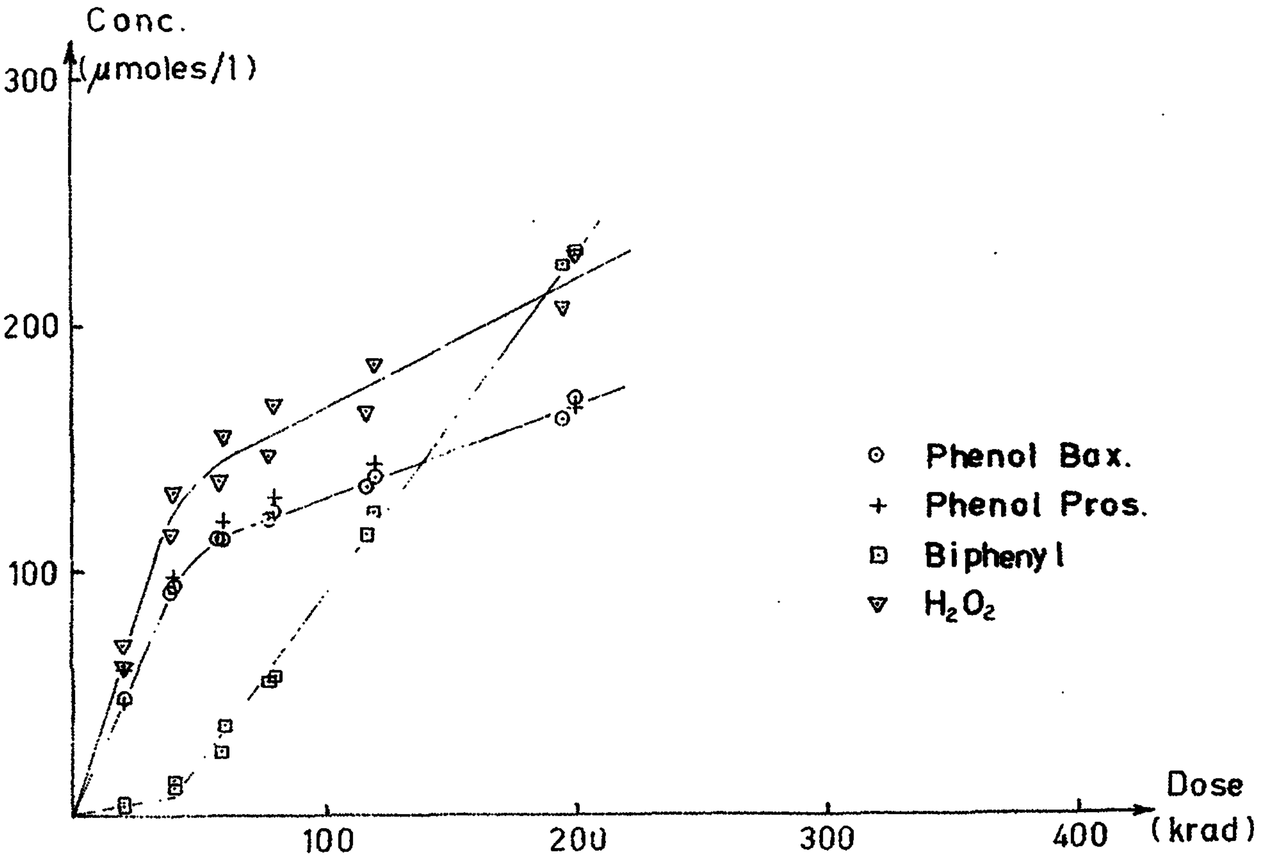

Fig. 7. Yields in aerated 0.1 N H_2SO_4 solutions.

