on the reactivity of organophosphorus insecticides with cholinesterase has assisted in the elucidation of the mechanism of their physiological action, which is extremely important for the understanding of a whole series of biochemical processes.

Your amazing capacity for work and keen intellect combined with encyclopaedic knowledge leave us no doubt about further successes of the school which you have established. We value greatly the opportunity of working with you.

We wish you health and new creative successes in your scientific and public activities.

Editorial Board of "Uspekhi Khimii"

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Oxidation of Benzene

E.T.Enisov and D.I.Metelitsa

The review gives a systematic account of studies on the oxidation of benzene by different methods—with oxygen in the gas phase, with Fenton's reagent in aqueous solution, under the action of light and penetrating radiation, and also catalytic oxidation in aqueous solution. Particular attention has been paid to the mechanism of the oxidation of benzene; the main experimental evidence for individual mechanisms is discussed and unlikely schemes are criticised. Kinetic data and the mechanism of the catalytic oxidation of benzene to phenol with oxygen in aqueous solution in the presence of iron and copper ions which follows from them are discussed in detail. The bibliography incorporates 120 references.

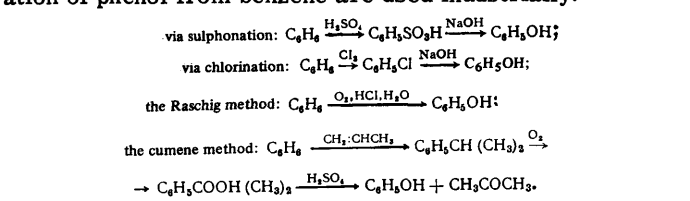
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I. INTRODUCTION

Benzene differs sharply from other hydrocarbons by its high stability with respect to oxidation, which is due to its structure. Hydrocarbons are known to be oxidised by a free-radical mechanism, the reaction including a stage involving the homolytic abstraction of a hydrogen atom. The high stability of the C–H bond in benzene (102 kcal mole^{-1}) is one of the reasons for its stability. No less important is another factor, namely the major role played in the oxidation of hydrocarbons by hydroperoxides, which break down into free radicals and initiate further chain oxidation. The corresponding hydroperoxide is not known for benzene and attempts to synthesise it have proved unsuccessful, and it appears that it does not exist as a stable molecular compound. The absence of a hydroperoxide as the species initiating the reaction does not favour rapid oxidation. Finally, it is very significant that the oxidation of benzene yields phenol and products of its further oxidation, which behave as inhibitors of chain reactions involving the oxidation of hydrocarbons. All these factors explain the stability of benzene with respect to oxidation.

The oxidation of benzene to phenol is of practical importance. Nowadays the following methods for the preparation of phenol from benzene are used industrially:



These procedures, including the cumene method which is the most economical, consist of many stages. Therefore the development of an effective single-stage process is important. As will be seen from the present review, under certain conditions it is possible to oxidise benzene to phenol with a fairly high yield. The theoretical possibility of oxidising benzene to phenol under mild conditions is a consequence of the existence of enzymes which can, for example, oxidise phenylalanine to tyrosine.

II. GAS-PHASE OXIDATION OF BENZENE

The first studies on the oxidation of benzene with molecular oxygen in the gas phase were performed in the 1920's. The gas-phase oxidation of benzene takes place at 500–700°C.[1-31] The oxidation yields phenol, resins, carbon monoxide, and carbon dioxide. At these high temperatures the oxidation of benzene is accompanied by its cracking on the wall of the reaction vessel. Glass packing favours the cracking process[27]. As a result of cracking, low-molecular hydrocarbons (methane, ethylene, acetylene, etc.) are formed together with the oxidation products[19,20,27]. In a number of investigations homogeneous catalysts, such as hydrogen chloride, nitrogen dioxide, and iodine were used. As an example, one may quote the experiments with iodine in which the introduction of 0.02% of iodine into air at 604°C increased the yield of phenol from 40.4% (without iodine) to 56.5% with respect to unreacted benzene[12]. In order to accelerate the oxidation of benzene, atomic oxygen obtained in an electric discharge has also been used[13,21,22]. The oxidation of benzene has been stimulated by readily

oxidisable organic compounds: cyclohexane, cyclohexanol, cyclohexanone, n-hexane, aniline, cyclohexene, etc.[15,23,28].

Photochemical oxidation of benzene at room temperature leads to the formation of phenol and a peroxide[24]. The phenol undergoes further photochemical decomposition.

The heterogeneous oxidation of benzene to maleic anhydride on vanadium pentoxide is an industrial method. The rate-limiting stage of this process is the heterogeneous oxidation of benzene to phenol, which is then rapidly oxidised to quinone and the latter is oxidised to maleic anhydride[8]. Table 1 gives the benzene oxidation conditions and the yields of phenol obtained in a number of the most interesting studies.

Table 1. Oxidation of benzene.

Oxidation conditions	Oxidation products	Yield of phenol, %	References
Benzene–air mixture, 300–500°C	phenol, biphenyl, maleic and formic acids	0.5—1.0 by weight	19,20
Benzene–air, 520–685°C, column without packing	phenol, resins, CO, CO_2, CH_4	20—26	27
Benzene–air, packed column	phenol, resins, CO, CO_2, CH_4, C_2H_2	16—18	
$O_2 + N_2$ + benzene, 660°C	phenol, resins	30	14
Atomic oxygen + benzene, 180–230°C		4.5—27	22
Atomic oxygen + benzene	phenol, biphenyl, CO, CO_2	43	13
Benzene–air, I_2(0.02%), 604°C	phenol, biphenyl	56.5	12
5% O_2 + benzene, 400–500°C	phenol, resins	to 75	5
Chromium, molybdenum, vanadium, and tantalum oxides			
Benzene–air, V_2O_5, 316°C	phenol, maleic acid	1.9	16
Benzene + cyclohexane (10%), 585°C		62	23
Benzene + readily oxidisable organic substances, 400°C	phenol, CO, CO_2, resins, CH_4, C_2H_2	20—26	28
Benzene + cyclohexane (0.2–0.3%), 449°C		30	15

The kinetics of the gas-phase oxidation of benzene were investigated by Ioffe[26-30] and Norrish et al.[31] The kinetic curves for the disappearance of benzene and the accumulation of phenol have the S-shape characteristics of auto-oxidation processes. In the initial period the reaction kinetics are described by the following equation: conversion = const. $\times e^{\varphi t}$, where φ = const. $\times e^{-32\,000/T}$ at 660–685°C for $(C_6H_6):(O_2) = 2:1$.[30] It is suggested that the acceleration of the reaction occurs as a result of the oxidation of side products such as methane, ethylene, etc.[30] The following mechanism has been proposed for the initial stage of the oxidation[30,31]:

$$C_6H_6 + O_2 \rightarrow C_6H_5^{\cdot} + HO_2^{\cdot},$$
$$C_6H_5^{\cdot} + O_2 \rightarrow C_6H_5OO^{\cdot},$$
$$C_6H_5OO^{\cdot} + C_6H_6 \rightarrow C_6H_5O^{\cdot} + C_6H_5OH,$$
$$C_6H_5O^{\cdot} + C_6H_6 \rightarrow C_6H_5OH + C_6H_5^{\cdot},$$
$$C_6H_5^{\cdot} + C_6H_5^{\cdot} \rightarrow C_6H_5{-}C_6H_5.$$

The available experimental data are still insufficient to decide whether this mechanism of the gas-phase oxidation at high temperatures should be accepted or rejected. One can only note that the reaction of phenoxy-radicals with benzene is endothermic to the extent of 17 kcal mole^{-1} and should be extremely slow. The reactions of phenoxy-radicals with O_2, benzene ("addition"), and phenyl radicals should be faster.

Phenol is an intermediate and undergoes further oxidation. The oxidation of phenol was investigated by Ioffe at 650°C and a mechanism was proposed for the oxidation of phenol in the presence of benzene (RH is benzene)[26]:

$$C_6H_5OH + R^{\cdot} \rightarrow C_6H_4OH^{\cdot} + RH,$$
$$C_6H_4OH^{\cdot} + O_2 \rightarrow HOC_6H_4OO^{\cdot},$$
$$HOC_6H_4OO^{\cdot} + RH \rightarrow HOC_6H_4OH + RO^{\cdot},$$
$$C_6H_4OH^{\cdot} + R^{\cdot} \rightarrow RC_6H_4OH.$$

In this mechanism the first reaction, the removal of H from the C–H bond in phenol, is doubtful. The weakest bond in the phenol molecule is O–H and this should in fact be the point of attack by the radical on the phenol molecule which yields a phenoxy-radical.

