511. *The Oxidation of Aromatic Compounds by Means of the Free Hydroxyl Radical.*

By J. H. Merz and W. A. Waters.

Aromatic compounds are oxidised by hydrogen peroxide in presence of ferrous ions according to a non-chain mechanism, and free aryl radicals are formed. The free phenyl radical does not react with water, but in part dimerises to diphenyl and in part combines with the hydroxyl radical to form phenol.

Toluene yields dibenzyl, benzaldehyde, and cresols. Benzoic acid, benzamide, nitrobenzene, and chlorobenzene yield *o*-substituted phenols and further oxidation products, but not diaryls. The further oxidation of phenols is too complex for kinetic study, since the reaction products include catechol derivatives which reduce ferric salts. Again, phenols are retarders of the free-radical oxidation of other substances.

The theoretical implications of these findings are reviewed, particularly in connection with the chemical reactivity of the free phenyl radical.

In a previous paper (this vol., p. S 15) we showed that the free hydroxyl radical, produced by the action of hydrogen peroxide on acidified ferrous sulphate, was able to oxidise many water-soluble aliphatic compounds by way of a dehydrogenation (1) which was followed *either* by a reaction

$$(1)\quad R{-}H + {\cdot}OH \xrightarrow{k_3} R{\cdot} + H{-}OH$$

(2) between the organic radical, R·, and molecular hydrogen peroxide which continues a chain

$$(2)\quad R{\cdot} + HO{-}OH \longrightarrow R{-}OH + {\cdot}OH$$

reaction, *or* by a combination (3, 4) or disproportionation (5) of a pair of radicals which does not allow of the continuation of a reaction chain

$$(3)\quad 2R{\cdot} \longrightarrow R{-}R$$

$$(4)\quad R{\cdot} + {\cdot}OH \longrightarrow R{-}OH$$

$$(5)\quad 2R_2CH{-}\dot{C}R_2' \longrightarrow R_2C{=}CR_2' + R_2CH{-}CHR_2'$$

The evaluation of the ratio $[\Delta H_2O_2]/[\Delta R{-}H]$, calculated in equivalents, and measured most simply as $[\Delta H_2O_2]/[\Delta H_2O_2 - \Delta Fe^{++}]$, for a series of mixtures of the organic substrate, R—H, with ferrous sulphate solution enabled us to discriminate quite clearly between the chain (2) and the non-chain (3—5) mechanism.

We have now extended our studies to a number of aromatic compounds, and have found that the hydroxyl radical quite easily attacks the benzene ring to give a free aryl radical which then reacts further *according to the non-chain mechanisms* (3) *and* (4) *only*. Thus Fig. 1 shows that quite a range of organic compounds can be oxidised so that the kinetic equation

$$-\Delta H_2O_2/-\Delta R—H = 2 + k_2[Fe^{++}]/k_3[R—H]$$

characteristic of the non-chain process is valid, whilst Table I shows that the ratio k_3/k_2 is greater for aromatic substances than for many aliphatic substances which oxidise in the same manner: indeed, the ratio is often greater than that observed for the chain oxidations of alcohols or aldehydes.

FIG. 1.

Stoicheiometry of oxidation of aromatic compounds showing that the non-chain relationship $\Delta H_2O_2/\Delta R—H = 2 + k_2[Fe^{++}]/k_3[R—H]$ *holds.*

