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REVIEW

On the mechanism of catalytic hydroxylation of aromatic hydrocarbons by hydrogen peroxide

E A Karakhanov,* S Yu Narin and A G Dedov
Petrochemistry and Organic Catalysis, Department of Chemistry, Moscow State University, Moscow, 119899, USSR

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1 INTRODUCTION

The catalytic hydroxylation of organic compounds by hydrogen peroxide has been studied by many researchers since this reaction was discovered by Fenton.[1-3] The search for new catalysts for the oxidation under mild conditions is still going on.[4-7] The hydroxylation of aromatic hydrocarbons is especially attracting attention.

However, in most cases the mechanism of catalytic oxidation of aromatic compounds to phenols and the nature of the hydroxylating moieties have not been discovered completely yet, and so the reports of different authors are rather contradictory.

In this connection the present review systematizes available literature data on the mechanism of catalytic hydroxylation of aromatic compounds by hydrogen peroxide under mild conditions. A more thorough consideration of the mechanism of hydroxylation will help to understand some reactions more profoundly. This will help to suggest further research for suitable catalysts for effective oxidation of different compounds under mild conditions (room temperature, atmospheric pressure, etc.). The catalytic systems known so far, e.g. Fenton's, Hamilton's, Udenfriend's, are nonactive—the reaction selectivity and the yield of the final products are not high. However, effective oxidation of aromatic compounds to the corresponding oxy derivatives is exhibited with a number of enzymes.[8-15]

The use of hydrogen peroxide as an oxidant is relevant to these reactions since it is a highly active and a non-wasteful reagent, which easily interacts with different media—homogeneous and heterogeneous, polar and non-polar.[17-19]

The study of the mechanism of oxidation by hydrogen peroxide is closely connected with the investigation of its catalytic and non-catalytic (radiation, thermal) decomposition, which leads to the formation of moieties active in hydroxylation. Since the decomposition of hydrogen peroxide has been studied very intensively and many publications have already dealt with the problem (see, e.g., Refs 17, 20–30), we will only dwell on some of the more general peculiarities of the decompositon of hydrogen peroxide which are necessary for the discussion of the mechanism of catalytic hydroxylation of aromatic compounds.

The mechanisms under review can be conventionally divided into three groups in accordance with the supposed nature of the hydroxylating moieties postulated in many papers by different authors, viz. free-radical, 'complex' and oxenoid.

2 FREE-RADICAL MECHANISMS

In most papers devoted to catalytic hydroxylation of aromatic compounds by hydrogen peroxide in a liquid phase, the authors adhere to a free-radical chain mechanism. Different radical species can act as the hydroxylating agent depending on the conditions of the reaction and the catalysts employed.

The first investigations on catalytic oxidation of aromatic compounds by hydrogen peroxide were carried out for the Fenton system, which was already known at the end of the nineteenth century.[1,2] The reagent used by Fenton was a solution of equimolar amounts of iron(II) sulfate

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* Author to whom correspondence should be addressed.

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($FeSO_4$) and hydrogen peroxide. According to most authors,[26,31–40] the species which is active in oxidation by Fenton's reagent in an aqueous medium is the hydroxyl radical, HO· Ruff's reagent, Iron(III)–hydrogen peroxide,[41] behaves similarly.

The mechanism of hydrogen peroxide decomposition in the Fenton system with the formation of the hydroxyl radical HO· was suggested by Haber and Weiss in 1934.[42] At present the following scheme of interaction of iron(II) with hydrogen peroxide in the absence of an organic compound is adopted (Eqns [1]–[7]).[5,18,20,24–26,29,33,43–48]

$$Fe^{2+} + H_2O_2 \xrightarrow{k_1} Fe^{3+} + HO^- + HO^{\cdot} \qquad [1]$$

$$Fe^{2+} + HO^{\cdot} \xrightarrow{k_2} Fe^{3+} + HO^- \qquad [2]$$

$$H_2O_2 + HO^{\cdot} \xrightarrow{k_3} H_2O + HO_2^{\cdot} \qquad [3]$$

$$Fe^{3+} + H_2O_2 \xrightarrow{k_4} Fe^{2+} + HO_2^{\cdot} + H^+ \qquad [4]$$

$$Fe^{3+} + HO_2^{\cdot} \xrightarrow{k_5} Fe^{2+} + O_2 + H^+ \qquad [5]$$

$$Fe^{2+} + HO_2^{\cdot} \xrightarrow{k_6} Fe^{3+} + HO_2^- \overset{H^+}{\rightleftarrows} H_2O_2 \qquad [6]$$