III. OXIDATION OF BENZENE WITH FENTON'S REAGENT

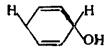
Fenton's reagent (aqueous solution of ferrous sulphate and hydrogen peroxide) is a source of hydroxy-radicals and is used for the oxidation of organic compounds[32-45]. In the absence of a substance undergoing oxidation, hydrogen peroxide breaks down as a result of the following reactions[41,45]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + OH^{-},$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^{+},$$
$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + OH^{-},$$
$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2 + H^{+},$$
$$HO^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot},$$
$$Fe^{2+} + HO_2^{\cdot} \rightarrow Fe^{3+} + HO_2^{-} \overset{H^+}{\rightleftarrows} H_2O_2.$$

According to Baxendale et al.[46], the rate constant is $k = 1.8 \times 10^9 \exp(-10\,000/RT)$ litre mole^{-1} s^{-1}. In the oxidation of benzene with Fenton's reagent the benzene molecule is attacked by hydroxy-radicals. The oxidation products are phenol and biphenyl (in the presence of oxygen, biphenyl does not form). In the first studies on the oxidation of benzene[33,37] the following reaction mechanism was put forward:

$$PhH + HO^{\cdot} \rightarrow Ph^{\cdot} + H_2O,$$
$$Ph^{\cdot} + Fe^{3+} + HO^{-} \rightarrow PhOH + Fe^{2+},$$
$$Ph^{\cdot} + Ph^{\cdot} \rightarrow Ph{-}Ph.$$

If the oxidation involves the removal of a hydrogen atom from the benzene molecule, an isotope effect should be observed in the oxidation of deuteriated benzene. However, there is no isotope effect in the oxidation of benzene with Fenton's reagent[41]. Dixon and Norman[45] investigated by the ESR method the free radicals formed in the systems H_2O_2–Ti^{3+} and H_2O_2–Ti^{3+}–benzene and established that in the presence of benzene hydroxyl radicals vanish and new radicals appear, to which the following structure is attributed:

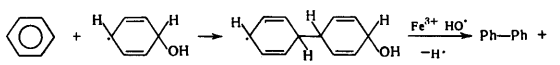


i.e. hydroxyl radicals add to benzene. The existence of the above radicals was also demonstrated spectroscopically[47]; the rate constant for the addition of HO$^{\cdot}$ to benzene has been calculated as 4.3×10^9 litre mole^{-1} s^{-1} (at 23°C). The high rate of addition of free hydroxy-radicals to benzene and the absence of an isotope effect are evidence that the oxidation of benzene with Fenton's reagent begins with the addition of OH$^{\cdot}$ to the benzene molecule:

$$C_6H_6 + HO^{\cdot} \rightarrow C_6H_6OH^{\cdot}.$$

The radical $C_6H_6OH^{\cdot}$ is then oxidised to phenol by the reaction with Fe^{3+} and HO$^{\cdot}$. Together with the oxidation to

phenol, this radical probably interacts with benzene and the product of such interaction is oxidised to biphenyl:



In the presence of oxygen the radical $C_6H_7O^{\cdot}$ is oxidised to phenol by the reaction with O_2 and this reaction is probably so fast that it successfully competes with the addition of $C_6H_7O^{\cdot}$ to benzene; this is why biphenyl does not form in the presence of oxygen. However, one cannot exclude the possibility that, as the temperature is raised, the reaction involving the "adhesion" of $HO^{\cdot}$ to benzene begins to be accompanied to a slight extent by the reaction involving the abstraction of a hydrogen atom. This is shown by the increase of the isotope effect: $k_H/k_D = 1.25$ (at 20°) and $k_H/k_D = 1.37$ (at 70°C) in the oxidation of a mixture of ordinary and deuteriated benzene with Fenton's reagent[48].

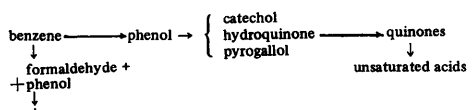
Aromatic compounds can be hydroxylated not only with Fenton's reagent but also with systems such as $Fe^{2+}-O_2$ and $Ti^{3+}-O_2$, but in such systems the hydroxylating agent is not $HO^{\cdot}$ but probably[49] the $HO_2^{\cdot}$ radical. For example, in the hydroxylation of *N*-acetanilide with the reagent hydrogen peroxide–iron(II) complex of EDTA (in this system the reactive species is $HO^{\cdot}$) the following mixture of isomeric *N*-acetamidophenols is obtained: *ortho*-isomer 46.5%, *meta*-isomer 2.5%, and *para*-isomer 51%. On the other hand, hydroxylation of *N*-acetanilide by the system $Fe^{2+}-O_2$ or $Ti^{3+}-O_2$ leads to a mixture of 35% of the *ortho*-isomer, 33% of the *meta*-isomer, and 32% of the *para*-isomer. This is evidence that *N*-acetanilide molecules are not attacked by hydroxy-radicals but by another species (for example $HO_2^{\cdot}$ radicals).

IV. RADIATION-CHEMICAL AND PHOTOCHEMICAL OXIDATION OF BENZENE

Much work has been done on the oxidation of benzene in aqueous solutions initiated by radiation of various kinds[50-71]. When a solution of benzene in water containing Fe^{3+} ions is irradiated with the light of the mercury lamp ($\lambda = 313$ nm), phenol, biphenyl, and Fe^{2+} ions are formed[50]. The addition of Cu^{2+} ions reduces the fraction of biphenyl. A mechanism has been suggested in which the hydroxy-radical removes a hydrogen atom from the benzene molecule. The results of the oxidation of benzene with Fenton's reagent convincingly demonstrate the addition of $HO^{\cdot}$ to benzene. Therefore the following mechanism can be suggested for the oxidation of benzene by Fe^{3+} ions:

$$Fe^{3+}_{aq} + h\nu \rightarrow Fe^{2+} + H^+ + HO^{\cdot},$$
$$HO^{\cdot} + C_6H_6 \rightarrow C_6H_7O^{\cdot},$$
$$C_6H_7O^{\cdot} + Fe^{3+} \rightarrow C_6H_5OH + Fe^{2+} + H^+,$$
$$C_6H_7O^{\cdot} + Cu^{2+} \rightarrow C_6H_5OH + Cu^{1+} + H^+,$$
$$C_6H_7O^{\cdot} + C_6H_6 \rightarrow HOC_6H_6{-}C_6H_6 \xrightarrow{Fe^{3+}} C_6H_5{-}C_6H_5 + H_2O + Fe^{2+} + H^+.$$

The oxidation of benzene in aqueous solution in an ultrasonic field yields phenol, which readily reacts further by the mechanism[52]

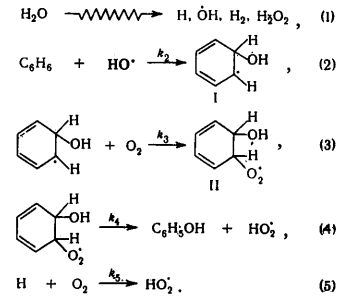


The radiolysis of aqueous benzene solutions under the action of cobalt-60 γ-rays has also been investigated[54-64]. At room temperature in the absence of oxygen oxidation in the two-phase system benzene–water takes place due to the water radiolysis product – H_2O_2, $HO^{\cdot}$, and $HO_2^{\cdot}$. The yields of phenol are slight: 2.64–2.94 m mole litre^{-1} kr^{-1}.[54,55] In the presence of oxygen the radiation-yield of phenol increases and reaches $G = 2$ molecules/100 eV. Proskurin and Barelko[55] established for the first time that the addition of Fe^{2+} or Fe^{3+} ions increases the yield of phenol to $G = 6$ and investigated the oxidation of benzene (under the action of γ-rays at an oxygen pressure of 10 atm) over a wide temperature range, between 20° and 220°C. The main products of the radiolysis of water–benzene mixtures (water : benzene = 32 : 1) under these conditions are phenol and a resin. The maximum yield of phenol at 200°C is 0.035 M with simultaneous formation of 0.025 M resin. The resin contains both phenolic derivatives and polyphenyls. Above 200°C the yield of phenol falls. When irradiation is stopped, the reaction continues with self-acceleration. The authors suggest that at high temperatures the oxidation of benzene is a branched-chain process.

The oxidation of benzene with X-rays yields phenol, biphenyl (in the absence of oxygen), hydrogen peroxide[68], and dialdehydes[69]. In the absence of oxygen the radiation yields G of the main oxidation products are 0.34 for phenol, 0.55 for biphenyl, 0.60 for hydrogen, and more than 0.60 for hydrogen peroxide. In the presence of oxygen or Fe^{2+} and Cu^{2+} ions the yield of phenol increases.