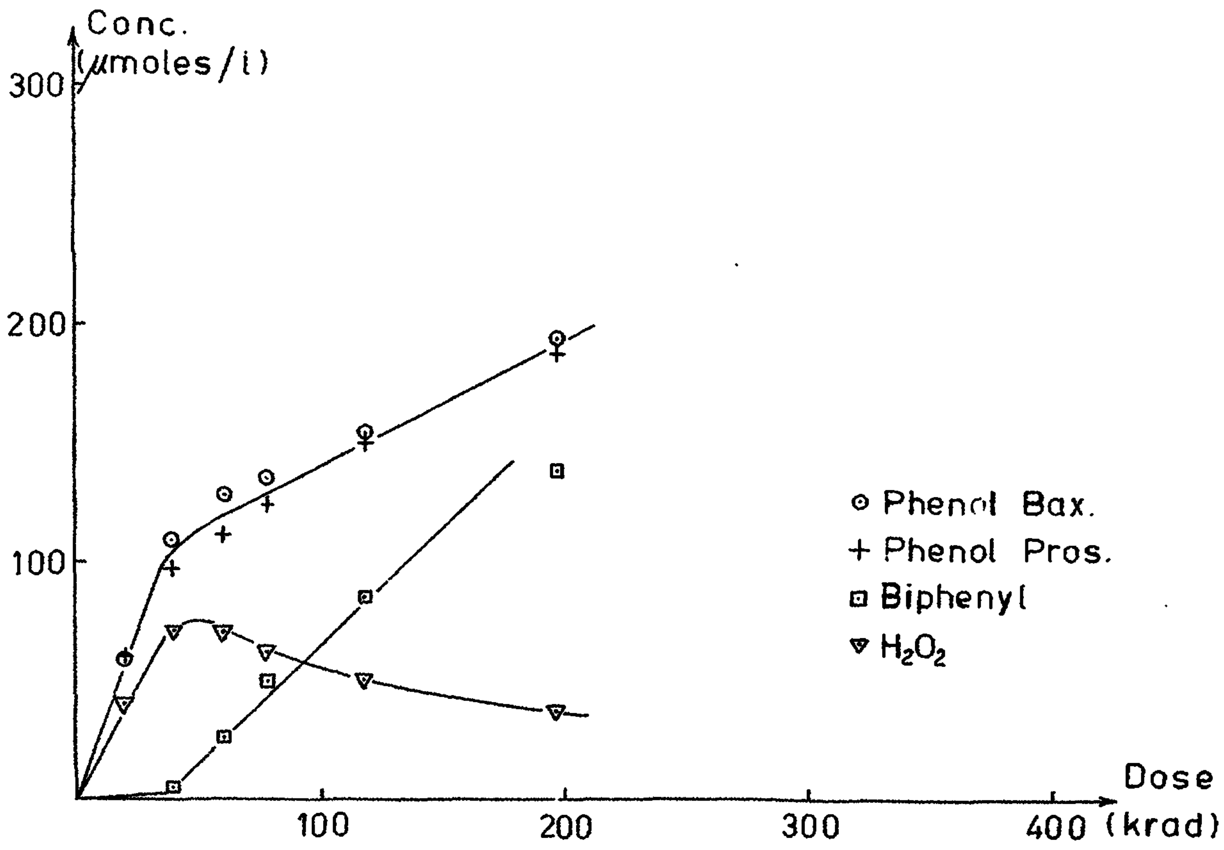

Fig. 8. Yields in aerated 0.1 N NaOH solutions.