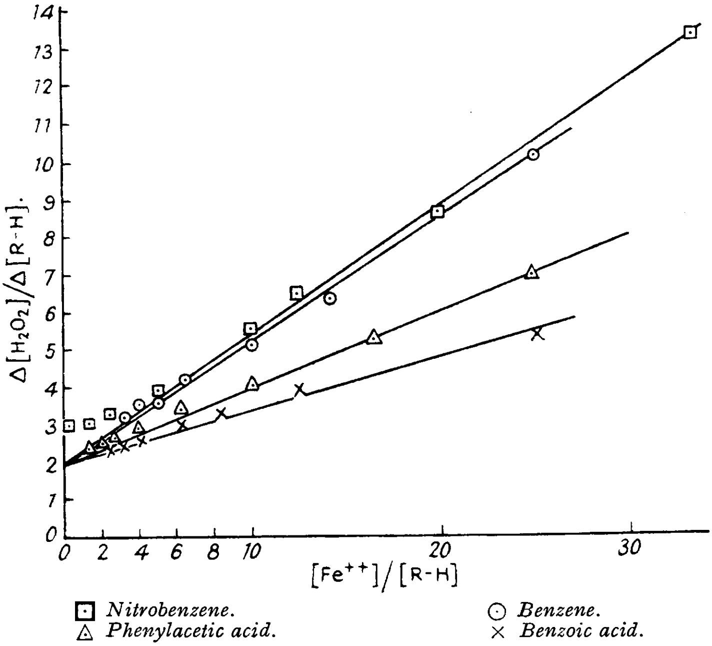


TABLE I.

$$\frac{k_3}{k_2} = \frac{\text{Velocity constant for reaction } R—H + \cdot OH \longrightarrow R\cdot + H_2O}{\text{Velocity constant for reaction } Fe^{2+} + \cdot OH \longrightarrow Fe^{3+} + (OH)^-}.$$

Substance.	k_3/k_2.	Substance.	k_3/k_2.
Benzene	3·2	Nitrobenzene	2·9
Benzoic acid	7·0	Benzenesulphonic acid	4·7
Benzamide	6·6	Dimethylaniline (sulphate)	6·6
Phenylacetic acid	4·8		

For comparison:

Non-chain oxidations.		Chain oxidations.	
tert.-Butyl alcohol	0·65	Ethyl alcohol	3·8
Chloral hydrate	4·7	*iso*Propyl alcohol	3·0
Ethyl acetate	1·1	Acetaldehyde	2·2
Diethylamine (sulphate)	0·4	Diethyl ether	6·4

We have been able, in a number of cases, to isolate reaction products which reveal further features of the courses of these oxidations.

The oxidation of benzene by hydrogen peroxide and a ferrous salt was first mentioned by

Cross, Bevan, and Heiberg (*Ber.*, 1900, **33**, 2017) who showed that phenol and pyrocatechol were obtainable, though in poor yield. This has been confirmed by Ono, Oyamada, and Katuragi (*J. Soc. Chem. Ind. Japan*, 1938, **41**, 209B; *Brit. Chem. Abs.*, 1938, *B*, 1265), but hitherto it does not seem to have been noticed that diphenyl is also formed in this reaction, though recently Stein and Weiss (*Nature*, 1948, **161**, 650) have reported that traces of diphenyl accompany the phenolic products which are obtained when aqueous solutions of benzene are irradiated with *X*-rays or γ-rays.

Actually, the chemical oxidation of benzene to diphenyl in aqueous solution can be demonstrated in a striking manner. When a saturated (*ca.* M/100) solution of benzene in cold, acidified, aqueous ferrous sulphate solution is injected, with shaking, with a dilute solution of hydrogen peroxide then the mixture immediately turns cloudy owing to the separation of diphenyl which eventually flocculates. The diphenyl can be obtained in larger quantity by adding dropwise from two burettes, to a dilute mechanically-stirred emulsion of benzene in dilute sulphuric acid, both ferrous sulphate and hydrogen peroxide solutions at rates which are controlled so that a little ferrous sulphate enters initially and thereafter remains in permanent excess, whilst the ratio [dissolved benzene]/[Fe^{++}] is maintained at as high a value as is conveniently possible. Alternatively, a homogeneous mixture of the aromatic compound and concentrated hydrogen peroxide in the minimum quantity of glacial acetic acid can be added dropwise to a stirred ice-cold solution of ferrous sulphate in dilute sulphuric acid.

Although some diphenyl is formed from benzene, phenolic products constitute the main yield. Hence, both the reactions $2C_6H_5\cdot \longrightarrow C_6H_5{-}C_6H_5$ and $C_6H_5\cdot + \cdot OH \longrightarrow C_6H_5{-}OH$ must occur concurrently in the aqueous phase. One typical experiment indicated that only about 20% of the phenyl radicals was converted into diphenyl.