It has been shown[69] that phenol and dialdehydes are formed at the same time and approximately in the same amounts: G(phenol) = 1.8 and G(dialdehydes) = 1.5.

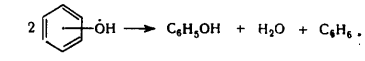
Let us now consider the mechanism of the radiolysis of aqueous benzene solutions[62,69]:



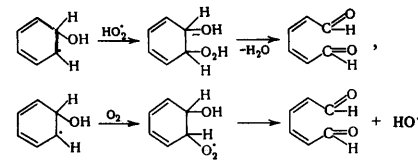
Reaction (2) is faster than reaction (3). Dorfman et al.[62] measured the rate constants k_2 and k_3 at 23°C:

$$k_2 = (4.3 \pm 0.9) \times 10^9 \text{ litre mole}^{-1}\text{ s}^{-1},$$
$$k_3 = (5.0 \pm 0.6) \times 10^9 \text{ litre mole}^{-1}\text{ s}^{-1}.$$

The mechanism shows that phenol forms by the oxidation with oxygen of radicals (I) and that at the same time the radicals disproportionate[41,69]:



It is more logical to assume that reactions (3) and (4) take place in one stage. The formation of dialdehyde together with phenol can take place by the following hypothetical reactions[64,70]:

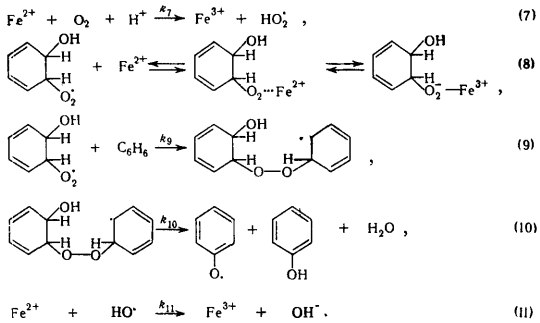


Thus, regardless of the source of radiation, the oxidation of benzene is initiated by the water radiolysis products HO· and $HO_2^·$. The mechanism of the oxidation of benzene is similar to that of the oxidation by Fenton's reagent: an HO· radical adds to benzene and the resulting radical is then oxidised with oxygen to phenol and other products. Some workers believe[71] that the oxidation of benzene under the action of radiation is suitable for the manufacture of phenol, particularly when iron ions are added. However, a considerable disadvantage of the radiation-chemical oxidation is the formation of a large amount of resins by the condensation of phenol and side products. Catechol, hydroquinone, hydroxybenzoic acids, maleic acid, and other compounds are formed in small amounts together with the resins.

As already noted several times, the addition of Fe^{2+}, Fe^{3+}, and Cu^{2+} ions in small amounts (at concentrations between 10^{-4} and 10^{-3} M) in the radiation-induced oxidation of benzene greatly increases the yield of phenol. Quite recently a group of Japanese investigators used the catalytic effect of iron and copper ions for the radiation-catalytic oxidation of benzene[72-79]. Benzene was oxidised in aqueous solutions of $FeSO_4$, $FeCl_2$, $CuCl_2$, and $Fe_2(SO_4)_3$ at concentrations between 10^{-4} and 0.1 M. At an oxygen pressure of 30 atm the reaction mixture was irradiated with cobalt-60 γ-rays for 25 min at different temperatures ranging from 100° to 200°C. When the reaction is carried out in the presence of Fe^{2+} ions, the maximum yield of phenol is 27 mg per ml of benzene, i.e. 2.5%. In the presence of Cu^{2+} ions, 1 ml of benzene yields 40 mg of phenol, i.e. 3.7% relative to the initial benzene. Biphenyl is not formed in the presence of iron and copper ions. It has been established that ferrous sulphate ensures a high yield of phenol both with and without γ-irradiation. In catalysis by Fe^{3+} ions considerable amounts of phenol are formed only on γ-irradiation; without it the yield of phenol is appreciable only at high temperatures (in excess of 180°C). In catalysis by cupric sulphate the yield of phenol is fairly high, both with and without irradiation[74] above 180°C. The catalytic effect of iron and copper chlorides is less than that of the corresponding sulphates[73,74]. The reaction is greatly influenced by the purity of the benzene; impurities such as toluene and thiophen increase the yield of phenol[75]. The addition of SO_4^{2-} ions greatly reduces the amount of phenol formed. When copper filings are introduced into the reaction vessel, the yield of phenol increases. An increase of the concentration of cupric sulphate from 10^{-4} M to 10^{-2} M at 198°C also increases the yield of phenol.

Phenol is the main reaction product but dihydroxybenzenes and also carbon dioxide, acetaldehyde formaldehyde, acetone, acetic acid, formic acid, and maleic acid are formed with it in small amounts (about 10^{-4} M).[77] All these compounds are formed as a result of the oxidation of phenol[76]. This conclusion was arrived at after the investigation of the products of the oxidation of phenol under the same conditions as those in the oxidation of benzene. All the compounds enumerated above were detected in the oxidation of phenol.

The study of the migration of oxygen with the aid of oxygen-18 shows that oxygen is incorporated into phenol both from water[78] and from O_2. In the oxidation of an equimolar mixture of benzene and hexadeuteriobenzene isotope analysis yielded $k_H/k_D = 1.2$. The low isotope effect suggests that a hydrogen atom is removed not from the benzene molecule but from a free radical, for example $\dot{C}_6H_6OH$. On the basis of experimental and literature data, Japanese investigators have suggested a mechanism for the oxidation of benzene under the action of γ-irradiation and in the presence of iron and copper ions. Without reservations, they extend the mechanism of radiation-induced initiation [reactions (1)–(5)], adopted for room temperature, to the high-temperature range:



(7)

(8)

(9)

(10)

$$Fe^{2+} + HO^· \xrightarrow{k_{11}} Fe^{3+} + OH^-. \quad (11)$$

At 25°C and pH 2 $k_{11} = 2.6 \times 10^8$ litre mole^{-1} s^{-1}.[80] It has been stated[81] that at 25°C k_2 is greater by a factor of 3.2 than k_{11}.

$$Fe^{2+} + H_2O_2 \xrightarrow{k_{12}} Fe^{3+} + OH^- + HO^·. \quad (12)$$

At 150°C $k_{12} = 6.6 \times 10^{-3}$ litre mole^{-1} s^{-1} and is therefore smaller than k_2.[82] If the catalyst is Fe^{3+} or Cu^{2+} ions, then reaction (13) is the initiating process:

$$Fe^{3+} + H_2O \rightarrow Fe^{2+} + H^+ + HO^·. \quad (13)$$

In a number of studies the possibility of this reaction has been demonstrated[83,84]. According to the above mechanism, the role of the Fe^{2+} ion is determined by reaction (7), which leads to the formation of $HO_2^·$ radicals. It is also suggested that Fe^{2+} ions stabilise the peroxy-radicals by reaction (8) and make possible the occurrence of reaction (9). As mentioned above, the reaction of $C_6H_7O^·$ radicals with O_2 takes place in one step. Therefore reactions (8)–(10) seem to be extremely unlikely and are superfluous in the mechanism. The inhibiting effect of Cl^- on the oxidation of benzene can be accounted for by the destruction of HO· radicals by the reaction

$$Cl^- + HO^· \xrightarrow{k_6} Cl^· + OH^-. \quad (6)$$

At 25°C $k_6 = 1.8 \times 10^8$ litre mole^{-1} s^{-1} (at pH 2). In 0.8 N sulphuric acid k_6 is greater by a factor of eight[80], while $k_2 = (4.3 \pm 0.9) \times 10^9$ litre mole^{-1} s^{-1} at 23°C. If the same temperature variation of k_2 and k_6 is assumed, then reactions (1) and (6) may compete at high temperatures.

Japanese investigators believe the oxidation of benzene to be a branched-chain process and on the basis of literature data[85] suggest the following branching mechanism:

$$PhO^· + PhH \rightarrow PhOH + Ph^·, \quad (14)$$

$$Ph^· + O_2 \rightarrow PhO_2^·, \quad (15)$$

$$PhO_2^· + PhH \rightarrow PhO_2H + Ph^·, \quad (16)$$

$$PhO_2H + Fe^{3+} \rightarrow PhO_2^· + Fe^{2+} + H^+, \quad (17)$$

$$PhO_2H + Fe^{2+} \rightarrow PhO^· + Fe^{3+} + OH^-, \quad (18)$$

$$PhO_2H = PhO^· + HO^·. \quad (19)$$

This mechanism is open to a number of significant objections. Reaction (14) cannot occur at an appreciable rate, since PhO· radicals show little activity and the C–H bond in benzene is strong. The reaction is endothermic (–17 kcal mole^{-1}) and cannot compete successfully to any extent with other reactions of phenoxy-radicals, such as

oxidation and addition to benzene. The hydroperoxide PhOOH does not exist as a molecular compound (particularly at a high temperature). Therefore all the reactions involving its participation must be excluded. The mechanism of the acceleration of the oxidation of benzene in the presence of iron and copper ions is discussed in greater detail in the section dealing with the catalytic oxidation of benzene.