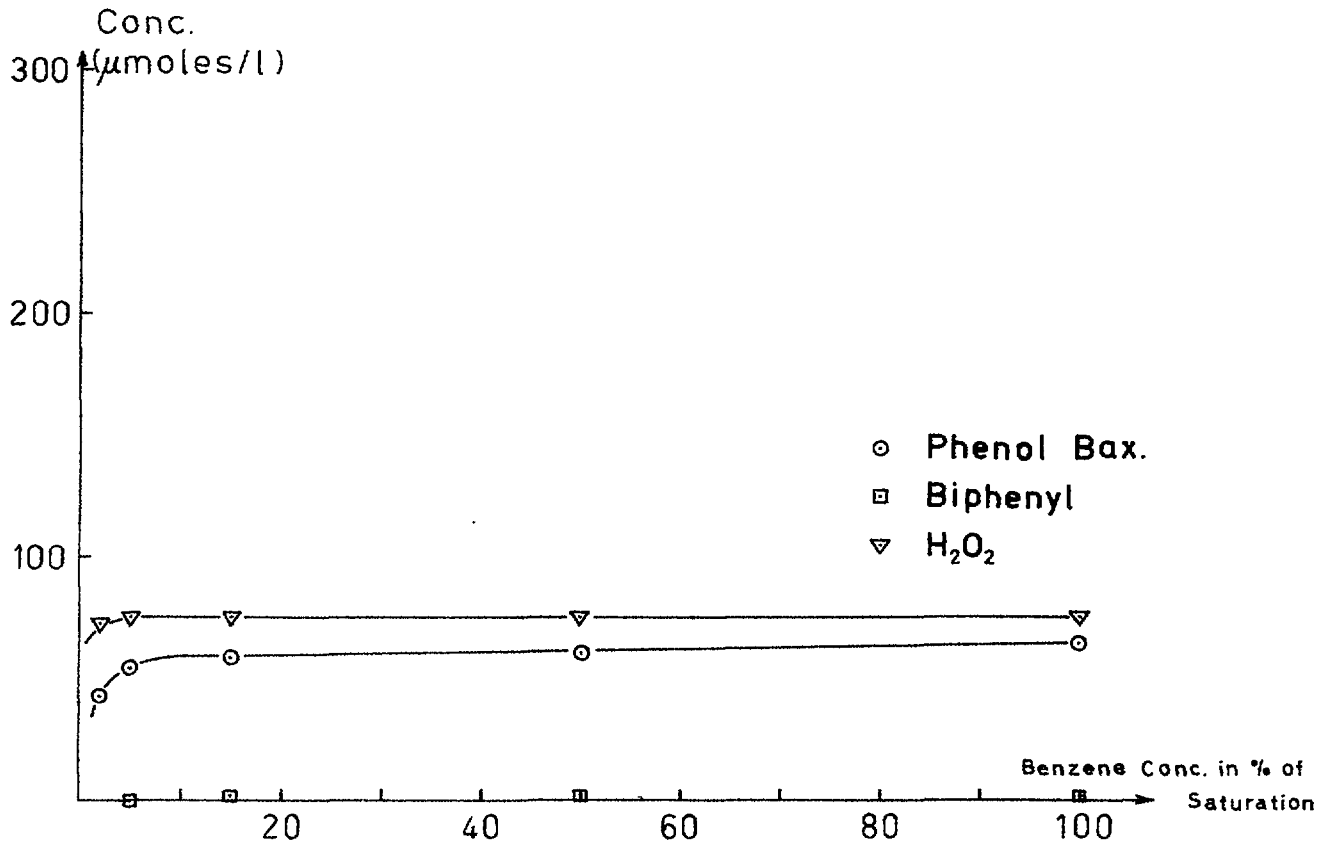

Fig. 9. Yields in aerated unbuffered solutions. Dependence on benzene concentration.