Toluene, which is much less soluble in water than is benzene, gives a just perceptible turbidity when treated similarly in aqueous solution, but the product of oxidation of an aqueous emulsion by the simultaneous addition technique described above is a mixture containing dibenzyl, benzaldehyde, and cresols. Evidently toluene is attacked by free hydroxyl radicals both in the side chain and in the nucleus. The oxidation of ethylbenzene yielded mainly acetophenone, and phenylacetic acid too was attacked mainly in the side chain. Anisole and dimethylaniline both yielded some formaldehyde, and thus resembled the aliphatic ethers and amines. Nitrobenzene darkened rapidly when oxidised in solution or emulsion; a little *o*-nitrophenol, together with more complex polyphenolic products, but no dinitrodiphenyls were formed. Again, the oxidation of a mixture of benzene with nitrobenzene did not yield any nitrodiphenyl. Chlorobenzene, similarly, gave no dichlorodiphenyl, but a little *o*-chlorophenol, together with more extensively oxidised products.

Benzoic acid oxidises to a red solution which was shown to contain salicylic acid. Evidently, therefore, the well-known microchemical colour reaction for the determination of traces of benzoic acid as salicylic acid (Hanriot, *Compt. rend.*, 1886, **102**, 1250; compare Milton and Waters "Methods of Quantitative Micro-analysis," 1949, p. 328) depends on a similar oxidation. Benzamide oxidises in a similar manner, and salicylamide could be separated from the reaction product. Isomeric hydroxybenzamides may perhaps be present but could not be isolated. Benzenesulphonic acid gave a solution which when treated with bromine-water precipitated tribromophenol, and evidently therefore some *o*- and/or *p*-hydroxybenzenesulphonic acids had been formed.

In none of these cases, however, was it possible to obtain the primary oxidation products in significant yield, since the various phenols themselves are extensively oxidised too. The oxidation of phenol by hydrogen peroxide in the presence of a ferrous salt has been studied by many workers (Cross, Bevan, and Heiberg, *loc. cit.*; Goldhammer, *Biochem. Z.*, 1927, **189**, 81; Chwala and Pailer, *J. pr. Chem.*, 1936, **11**, 132; Ono and Oyamada, *Bull. Soc. Chem. Japan*, 1936, **11**, 132), usually with inconsistent results, since the requisite conditions for the attainment of reproducibility with this reagent (see Merz and Waters, *Faraday Soc. Discussions*, 1947, **2**, 180) were not then known. The earlier work, however, makes it quite evident that the *o*-hydroxylation of the aromatic nucleus, noted above, occurs with phenol too, since catechol can be isolated more easily than other reaction products such as quinol or diphenols, though these too are formed.

Our own colorimetric measurements, both with phenol and with *p*-cresol, have as yet failed to reveal the detailed course of this oxidation for, as Fig. 2 shows, the final concentration of ferric ion in the solution is nearly independent of the initial [phenol]/[Fe^{++}] ratio. This result can, in part, be accounted for by the fact that catechol and its analogues reduce ferric salts to ferrous salts, but are thereby oxidised to 1 : 2-quinones which are unstable in water. More important, however, is the fact that phenol is a strong " retarder " of oxidations involving free hydroxyl, since the interchange process (6) yields mesomeric phenoxy-radicals which are much

$$(6)\quad C_6H_5{-}O{-}H + \cdot OH \xrightarrow{k_x} C_6H_5{-}O\cdot + H{-}OH$$

less reactive than free hydroxyl. Thus the addition of phenol significantly reduces the rate of oxidation of *iso*propyl alcohol (Fig. 3), its apparent * retardation coefficient, k_x/k_2, being 9·3. The full details of phenol oxidation would thus appear to be too complex for quantitative evaluation by our present techniques. The occurrence of these further complex oxidations of phenols naturally renders the direct oxidation of aromatic ring systems by free hydroxyl radicals a process of no preparative value.

FIG. 2.

The oxidation of phenols.