V. INITIATED LIQUID-PHASE OXIDATION OF BENZENE

Various methods for the oxidation of benzene in aqueous solutions were discussed above. It has been shown[86,87] that the oxidation of liquid benzene to phenol under pressure below the critical temperature (t_{cr} = 288°C) is possible in principle. The oxidation was carried out in an autoclave at 230–270°C and a pressure of 50 atm. The oxidation results in the formation of phenol and resins.

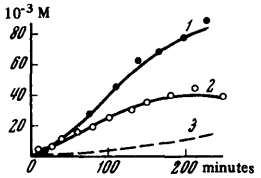


Figure 1. Kinetic curves for the accumulation of phenol at 250°C: *1*) in the experiment with continuous initiation by nitrogen dioxide; *2*) in the experiment with initial 40 min gas-phase initiation; the dashed curve indicates the accumulation of phenol in the experiment without initiation.

Table 2. Initiated oxidation of benzene.

t, °C	Conditions	Rate of formation of phenol, 10^{-3} mole litre min^{-1}	Phenol, mole %	Degree of oxidation, wt. %
250	No additive	0.07	0.16	0.7
230	2% C_6H_{12}	0.18	0.23	6.5
250	1% $C_6H_{10}O$	1.70	0.50	6.0
250	NO_2 continuous	0.49	0.80	5.3
250	NO_2 40 min	0.23	0.33	2.0
250	NO_2 + 1% C_6H_{12}	0.31	0.48	2.7
267	NO_2 continuous	0.88	1.10	4.0

The reaction takes place with self-acceleration, the concentration of phenol tending to a limit during the reaction. In the absence of initiating effects the maximum concentration of phenol at 250°C is 1.8×10^{-3} M and is attained 6 h after the start of the reaction. The oxidation of benzene can be stimulated by the introduction of readily oxidisable substances (cyclohexane, cyclohexanone) and by passing through the system nitrogen dioxide (gaseous initiator) together with air. Fig. 1 presents kinetic curves for the accumulation of phenol in experiments with nitrogen dioxide (2% NO_2 in the 1 : 1 N_2–O_2 mixture). Nitrogen dioxide accelerates the reaction and increases the amount of phenol formed. The results of the experiments are presented in Table 2.

The available data are so far insufficient for the discussion of a concrete mechanism of liquid-phase oxidation of benzene. However, the observed features of the kinetics indicate a free-radical oxidation mechanism (possibly of a chain type). These include the accelerating effect on the oxidation of benzene of the addition of substances readily oxidisable by a chain mechanism such as cyclohexane and cyclohexanone, the powerful effect of nitrogen dioxide which accelerates the oxidation of other hydrocarbons, and the S-shaped kinetic curves for the accumulation of phenol, which is a characteristic of chain auto-oxidation reactions. It should be noted that the oxidation of benzene is a self-inhibiting process, as shown by experiments where the initiation of this reaction by nitrogen dioxide was interrupted (Fig. 1).

VI. CATALYTIC OXIDATION OF BENZENE IN AQUEOUS SOLUTION

The possibility of the oxidation of benzene in aqueous solution at 170–200°C in the presence of iron and copper ions was established by Japanese investigators, who obtained interesting experimental data on this process[72-79,88].

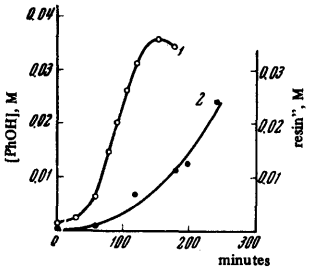


Figure 2. Kinetic curves for the accumulation of phenol (curve *1*) and resins (curve *2*) at 200°C and an air pressure of 35 atm in the presence of 0.012 M Cu^{2+} and 5 ml of benzene; the content of the $C_6H_4O_4$ resins (mole $litre^{-1}$) is plotted.

A detailed study of the kinetics and mechanism of this reaction has been made[89-94]. Benzene dissolved in water (at 185°C the solubility of benzene in water is 0.21 mole $litre^{-1}$) was oxidised with oxygen in an autoclave under pressure. In the presence of iron and copper ions benzene was scarcely oxidised at 185–200°C; Co^{2+}, Mn^{2+}, and Ti^{3+} ions do not catalyse the oxidation of benzene. In the presence of copper and iron ions benzene was oxidised fairly rapidly with formation of phenol. An appreciable quantity of phenolic resin with the elemental composition $C_6H_4O_4$ (Fig. 2) and a small amount of low-molecular products (acetaldehyde, formaldehyde, acetone, acetic acid, and carbon dioxide) were formed together with phenol[92]. The low-molecular products are formed as a result of the oxidation of phenol[76]. The catalytic oxidation of benzene is an autocatalytic reaction[89,92] (Fig. 2). The kinetics of phenol accumulation obey the equation for autocatalysis of the second kind: $dx/dt = k(1 - x)x^2$, where $x = [C_6H_5OH]/[C_6H_5OH]_{max}$. Phenol is an intermediate in this reaction, as can be clearly seen from experiments in which various

amounts of phenol were introduced into the initial benzene (Fig. 3). If the initial concentration of phenol is less than the maximum concentration, phenol accumulates, but if it is greater the concentration of phenol falls. It follows from the kinetic curve for the accumulation of phenol and the resin (Fig. 2), that the latter does in fact form as a result of the oxidation of phenol. Experiments with the introduction of phenol at the beginning of the reaction (Fig. 4) showed that phenol is the main product responsible for the autocatalysis of the reaction[92]. Surprisingly, the accumulation of phenol accelerates the oxidation of the initial benzene (usually in hydrocarbon oxidation reactions phenol behaves as an inhibitor).

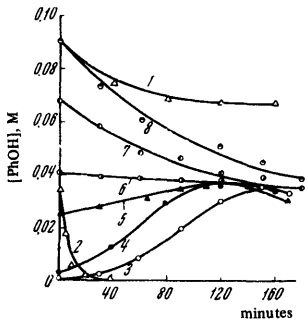


Figure 3. Kinetic curves for the accumulation and consumption of phenol at 200°C and a pressure of 35 atm (50% O_2) in the presence of 0.0125 M $CuSO_4$:
1) oxidation of phenol in benzene; *2*) oxidation of phenol in aqueous cupric sulphate without benzene; *3*)-*8*) kinetic curves for the accumulation and consumption of phenol in aqueous cupric sulphate solution in the presence of benzene (5 ml) in experiments with initial addition of phenol.

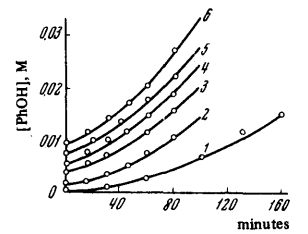


Figure 4. Initial sections of the kinetic curves for the accumulation of phenol at 200°C at pH 1.2 in the presence of 5 ml of benzene and 90 ml of 0.006 M Fe^{3+} solution and different concentrations of added phenol (M):
1) no phenol added; *2*) 0.0018; *3*) 0.0046; *4*) 0.0057; *5*) 0.0074; *6*) 0.0100.

It has been established for iron ions that during the reaction their valence state changes. If trivalent iron is introduced into the initial benzene solution in water, then divalent iron appears and accumulates in the reaction, and conversely. The oxidation in the presence of copper ions is accelerated when a copper plate is introduced into the reactor, metallic copper dissolving during the reaction, i.e. the appearance in the system of copper(I) ions at a certain rate (formed by the reaction $Cu^0 + Cu^{2+} \rightarrow 2Cu^+$) stimulates the oxidation process. There is no doubt that oxidation-reduction reactions with participation of lower- and higher-valence ions play an important role in the catalytic oxidation of benzene.