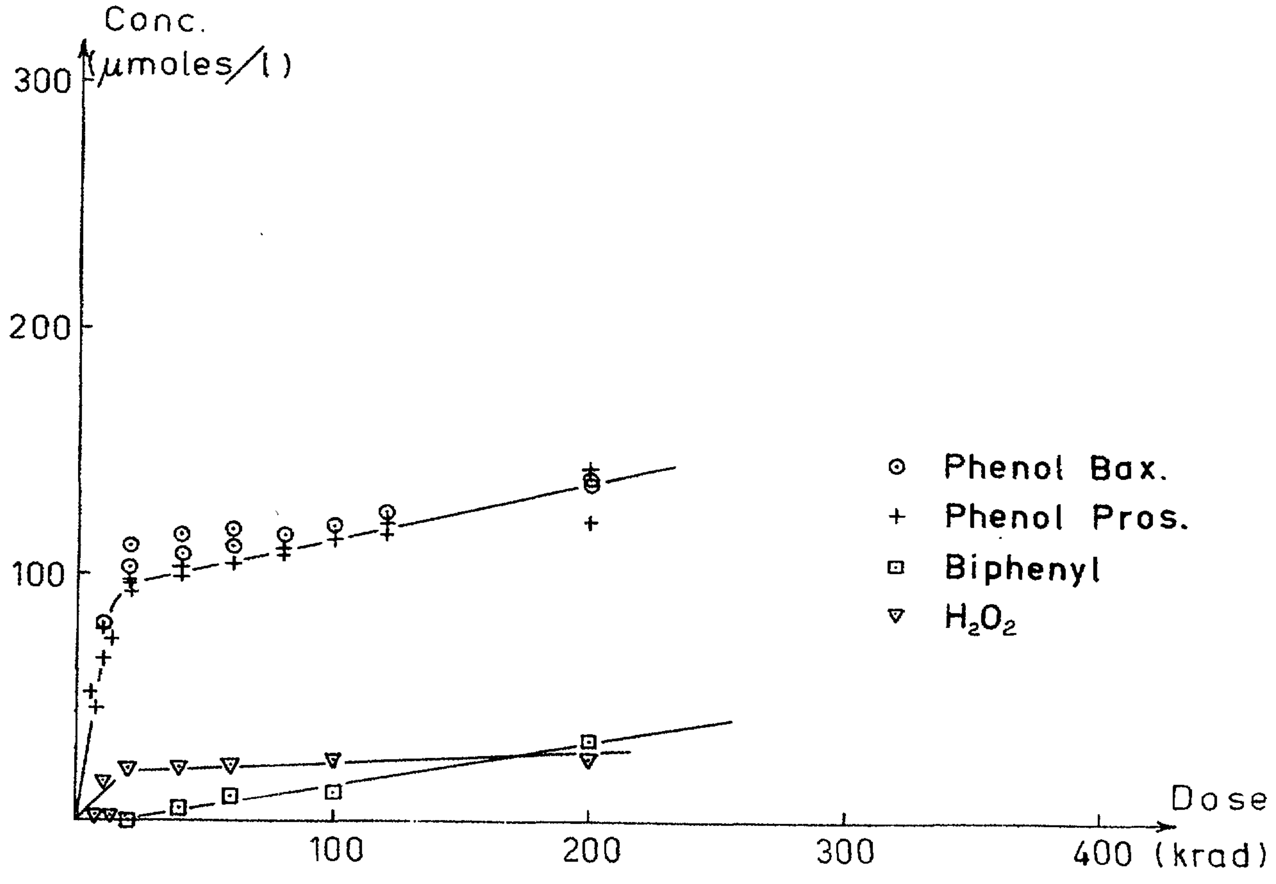

Fig. 10. Yields in aerated solutions, 0.1 N H_2SO_4 + 10^{-2} N Fe^{2+}.