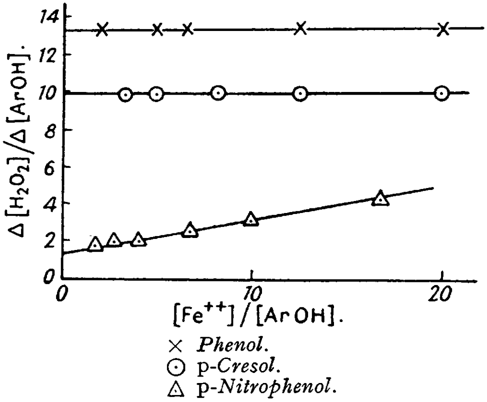
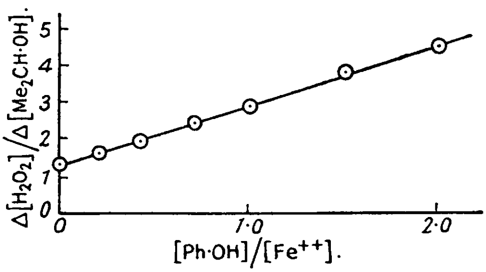


FIG. 3.

Retardation of the oxidation of iso*propyl alcohol by phenol.*



Discussion.—This work shows clearly that free phenyl radicals do not react with cold water, for reaction (*a*) would not allow of the oxidation of any benzene, whilst reaction (*b*), unless extremely slow, would so dominate the oxidation that no diphenyl would be formed.

$$(a)\quad C_6H_5\cdot + H{-}OH \longrightarrow C_6H_5{-}H + \cdot OH$$

$$(b)\quad C_6H_5\cdot + HO{-}H \longrightarrow C_6H_5{-}OH + \cdot H$$

This confirms the surmise made by one of us (*J.*, 1937, 2015) that the very small quantities of aromatic hydrocarbons which are formed in decompositions of aqueous solutions of diazoates (compare Jolles, *Gazzetta*, 1931, **61**, 403; *Atti R. Accad. Lincei*, 1932, **15**, 292, 395) originate from reactions between aryl radicals and aromatic molecules, *i.e.*, chiefly from homolyses occurring in the tar phase (compare Saunders and Waters, *J.*, 1946, 1156). Until now, however, it has not been possible decisively to reject the alternative mechanism involving reaction (*a*), improbable though it has always seemed.

Since the work of Hey, Wieland, and others (compare Waters, "The Chemistry of Free Radicals," 1946, Chap. VIII) has indicated that diphenyl may easily be formed by reaction (*c*)

$$(c)\quad C_6H_5\cdot + H{-}C_6H_5 \longrightarrow C_6H_5{-}C_6H_5 + \cdot H$$

it is possible that in our present oxidation the production of the diphenyl might be due to the occurrence of reaction (*c*) in the aqueous phase between the free phenyl radicals and the dissolved benzene molecules, and not by the dimerisation of the free phenyl radicals (reaction 3), since atomic hydrogen would at once be removed by the free hydroxyl radicals that are also present. In considering this possibility it must be borne in mind that the velocity of reaction (*c*) would have to be abnormally high if any appreciable formation of diphenyl is to be accounted for in this way. Our failure to isolate appreciable amounts of substituted diaryls from either nitrobenzene or chlorobenzene points against the significant occurrence of reaction (*c*) in very dilute aqueous solution, for the corresponding reactions of the radicals $\cdot C_6H_4Cl$ and $\cdot C_6H_4{\cdot}NO_2$ with chlorobenzene and nitrobenzene occur quite easily when these two liquids are also the solvents. Again,

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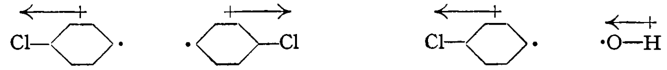
* This computation assumes that the phenoxy-radical is not oxidised further in the presence of Fe^{++}, and that the reaction $HO\cdot + C_6H_5{-}OH \longrightarrow H{-}OH + \cdot C_6H_4{-}OH$ can be neglected. Neither of these assumptions is quite true, but Fig. 2 shows that 90% of the hydrogen peroxide taken is consumed by oxidising Fe^{++} ions.

toluene gave some dibenzyl and not phenyltolylmethane or ditolyl: hence dissolved benzyl radicals do not seem to substitute the benzene ring. The present evidence therefore indicates strongly that the diphenyl is formed by the dimerisation of the free phenyl radicals in the aqueous solution (reaction 3).