The kinetics of the oxidation of benzene in the presence of iron and copper ions are very similar[89,90]. As the concentration of benzene increases, the maximum reaction rate w_{max} passes through a maximum, and the maximum concentration of phenol $[PhOH]_{max}$ increases linearly. With increase in the partial pressure of oxygen, both $[PhOH]_{max}$ and w_{max} increase. As the concentration of the catalyst is raised, w_{max} passes through a maximum and $[PhOH]_{max}$ increases in the presence of Cu^{2+} ions. An increase of the concentration of hydrogen ions entails a decrease of the reaction rate. Anions such as F^-, Cl^-, Br^-, CH_3COO^-, and SO_4^{2-} lower both the rate of accumulation of phenol and $[PhOH]_{max}$. Hydrocarbons (cumene, cyclohexene) and alcohols (isopropyl alcohol, cyclohexanol), introduced in an amount of 2% of the initial benzene, retard the oxidation of benzene. The maximum yield of phenol relative to benzene consumed (57%) was obtained in an experiment performed under the following conditions: 200°C, 0.012 M Cu^{2+}, 5 ml of benzene per 100 ml of water, duration 2 h, and P_{O_2} = 17.5 atm. The extent of reaction was 66%.

The mechanism of the oxidation of benzene in this reaction proved to be closely related to the mechanism of the oxidation of phenol and to the valence changes. Therefore a detailed study was made[93] of the oxidation of phenol under conditions similar to those in the oxidation of benzene and also of the oxidation of iron(II) ions. It was found that at 200°C in aqueous solution phenol is oxidised in three different ways: by reaction with molecular oxygen, by reaction with iron(III) ions, and by reaction with free radicals ($HO^\cdot$ and $HO_2^\cdot$).

Molecular phenol and phenoxide ions react with oxygen:

$$PhOH + O_2 \xrightarrow{k_0'} PhO^\cdot + HO_2^\cdot , \qquad (0')$$

$$PhOH + H_2O \rightleftarrows PhO^- + H_3O^+ ,$$

$$PhO^- + O_2 \xrightarrow{k_0''} PhO^\cdot + O_2^{-\cdot} , \qquad (0'')$$

$$O_2^{-\cdot} + H^+ \rightleftarrows HO_2^\cdot ,$$

$$PhOH + HO_2^\cdot \rightarrow PhO^\cdot + H_2O_2 ,$$

$$PhO^\cdot + O_2(HO_2^\cdot) \rightarrow \text{products of further oxidation}$$

(K_0 is the equilibrium constant).

It has been established experimentally that at 200°C $w = 2k[PhOH][O_2]$, $2k = a + b[H^+]^{-1}$, $a = (1.13 \pm 0.17) \times 10^{-5}$ litre mole^{-1} s^{-1}, and $b = (2.9 \pm 0.3) \times 10^{-6}$ s^{-1}. Comparison with the mechanism yields $\frac{1}{2}a = k_{0'}$ and $\frac{1}{2}b = K_0 k_{0''}$.

The reaction between phenol and Fe^{3+} ions was investigated under pressure in an atmosphere of argon. It was established that the reaction rate $w = k[PhOH][Fe^{3+}][H^+]^{-1}$ and $k = (3.5 \pm 0.2) \times 10^{-4}$ s^{-1} at 200°C.

It is suggested that the oxidation takes place according to the reaction

$$PhO^- + Fe^{3+} \rightarrow Fe^{2+} + PhO^\cdot \xrightarrow{Fe^{3+}} \text{molecular products.}$$

At 200°C Fe^{2+} ions (these were introduced in the form of Mohr's salt) are oxidised at the rate

$$w = (4.25 \cdot 10^{-3} + 9.0 \cdot 10^{-5}\,[H^+]^{-1})\,[Fe^{2+}]\,[O_2] \text{ mole litre}^{-1}\,\text{s}^{-1}.$$

According to the literature[95-103], the mechanism of the oxidation of Fe^{2+} ions is as follows

$$Fe^{2+} + O_2 \xrightarrow{k_2'} Fe^{3+} + O_2^- , \quad (2')$$

$$Fe^{2+}\,aq \overset{K_1}{\rightleftarrows} FeOH^+ + H^+ ,$$

$$FeOH^+ + O_2 \xrightarrow{k_2''} FeOH^{2+} + O_2^- , \quad (2'')$$

$$O_2^- + H^+ \rightleftarrows HO_2^\cdot ,$$

$$Fe^{2+} + HO_2^\cdot \rightarrow Fe^{3+} + HO_2^- ,$$

$$HO_2^- + H^+ \rightleftarrows H_2O_2 ,$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\cdot + OH^- ,$$

$$Fe^{2+} + HO^\cdot \rightarrow Fe^{3+} + OH^- .$$

Reactions (2′) and (2″) constitute the rate-limiting stage. Subsequent reactions with participation of $HO^\cdot$, HO_2, and H_2O_2 are very rapid and the concentrations of the reacting species (radicals and hydrogen peroxide) correspond to kinetic equilibrium. Since one oxygen molecule oxidises ultimately four Fe^{2+} ions, the rate of oxidation of Fe^{2+} according to the mechanism is $w = 4k_{2'}[Fe^{2+}][O_2] + 4k_{2''}K_2[Fe^{2+}][O_2][H^+]^{-1}$. Comparison with the experimental relations yields (for 200°C) $k_{2'} = 1.06 \times 10^{-3}$ litre mole^{-1} s^{-1} and $k_{2''}K_2 = 2.25 \times 10^{-5}$ s^{-1}. Sulphate ions accelerate the oxidation of Fe^{2+}.

The radicals $HO^\cdot$ and $HO_2^\cdot$, formed in the reactions of O_2 with Fe^{2+} and phenol, react with phenol. Therefore the mechanism for the oxidation of phenol can be represented by the following set of reactions (r$^\cdot$ is a general symbol for an active radical):

$$PhOH + O_2 \xrightarrow{k_0'} PhO^\cdot + HO_2^\cdot ,$$

$$PhO^- + O_2 \xrightarrow{k_0''} PhO + O_2^- ,$$

$$Fe^{2+} + O_2 \xrightarrow{k_2'} Fe^{3+} + r^\cdot ,$$

$$FeOH^+ + O_2 \xrightarrow{k_2''} FeOH^{2+} + r^\cdot ,$$

$$Fe^{2+} + r^\cdot \xrightarrow{k_3} Fe^{3+} + r^- ,$$

$$PhOH + r^\cdot \xrightarrow{k_4} PhO^\cdot + rH .$$

According to this mechanism, the rate of oxidation of phenol is

$$w = (k_0[O_2] + k_1[Fe^{3+}] + k_4[r^\cdot])[PhOH].$$

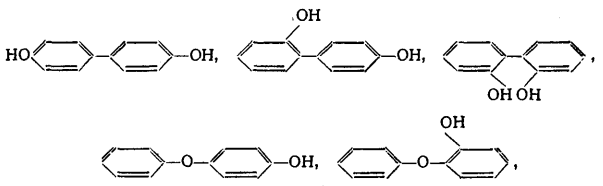
Table 3. Contribution of various reactions to the overall rate of oxidation of phenol at 200°C.

$[O_2]$, M	$[H^+]^{-1}$, litre mole^{-1}	$10^3[Fe^{3+}]$, M	$2 \times 10^5 k_0 \times [O_2]$, s^{-1}	$10^5 k_1 \times [Fe^{3+}]$, s^{-1}	$10^5 k_1 \times [r^\cdot]$, s^{-1}	$\frac{10^5 w}{[PhOH]}$, s^{-1}
0.22	12.6	2.2	1.05	0.97	0.73	2.75
0.22	12.6	1.1	1.05	0.48	0.47	2.00
0.22	12.6	0.5	1.05	0.22	0.03	1.30
0.22	12.0	0.9	0.88	0.38	0.50	1.76
0.44	6.0	17.0	1.20	4.10	5.70	11.00
0.22	52.4	0.2	3.00	0.36	0.81	4.17

Table 3 lists the rates of each of the three phenol consumption reactions for experiments with different initial conditions[93] and shows that the contribution of free-radical reactions ranges from 2 to 50% (in different experiments).