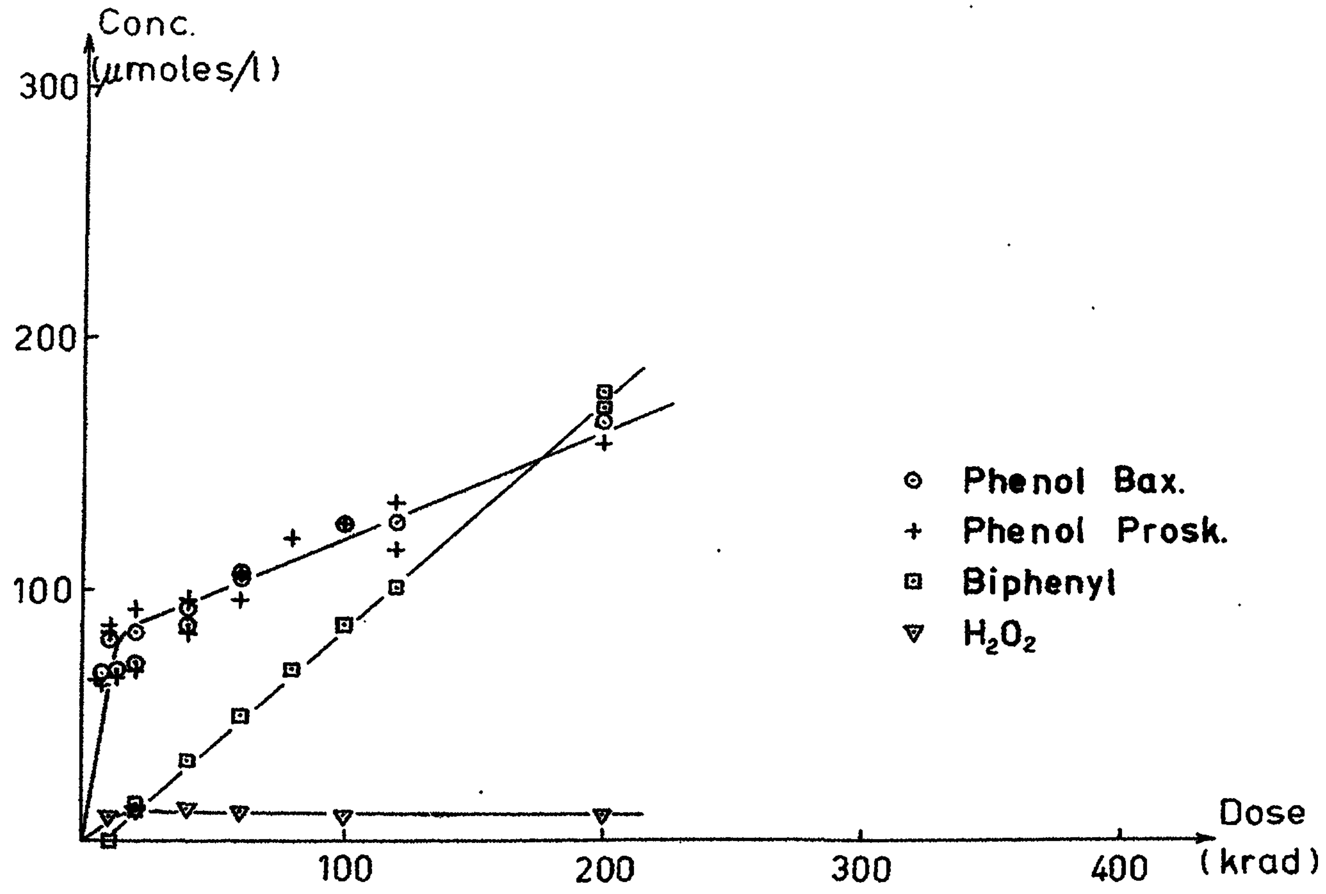

Fig. 11. Yields in aerated solutions, 0.1 N H_2SO_4 + 10^{-3} N Fe^{2+}.

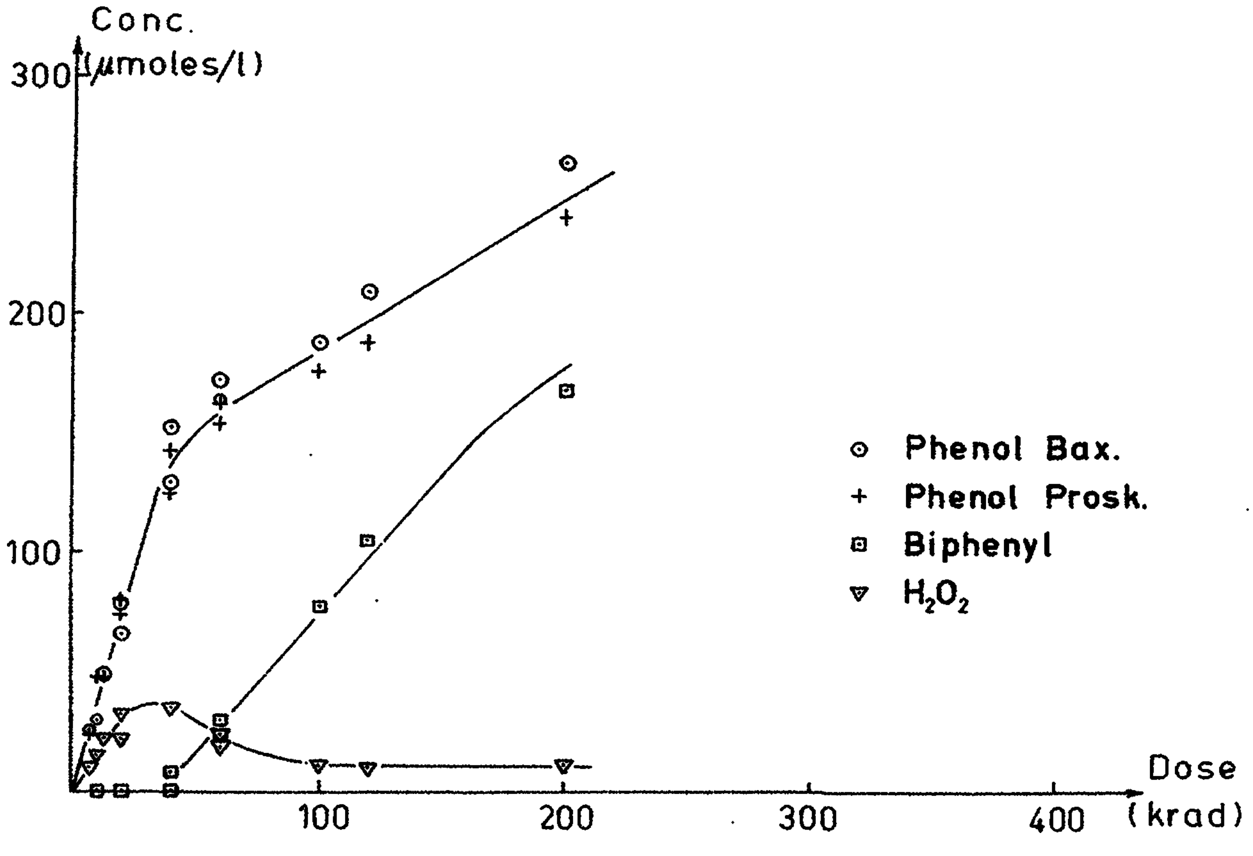

Fig. 12. Yields in aerated solutions, 0.1 N H_2SO_4 + 10^{-3} N Fe^{3+}.

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