The absence of detectable diaryl formation by the dimerisation of chlorophenyl, or nitrophenyl, radicals is curious, but it may perhaps be explained * by the fact that these radicals are both dipoles, owing to their substituents, and that their combination in pairs would have to overcome electrostatic repulsions between like charges, a circumstance which would not arise in their reactions with hydroxyl radicals (compare Weiss, *Trans. Faraday Soc.*, 1940, **36**, 856):



In our study of the aliphatic free radicals (this vol., p. 15) we discovered many that were sufficiently reactive to attack molecular hydrogen peroxide. To those which did not do so, but oxidised further by the non-chain sequence, we ascribed structures in which the wave-system of the odd electron had been appreciably drawn away from the immediate vicinity of the tervalent carbon atom by electrophilic groups situated in the remainder of the molecule. A similar explanation cannot be given for the comparative stability of the free phenyl radical under our reaction conditions. Again, this stability cannot be due to resonance with the "aromatic sextet" since (i) one cannot write down any alternative, stereochemically rational, canonical structures to the Kekulé formula with the odd electron situated at the carbon atom which has been deprived of its hydrogen (compare Waters, *Faraday Soc. Discussions*, 1947, **2**, 373), and (ii) the axis of symmetry of the odd electron of the phenyl radical (along the line of the original C–H bond) is at right angles to that of the *p–p* bonds of the aromatic sextet and hence there cannot be any interaction between these two wave-systems.

No satisfactory explanation can therefore be offered for our demonstration that free phenyl, *in water*, appears to be a comparatively stable radical. The observation was most unexpected since free phenyl *sometimes* appears to be even more reactive than free methyl. For example, Cramer (*J. Amer. Chem. Soc.*, 1934, **56**, 1234; 1938, **60**, 1406) failed to alkylate benzene at temperatures below 300° by free ethyl radicals generated from tetraethyl-lead. Again, Fieser, Clapp, and Daudt, *ibid.*, 1942, **64**, 2053) obtained only benzyl acetate from toluene under conditions in which both free methyl and free acetate radicals were probably present, whilst Hey, (*J.*, 1934, 1936) found that toluene reacted quite easily with free phenyl radicals derived from both dibenzoyl peroxide and benzene diazoacetate to give a mixture of methyldiphenyls. It may be, therefore, that the reactions of free hydrocarbon radicals exhibit more specificity than has hitherto been supposed, and that their interactions with aromatic nuclei are conditioned by special steric conditions (compare Mayo, *Faraday Soc. Discussions*, 1947, **2**, 372; Waters, *idem*).

The absence of a reaction between a free organic radical and water is not surprising, because a process such as (*a*) or (*b*) (p. 2430) would require the severance of a strong H–O bond. The reactions between free radicals and organic molecules involve only much weaker bonds, such as C–H, or C–Cl, and hence water may be the one unique solvent with which organic free radicals do not react.

Finally, attention may be directed to our observation that substituted benzene derivatives can regularly be hydroxylated in the *o*-position, but the implications of the fact must be viewed with caution. First, it must be pointed out that the isolated yields of *o*-substituted products are small, even in the case of phenol, and secondly, it may be that the isomeric hydroxy-compounds are more rapidly destroyed by the reagent used in spite of the fact that catechol has a higher oxidation potential than either quinol or resorcinol. It may be noted, however, that computations of the local electron densities at the carbon centres of substituted benzene derivatives invariably exhibit the greatest divergencies from the mean at points vicinal (*i.e.*, *ortho*) to the substituent group (Coulson, private communication). These calculations concerning the structures of normal molecules are particularly relevant in connection with their homolytic reactions, such as those discussed in this paper. They possibly may be used to predict the points at which free-radical attack can occur with the least energy demand, though as one of us has pointed out (*J.*, 1948, 727) the simplified approach to this used by Wheland (*J. Amer. Chem. Soc.*, 1942, **64**, 900) may be inadequate.