The reaction of hydroxy-radicals with phenol in aqueous solutions has been investigated[62,104-108]. Dixon and Norman[104] obtained hydroxy-radicals by the reaction of Ti^{3+} with hydrogen peroxide; in this system the formation of phenoxy-radicals from phenol was observed by the ESR method. It was reasonable to postulate the following reaction: $HO^\cdot + PhOH \rightarrow H_2O + PhO^\cdot$. However, it has been established by pulse radiolysis[62] that the primary radical product of the reaction of $HO^\cdot$ with phenol is dihydroxycyclohexadienyl, i.e. the hydroxy-radical adds to the phenol molecule: $HO^\cdot + C_6H_5OH \rightarrow HOC_6H_5\dot{O}H$. This contradiction has been resolved by Lamb and coworkers[105,106]. It was established by pulse radiolysis that the hydroxy-radical does indeed add to phenol but the $HOC_6H_5\dot{O}H$ radical formed is unstable and in aqueous solution is rapidly converted into the phenoxy-radical and water. The reaction is catalysed by H^+, OH^-, and $H_2PO_4^-$ ions. In aqueous solutions at pH 6.3 the rate constant for the decomposition of the radical[106] $HOC_6H_5\dot{O}H$ is 4.7×10^3 s^{-1}. This radical also reacts with other free radicals. The rate constant for the addition of $HO^\cdot$ to phenol in aqueous solution at room temperature is 1.06×10^{10} litre mole^{-1} s^{-1} at pH 6–7 [107] and 0.51×10^{10} at pH 9.[108]

In aqueous solutions phenoxy-radicals rapidly recombine with the ultimate formation of dimeric products. The recombination takes place with a rate constant $k = 5.6 \times 10^9$ litre mole^{-1} s^{-1} (determined by flash photolysis[109]). The following compounds have been observed among the products of the reaction of phenol in photolysis both in the presence and absence of oxygen[110]:



as well as dihydric phenols.

Thus kinetic data for the oxidation of phenol and modern ideas on the mechanism of the oxidation of Fe^{2+} show that in the catalytic oxidation of benzene in the presence of Fe^{2+} and Cu^{2+} ions benzene may be attacked by $HO^\cdot$ and $HO_2^\cdot$ radicals. At the initial point of the catalytic oxidation of benzene free radicals are formed by the reactions

$$Fe^{2+}aq + O_2 \rightarrow Fe^{3+}aq + O_2^- , \quad (2')$$

$$Fe^{3+} + HO^- \rightarrow Fe^{2+} + HO^\cdot . \quad (2'')$$

Reaction (2′) is much faster than reaction (2″) and therefore, on introduction of Fe^{2+} at the beginning of the reaction, the oxidation develops more rapidly than in the presence of Fe^{3+} ions. For the same reason, a copper surface in the presence of Cu^{2+} ions accelerates the process: the Cu^+ ions formed at a constant rate by the reaction of Cu^{2+} ions with metallic copper are then oxidised by O_2 with formation of O_2^- [by a reaction analogous to reaction (2′)]. Thus Fe^{2+} and Fe^{3+} ions (or Cu^{2+} and Cu^+) constitute the only source of $HO^\cdot$ and $HO_2^\cdot$ radicals at the beginning of the oxidation.

At an advanced stage of the reaction phenol begins to play a significant role in the formation of radicals. In the first place it reacts directly with O_2 forming O_2^-, which is then converted by a series of consecutive reactions into a hydroxyl radical:

$$O_2^- \overset{H^+}{\rightleftarrows} HO_2^\cdot \xrightarrow{Fe^{2+}} HO_2^- \overset{H^+}{\rightleftarrows} H_2O_2 \xrightarrow{Fe^{2+}} HO^\cdot .$$

In the second place, by reducing Fe^{3+} to Fe^{2+}, phenol increases the concentration of the latter and thus increases the rate of formation of radicals by reaction (2′). The increase in the rate of formation of radicals as phenol accumulates is in fact the reason for the autocatalytic course of the reaction.

The oxidation of benzene can be represented schematically by the following reactions:

$$\left.\begin{aligned} PhOH + O_2 &\xrightarrow{k_{0'}} PhO^{\cdot} + HO_2^{\cdot} \\ PhO^- + O_2 &\xrightarrow{k_{0''}} PhO^{\cdot} + O_2^- \\ Fe^{2+} + O_2 &\xrightarrow{k_{2'}} Fe^{3+} + O_2^- \\ FeOH^+ + O_2 &\xrightarrow{k_{2''}} FeOH^{2+} + O_2^- \end{aligned}\right\} \text{formation of free radicals}$$

$$\left.\begin{aligned} PhOH + r^{\cdot} &\xrightarrow{k_4} PhO^{\cdot} + rH \\ PhO^- + Fe^{3+} &\xrightarrow{k_5} PhO^{\cdot} + Fe^{2+} \end{aligned}\right\} \text{consumption of phenol}$$

$$C_6H_6 + r^{\cdot} \xrightarrow{k_6} PhOH \quad \text{formation of phenol.}$$

The present authors calculated[94] kinetic curves for the accumulation of phenol and consumption of benzene by this mechanism. The rate constants for reactions (0), (1), and (2) taken from experiments on the oxidation of phenol were used in the calculations and the ratio k_4/k_5 was evaluated from the ratio of the concentrations of benzene and phenol at the point corresponding to the maximum concentration of the latter, and the concentrations of Fe^{2+} and Fe^{3+} were determined experimentally. Under the experimental conditions (200°C, pH 1.90), the constants have the following values:

$$k_0 = k_{0'} + k_{0''}K_0[H^+]^{-1} = (2.43 \pm 0.30),\ 10^{-4} \text{ litre mole s}^{-1},$$
$$k_1 = (k_{1'}K_0 + k_{1''}K_1)[H^+]^{-1} = (2.80 \pm 0.20),\ 10^{-2} \text{ litre mole s}^{-1},$$
$$k_2 = k_{2'} + k_{2''}K_2[H^+]^{-1} = (2.86 \pm 0.20),\ 10^{-3} \text{ litre mole s}^{-1}.$$

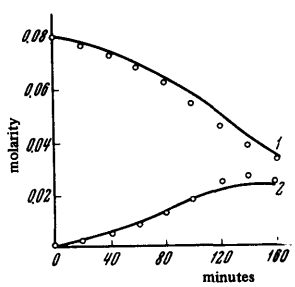


Figure 5. Experimental (circles) and calculated (lines) kinetic curves for the consumption of benzene (curve *1*) and accumulation of phenol (curve *2*).

Fig. 5 shows that the results of the calculations are in good agreement with experiment. The variation of the contribution of each reaction to the overall process of radical formation is plotted in Fig. 6. It is clearly seen that at an advanced stage the main source of radicals in the process is the reaction of phenol with oxygen.

The hydroxylation of benzene in this reaction takes place as a result of the addition of the radical to the benzene molecule. This is indicated by the closeness to unity of the isotope effect in the oxidation of C_6H_6 and C_6D_6 (k_H/k_D = 1.2) [78] and also the fact that the ratio of the rate constants for the reactions of radicals with benzene and phenol is close to unity[94]. Indeed if the free radical ($HO^{\cdot}$ or $HO_2^{\cdot}$) removed a hydrogen atom from benzene, then we should have $k_5 \ll k_4$, since the C–H bond energy in benzene is 102 kcal mole^{-1}, while the O–H bond energy in phenol is 85 kcal mole^{-1}. The available experimental data are so far insufficient for an estimate of the contribution of each radical ($HO^{\cdot}$ and $HO_2^{\cdot}$) to the hydroxylation of benzene.

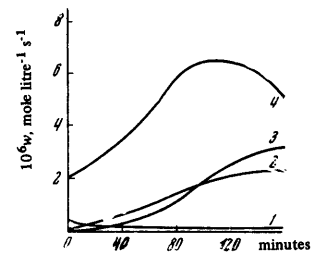


Figure 6. Rates of different reactions at 200°C, pH 1.90, and an oxygen pressure of 35 atm:
1) oxidation of Fe^{2+} ions; *2*) oxidation of phenol by oxygen; *3*) oxidation of phenol by reaction with radicals; *4*) consumption of benzene.

There is no doubt, however, that hydroxy-radicals hydroxylate benzene very vigorously, since it is known that at room temperature $k_{(HO^{\cdot}+C_6H_6)} = 4.3 \times 10^9$ litre mole^{-1} s^{-1},[45] i.e. the rate constant is very high. The question of the activity of the $HO_2^{\cdot}$ radical as a hydroxylating agent still remains obscure. Altogether, it has been shown that the catalytic oxidation of benzene in aqueous solution at 170–220°C is a coupled autocatalytic ion—radical reaction oxidising benzene and phenol by short chains, in which benzene is oxidised by radical addition; this in fact ensures a comparatively high yield of phenol. The chain length under the experimental conditions quoted in Fig. 5 is four units. Chain growth probably takes place by the reactions

$$C_6H_6 + HO^{\cdot} \rightarrow C_6H_7O^{\cdot},$$
$$C_6H_7O^{\cdot} + O_2 \rightarrow C_6H_5OH + HO_2^{\cdot},$$
$$HO_2^{\cdot} \xrightarrow{Fe^{2+}} HO_2^- \xrightarrow{H^+} H_2O_2 \xrightarrow{Fe^{2+}} HO^{\cdot}.$$

The benzene oxidation mechanism described above explains all the kinetic features of this reaction. The inhibiting effect of anions such as Cl^- and Br^- is due to the reactions

$$HO^{\cdot} + Cl^- \rightarrow HO^- + Cl^{\cdot},$$
$$Cl^{\cdot} + C_6H_5OH \rightarrow HCl + C_6H_5O^{\cdot}.$$

which lower the concentration of the hydroxylating agent, while phenol continues to disappear by reactions with $Cl^{\cdot}$ (or $Br^{\cdot}$). The inhibiting effect of certain organic additives[91] is also due to the fact that hydroxy-radicals are consumed in the oxidation of the organic compound and not in the hydroxylation of benzene.

VII. OTHER METHODS FOR THE OXIDATION OF BENZENE

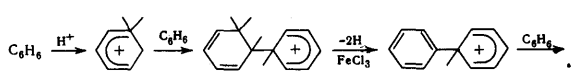
In a number of studies benzene was oxidised under pressure in liquid hydrofluoric acid[111-113]. The reaction at 200°C yields phenol, biphenyl, and carbon black, i.e. under these conditions oxidation is accompanied by dehydrogenation of benzene to carbon. Arsenic and selenium oxides make it possible to lower the oxidation temperature. The mixture hydrogen fluoride–boron trifluoride has also been employed as a catalyst[112], and O_2, ozone, sulphur dioxide, and atomic oxygen have served as oxidants. Phenol is formed in very small amounts.

Benzene can be oxidised to phenol using cupric sulphate as the oxidant by heating a mixture of benzene and aqueous cupric sulphate to 304°C.[114] The maximum yield of phenol (66%) is obtained when sodium phosphate is introduced together with cupric phosphate. Benzene can be oxidised to phenol with cupric acetate and benzoate (210–250°C, water)[115]. At 250°C 0.135 mole of phenol is formed in 5 h per mole of cupric sulphate consumed (benzene : water = 1 : 1). Phenol is obtained in the oxidation of benzene with oxygen at 300°C in the presence of water and the heterogeneous catalyst[116] 6% Cu–17% Mo on alumina. A high yield (75% relative to unreacted benzene) of phenol is obtained when benzene is oxidised with oxygen in benzoic acid in the presence of catalysts such as iron, copper, and silver oxides (260°C, water removed continuously by azeotropic distillation)[117].

The attempt to oxidise benzene in a hydrocarbon medium in the presence of suspended titanium salts and oxides at 25–100°C showed that under these conditions phenol is formed in negligible amounts[118].

Benzene can be polymerised to polyphenyl in the presence of Lewis acids, an oxidant, and water. When benzene is refluxed with anhydrous ferric chloride, a polyphenyl resin is formed[119]. Traces of water accelerate the reaction. Chlorobenzene is produced together with the polymer. Ferric chloride behaves as a catalyst of cationic polymerisation and as an oxidant:

$$H_2O + FeCl_3 \rightleftharpoons H^+ + Fe(OH)Cl_2 ,$$



A similar mechanism for the formation of polyphenyl from benzene has been suggested for the process in the presence of $MoCl_5$ and water[120] and in the presence of aluminium chloride, cupric chloride, and water. The polymer produced, parapolyphenyl, is thermally stable (up to 525°C) and has a high molecular weight.

REFERENCES

1. Dow Chemical Co., U.S.P. 1547725 (1925).
2. Dow Chemical Co., U.S.P. 1595299 (1926).
3. Federal Phosphorus Co., U.S.P. 1735327 (1929).
4. C.Bibb and H.Lucas, Ind.Eng.Chem., 21, 635 (1929).
5. I.G.Farbenindustrie, German P. 501467 (1930).
6. R.Fort and C.N.Hinshelwood, Proc.Roy.Soc., A127, 218 (1930).
7. E.W.Mardles, Trans.Faraday Soc., 27, 712 (1930).
8. Yu.S.Zalkind and A.Zolotarev, Zhur.Prikl.Khim., 6, 681 (1933).
9. J.H.Bergoine, Proc.Roy.Soc., A179, 539 (1940).
10. D.M.Newitt and J.H.Burgoyne, Proc.Roy.Soc., A153, 448 (1936).
11. W.I.Denton, H.G.Doherty, and R.H.Krieble, Ind.Eng. Chem., 42, 777 (1950).
12. R.A.Harman, U.S.P. 2382148 (1946); Chem.Abs., 40, 955 (1946).
13. F.Porter, U.S.P. 2392875 (1946); Chem.Abs., 40, 2470 (1946).
14. R.H.Krieble and W.I.Denton, U.S.P. 2415101 (1947); Chem.Abs., 41, 2751h (1947).
15. R.H.Krieble and W.I.Denton, U.S.P. 2440233, 2440234 (1948); Chem.Abs., 42, 6851a (1948).
16. C.H.Schlemsan, W.I.Denton, and R.B.Bishop, U.S.P. 2456597 (1949); Chem.Abs., 43, 1805e (1949).
17. G.G.Joris, U.S.P. 2546639, 2546640 (1951); Chem.Abs., 45, 9561e (1951).
18. Y.Hosaka, T.Naito, and Y.Urano, J.Chem.Soc.Japan, 57, 282 (1954).
19. Y.Hosaka, J.Chem.Soc.Japan, 57, 197 (1954).
20. Y.Hosaka, Y.Urano, and M.Yasumoto, J.Chem.Soc.Japan, 57, 375 (1954).
21. Chu Ju-Chin and D.F.Othmer, Ind.Eng.Chem., 45, 1266 (1953).
22. L.I.Avraamenko, I.I.Ioffe, and R.V.Lorentso, Dokl.Akad. Nauk SSSR, 66, 1111 (1949).
23. M.Donald and M.Darlington, Ind.Chemist, 34, 5 (1958).
24. G.L.Grigoryan, A.A.Mantashyan, and A.B.Nalbandyan, Arm.Khim.Zhur., 19, 140 (1966).
25. I.I.Ioffe and N.I.Shirokova, Vestnik Akad.Nauk SSSR, 11, 96 (1948).
26. I.I.Ioffe, Zhur.Fiz.Khim., 28, 772 (1954).
27. I.I.Ioffe, Ya.S.Levin, E.V.Sokolova, I.G.Kronich, and N.I.Shirokova, Zhur.Fiz.Khim., 28, 1386 (1954).
28. I.I.Ioffe, Ya.S.Levin, and I.G.Kronich, Zhur.Fiz.Khim., 28, 1395 (1954).
29. I.I.Ioffe, Zhur.Fiz.Khim., 28, 1555 (1954).
30. I.I.Ioffe, Symposium, "Voprosy Khimicheskoi Kinetiki, Kataliza i Reaktsionnoi Sposobnosti" (Problems of Chemical Kinetics, Catalysis, and Reactivity), Izd.Akad.Nauk SSSR, Moscow, 1955.
31. R.G.W.Norrish and G.W.Taylor, Proc.Roy.Soc., A234, 160 (1956).
32. K.Ono, T.Oyamada, and H.Katsuragi, J.Soc.Chem.Ind. Japan, 41, Suppl.binding, 209 (1938).
33. M.Merz and W.Waters, J.Chem.Soc., 2427 (1949).
34. J.Loeff, G.Stein, and J.Weiss, J.Chem.Soc., 2074 (1949).
35. G.Stein and J.Weiss, J.Chem.Soc., 3249 (1949).
36. J.Johnson, G.Stein, and J.Weiss, J.Chem.Soc., 3275 (1951).
37. J.H.Baxendale and J.Magee, Discuss.Faraday Soc., 14, 160 (1953).
38. C.M.Coppinger, J.Amer.Chem.Soc., 79, 2758 (1957).
39. R.Norman and G.K.Radda, Proc.Chem.Soc., 138 (1962).
40. J.A.Hamilton and J.P.Friedman, J.Amer.Chem.Soc., 85, 1008 (1963).
41. J.R.L.Smith and R.O.C.Norman, J.Chem.Soc., 2897 (1963).
42. N.Uri, Chem.Rev., 50, 375 (1952).
43. A.Haber and J.Weiss, Proc.Roy.Soc., A147, 332 (1934).
44. N.A.Vysotskaya, Zhur.Fiz.Khim., 38, 1688 (1964) [Russ.J. Phys.Chem., 922 (1964)].
45. W.T.Dixon and R.O.C.Norman, J.Chem.Soc., 2897 (1963).
46. J.H.Baxendale, M.G.Evans, and G.S.Park, Trans.Faraday Soc., 42, 155 (1946).
47. L.M.Dorfman, J.A.Taub, and R.E.Buhler, J.Chem.Phys., 36, 549 (1962).
48. H.Hotta, Bull.Chem.Soc.Japan, 40, 687 (1967).
49. H.Staudinger and V.Ulrich, Z.Naturforsch., 19b, H10, 877 (1964).
50. T.J.Sworski, J.Chem.Phys., 20, 1817 (1952).
51. J.H.Baxendale and J.Magee, Trans.Faraday Soc., 51, 205 (1955).
52. Yu.Yu.Lur'e, P.F.Kandzas, and A.A.Mokina, Zhur.Fiz. Khim., 36, 2616 (1962) [Russ.J.Phys.Chem., 1422 (1962)].