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* We thank Professor C. A. Coulson for this suggestion.

EXPERIMENTAL.

Kinetic measurements were carried out, at pH 1, at room temperature, as follows: 10 ml. of 0·1N-ferrous ammonium sulphate, dissolved in 0·5N-sulphuric acid, were mixed with the appropriate volume of a standard aqueous solution of the organic substrate, and diluted with distilled water to a total of 45 ml. 5 Ml. of 0·1N-hydrogen peroxide were then added with shaking. After a short time the Fe^{3+} content of the product was determined colorimetrically with potassium thiocyanate, a "Spekker" photo-absorptiometer being used. For this determination the reaction mixture was diluted to 250 ml.; 10-ml. portions were then mixed with 5 ml. of 10% potassium thiocyanate and diluted to 100 ml. with 0·2N-sulphuric acid. A similarly prepared mixture to which no organic substance had been added served as the reference blank.

Experiments involving the oxidation of phenols were carried out under an atmosphere of nitrogen. The retarding effect of the phenol was determined by adding the appropriate volume of standard aqueous phenol solution to a mixture of 10 ml. of 0·1N-ferrous ammonium sulphate with 10 ml. of 0·2M-*iso*propyl alcohol, diluting the mixture to 45 ml., and then proceeding as above.

The larger-scale investigations of oxidation products were conducted as follows:

Benzene.—To a mechanically stirred emulsion of 25 ml. of benzene in 750 ml. of 0·35N-ferrous sulphate, acidified with 5 ml. of concentrated sulphuric acid, 100 ml. of 1·4N-hydrogen peroxide were added dropwise from a burette. Extraction with ether gave 1·2 g. of a brownish solid which, after washing with alkali and crystallising from aqueous acetic acid and then methanol gave 0·26 g. of diphenyl of m. p. 70·5°; this was unchanged after admixture with authentic material. The alkali-soluble portion, on treatment with acidified bromide–bromate mixture gave 2·8 g. of tribromophenol, m. p. 93°. Pure diphenyl was also isolated from an oxidation carried out in homogeneous aqueous solution.

Toluene.—To a mechanically stirred emulsion of 10 ml. of toluene in 2 l. of 0·1N-sulphuric acid, N-solutions of ferrous sulphate and of hydrogen peroxide were added from two burettes at such a rate that the mixture contained a permanent slight excess of ferrous ions. Extraction with ether, followed by washing with dilute alkali to remove cresols, and evaporation gave a dark oil, smelling of benzaldehyde, which solidified on storage in a refrigerator. Two recrystallisations from methanol gave pure dibenzyl, m. p. and mixed m. p. 52·5°. The mother-liquor from the first crystallisation reduced ammoniacal silver nitrate, and, on treatment with phenylhydrazine in dilute acetic acid, benzaldehyde phenylhydrazone, m. p. and mixed m. p. 158°, was obtained. There remained only a very small amount of non-phenolic dark residue. The alkali-soluble extract gave, on acidification, a little brownish oil which exhibited positive reactions for cresols (ferric chloride colour, bromination, etc.) but was insufficient in quantity for separation into pure components.

Ethylbenzene.—This was oxidised in a similar manner, a mixture of 100 ml. of glacial acetic acid and 1 l. of N-sulphuric acid being used as the reaction phase. The product was extracted with ether, washed with alkali and treated with Girard's reagent P. This separated acetophenone, which was isolated and characterised by its 2 : 4 dinitrophenylhydrazone, and by a positive iodoform test.

Phenylacetic Acid.—A saturated aqueous solution of phenylacetic acid (0·1 mol.) was treated with 0·2 mol. each of hydrogen peroxide and acidified ferrous sulphate solutions. Extraction with ether gave a product containing mainly benzaldehyde (phenylhydrazone, m. p. and mixed m. p. 158°). A very feeble reaction for phenolic products was given; phenylglyoxylic acid could not be detected (no coloration with 2 : 4-dinitrophenylhydrazine in sodium carbonate solution).