53. G.Stein and J.Weiss, J.Chem.Soc., 3245 (1949).
54. G.R.Freeman, A.B.van Cleave, and J.W.T.Spinks, Canad. J.Chem., 31, 448 (1953).
55. M.A.Proskurin and E.V.Barelko, "Sbornik Rabot po Radiatsionnoi Khimii" (Collected Papers on Radiation Chemistry), Izd.Akad.Nauk SSSR, Moscow, 1955, p.99.
56. J.H.Baxendale and D.Smithies, J.Chem.Phys., 33, 604 (1955).
57. P.V.Phung and M.Burton, Radiation Res., 7, 199 (1957).
58. M.A.Proskurin, E.V.Barelko, and L.I.Kartasheva, Dokl. Akad.Nauk SSSR, 121, 671 (1958).
59. M.A.Proskurin and Yu.M.Kolotyrkin, "Trudy Vtoroi Konferentsii po Mirnomu Ispol'zovaniyu Atomnoi Energii, Zheneva" (Proceedings of the Second Conference on Peaceful Uses of Atomic Energy, Geneva), 1958, Vol.29, p.52.
60. E.J.Henley, J.Goodman, and J.Tang, Trans.Amer.Nucl. Soc., 3, 287 (1960).
61. H.Hotta and A.Terakawa, Bull.Chem.Soc.Japan, 33, 335 (1960).
62. L.M.Dorfman, J.A.Taub, and R.E.Buhler, J.Chem.Phys., 36, 3051 (1962).
63. G.C.Christensen, Nukleonik, 8, 121–124 (1966).
64. L.I.Kartasheva and A.K.Pikaev, Khim.Vysokikh Energii, 1, No.1, 22 (1967).
65. G.Stein and J.Weiss, J.Chem.Soc., 3254 (1949).
66. G.Stein and J.Weiss, J.Chem.Soc., 3265 (1951).
67. J.Loeff and G.Stein, Nature, 184, 901 (1959).
68. J.H.Baxendale and D.Smithies, J.Chem.Soc., 779 (1959).
69. J.Loeff and G.Stein, J.Chem.Soc., 2623 (1963).
70. M.Daniels, G.Sholes, and J.Weiss, J.Chem.Soc., 832 (1956).
71. N.Siborovski, Rev.Prod.Chim., 66, 1305 (1963).
72. H.Hotta and N.Suruki, Bull.Chem.Soc.Japan, 36, 717 (1963).
73. H.Hotta, A.Terakawa, K.Shimada, and N.Suzuki, Bull. Chem.Soc.Japan, 36, 721 (1963).
74. H.Hotta, N.Suzuki, and A.Terakawa, Bull.Chem.Soc. Japan, 36, 1255 (1963).
75. N.Suzuki and H.Hotta, Bull.Chem.Soc.Japan, 37, 244 (1964).
76. K.Shimada, N.Suzuki, N.Itatani, and H.Hotta, Bull.Chem. Soc.Japan, 37, 1143 (1964).
77. H.Hotta, N.Suzuki, N.Itatani, and K.Shimada, Bull.Chem. Soc.Japan, 37, 1147 (1964).
78. H.Hotta, N.Suzuki, and T.Abe, Bull.Chem.Soc.Japan, 39, 417 (1966).
79. N.Suzuki, H.Hotta, and H.Hashimoto, Bull.Chem.Soc. Japan, 39, 422 (1966).
80. H.A.Schwarz, J.Phys.Chem., 66, 255 (1962).
81. C.Ferradini, Adv.Inorg.Chem.Radiochem., 3, 171 (1961).
82. W.G.Barb, J.H.Baxendale, P.George, and K.R.Hargrave, Trans.Faraday Soc., 47, 462 (1951).
83. J.H.Baxendale and C.Wells, Trans.Faraday Soc., 53, 800 (1957).
84. N.K.King and M.E.Winfield, J.Amer.Chem.Soc., 80, 2060 (1958).
85. A.V.Tobolski and R.B.Mesrobian, "Organic Peroxides", Interscience Publ., New York, 1954.
86. N.M.Emanuel' and E.T.Denisov, Dokl.Akad.Nauk SSSR, 117, 458 (1957).
87. E.T.Denisov and N.M.Emanuel', Zhur.Fiz.Khim., 32, 2374 (1958).
88. A.Terakawa, Y.Hosaki, M.Nitto, and T.Hirayama, J.Chem. Soc.Japan, Ind.Chem.Sect., 66, 1328 (1963).
89. D.I.Metelitsa and E.T.Denisov, Zhur.Fiz.Khim., 40, 2162 (1966) [Russ.J.Phys.Chem., 1165 (1966)].
90. D.I.Metelitsa, E.T.Denisov, and A.E.Semenchenko, Zhur. Fiz.Khim., 41, 1905 (1967) [Russ.J.Phys.Chem., 1020 (1967)].
91. D.I.Metelitsa, E.T.Denisov, and A.E.Semenchenko, Zhur. Fiz.Khim., 41, 2708 (1967) [Russ.J.Phys.Chem., 1463 (1967)].
92. D.I.Metelitsa and E.T.Denisov, Neftekhimiya, 7, 65 (1967).
93. D.I.Metelitsa and E.T.Denisov, Kinetika i Kataliz, in the press.
94. D.I.Metelitsa and E.T.Denisov, Zhur.Fiz.Khim., in the press.
95. J.W.Lamb and L.W.Elder, J.Amer.Chem.Soc., 53, 137 (1931).
96. J.W.McBain, J.Amer.Chem.Soc., 5, 623 (1901).
97. J.Weiss, Naturwiss., 23, 64 (1935).
98. A.M.Posner, Trans.Faraday Soc., 49, 382 (1953).
99. P.George, J.Chem.Soc., 4349 (1954).
100. J.Weiss, Experientia, 9, 61 (1953).
101. E.Abel, Monatsh., 85, 227 (1954).
102. M.Cher and N.Davidson, J.Amer.Chem.Soc., 77, 793 (1955).
103. F.E.Hufman and N.Davidson, J.Amer.Chem.Soc., 78, 4836 (1956).
104. W.T.Dixon and R.O.C.Norman, Proc.Chem.Soc., 97 (1963).
105. G.E.Adams, B.D.Michael, and E.J.Land, Nature, 211, 293 (1966).
106. E.J.Land and M.Ebert, Trans.Faraday Soc., 63, 1181 (1967).
107. G.E.Adams, J.W.Boag, J.Currant, and B.D.Michael, Pulse Radiolysis, Acad.Press, 1965, p.131.
108. M.Anbar, D.Meyerstein, and P.Neta, J.Phys.Chem., 70, 2660 (1966).
109. G.Dobson and L.J.Grossweiner, Trans.Faraday Soc., 61, 708 (1965).
110. H.I.Joschek and S.I.Miller, J.Amer.Chem.Soc., 88, 3273 (1966).
111. J.H.Simons and R.E.McArthur, Ind.Eng.Chem., 39, 364 (1947).
112. A.P.Lien, U.S.P. 2499515 (1950); Chem.Abs., 44, 5908 (1950).
113. J.H.Simons, U.S.P. 2530369 (1951); Chem.Abs., 45, 2979a (1951).
114. J.B.Braunworth, U.S.P. 2976329 (1961).
115. M.Osamu, F.Kotaro, and H.Hatiro, J.Chem.Soc.Japan, 67, 1141 (1964).
116. J.B.Braunworth and W.T.Winstead, U.S.P. 3033904 (1963); Chem.Abs., 57, 11107 (1963).
117. I.I.Ioffe, V.V.Suchkov, V.I.Sushchenya, and E.A.Migge, USSR P. 1769/15 (1966); Ref.Zhur.Khim., 4N167P (1967).
118. W.E.Loeb, U.S.P. 3033903 (1962).
119. P.Kovacic and C.Wu, J.Polymer Sci., 47, 45 (1960).
120. P.Kovacic and R.M.Lange, J.Org.Chem., 28, 968 (1963).

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