Benzoic Acid.—A saturated aqueous solution of benzoic acid (15 g.) was mixed with 150 ml. of N-hydrogen peroxide and acidified ferrous sulphate was added, with stirring, until present in slight excess. The deep purple solution was extracted with ether, which dissolved out some of the ferric complex of salicylic acid. The extracted acids were esterified with methanol, by means of sulphuric acid, and the esters were taken up in ether and washed first with sodium hydrogen carbonate and then with sodium hydroxide. The latter solution, on acidification, gave about 2 ml. of methyl salicylate, b. p. 220—224°, and on hydrolysis pure salicylic acid.

Benzamide.—200 Ml. of a 0·5M-ferrous sulphate solution were added, with mechanical stirring, to an ice-cold, homogeneous mixture of benzamide (0·15 mol.) and hydrogen peroxide (0·1 mol.) in glacial acetic acid. The reaction mixture became deep violet. Extraction with ether separated the ferric complex of salicylamide in the form of a yellow solution, which immediately became deep violet again when water was added to the ethereal extract. Evaporation of the ether, followed by treatment with cold dilute sodium hydroxide, precipitated ferric hydroxide mixed with unchanged benzamide. The filtrate on acidification precipitated almost pure salicylamide (1·5 g.), which after recrystallisation from hot water had m. p. 139° and on hydrolysis yielded salicylic acid, m. p. and mixed m. p. 155°.

Nitrobenzene.—A concentrated mixture of nitrobenzene and hydrogen peroxide in glacial acetic acid was added, with vigorous stirring, to an excess of an ice-cooled solution of ferrous sulphate. Extraction of the product with ether gave a dark oil from which the excess of nitrobenzene and acetic acid was removed, together with *o*-nitrophenol, by steam-distillation. The last substance was characterised by extracting the steam-distillate with ether, washing out the nitrophenol with dilute sodium hydroxide, acidifying these washings and then re-extracting with ether. The final product (yield under 1%) had, after recrystallisation, m. p. and mixed m. p. 44°. The main involatile product of the oxidation was a black tarry solid which gave a red solution in sodium hydroxide and an amorphous precipitate with lead acetate solution. Attempts to isolate pure compounds from this were not successful. None of the material was sufficiently insoluble in water to be a dinitrodiphenyl. A similar product was obtained when a mixture of benzene and nitrobenzene was oxidised.

Chlorobenzene.—A mixture of chlorobenzene and hydrogen peroxide in glacial acetic acid solution was added in small portions to an excess of an ice-cooled, acidified, solution of ferrous sulphate. The reaction product was extracted with ether and the extract was evaporated and steam-distilled. The distillate contained some *o*-chlorophenol (yield *ca.* 5%) which was separated in the usual manner (see above). It was characterised as its dinitro-derivative, m. p. 111° (Found: C, 33·2; H, 1·33; N, 12·6. Calc. for $C_6H_3O_5N_2Cl$: C, 33·0; H, 1·37; N, 12·8%). The residue from the steam-distillation contained a black tarry phenolic solid, which gave a red solution in sodium hydroxide and was easily soluble in alcohol. It gave an insoluble lead salt, but further attempts to characterise this as a definite catechol derivative were unsuccessful.

Benzenesulphonic Acid.—The oxidation of an acidified solution of recrystallised sodium benzenesulphonate with ferrous sulphate and hydrogen peroxide gave a clear solution which when treated with bromide-bromate mixture gave an abundant precipitate of tribromophenol. Individual phenolsulphonic acids could not be isolated.

Dimethylaniline.—Dimethylaniline in N-sulphuric acid was promptly oxidised to a deep purple solution, indicative of dyes derived from *o*-aminophenol. On boiling, the aqueous product liberated formaldehyde, which was characterised as its dimedone derivative, m. p. 190°.

Anisole.—This was oxidised in a similar way to chlorobenzene, and the solution resulting from this reaction, too, liberated formaldehyde when heated.

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