$$HO_2^{\cdot} + HO_2^{\cdot} \xrightarrow{k_7} H_2O_2 + O_2 \qquad [7]$$

Iron ions change their valence state during the reaction. The stationary concentration of iron(II) ions is considered to be very small. At nearly equal concentrations of iron(II) ions and hydrogen peroxide in acid media, reactions [1], [2], [3] and [6] take place, and the role of the processes [4], [5] and [7] is insignificant: at pH 2.1 and 25 °C, $k_1 = 76$ (Ref. 49) ($k_1 = 50$ according to Ref. 26), $k_2 = 2.6 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$ (Ref. 50), $k_3 = 3 \times 10^7$, $k_4 = 1.56 \times 10^{-3}\ dm^3\ mol^{-1}\ s^{-1}$ (Ref. 49), $k_5 = 3.3 \times 10^5$ (Ref. 48), $k_6 = 2.1 \times 10^{-6}\ dm^3\ mol^{-1}\ s^{-1}$ (Ref. 51). With excess of iron(II) ions reactions [1] and [2] are preferred; with excess of H_2O_2 reactions [1], [3] and [6] are favored.

It was established[29] that the mechanism of disproportionation of hydrogen peroxide involves cyclic ion-radicals in the system iron(II)–hydrogen peroxide, and in the presence of iron(III)–hydrogen peroxide it is a radical-chain process.

In acid media with sufficient iron(II) ion (the stoichiometry of the reaction is 2 mol of iron(II)/1 mol of hydrogen peroxide). Fenton's system is an effective source of active hydroxyl radicals (HO·). The mechanism of oxidation of different compounds by Fenton's reagent is usually explained by this classical scheme. As a rule, in the presence of an organic substrate, the slowing of the reaction and the decrease of the length of the chain takes place due to the interaction of hydroxyl radical with an organic compound.

The hydroxylation of different aromatic compounds by the iron(II)–hydrogen peroxide system and its analogs has been thoroughly studied. Thus, for example, the oxidation of benzene is described in Refs 31, 52–64, of naphthalene in Refs 65–67, of anisole in Refs 31, 61–63, 68–70, of fluorobenzene in Refs 61, 62, of phenol and its substitutes in Refs 52, 62, 70–74, of toluene in Refs 31, 54, 58, 60, 61, 63, 70, 75, of nitrobenzene in Ref. 53, of benzoic acid in Ref. 55, of phenylacetic acid in Refs 54, 76, 77 and of trimethoxybenzene in Ref. 78.

The first attempts to systematize the data on the oxidation of organic compounds by Fenton's reagent appeared at the end of the 1940s and the beginning of the 1950s.[52,56]

Merz and Waters[52,79] supposed that the interaction of hydroxyl radical with aromatic compounds goes via abstraction of a hydrogen atom according to the scheme below (called 'non-chain oxidation' by the authors) in Eqns [8]–[10]:

$$RC_6H_4H + HO^{\cdot} \rightarrow RC_6H_4^{\cdot} + H_2O \qquad [8]$$

$$RC_6H_4^{\cdot} + HO^{\cdot} \rightarrow RC_6H_4OH \qquad [9]$$

$$RC_6H_4^{\cdot} + RC_6H_4^{\cdot} \rightarrow RC_6H_4 - C_6H_4R \qquad [10]$$

In the same papers another variant of Eqn [9] is discussed (Eqn [9a]):

$$RC_6H_4^{\cdot} + H{-}OH \rightarrow RC_6H_4OH + H^{\cdot} \qquad [9a]$$

To support the scheme the authors[52,79] refer to the formation of phenol and biphenyl in the reaction.

However, Smith and Norman[58] did not find a primary deuterium isotope effect ($k_H/k_D = 1$) in the oxidation of hexadeuterobenzene by Fenton's reagent, which testifies to either the absence of hydrogen atom abstraction, or the fact that this abstraction does not influence the rate of the reaction. Later similar data were obtained in Ref. 60. The mechanism of non-chain hydroxylation suggested in Ref. 52 was considered doubtful due to the use of labeled oxygen.[74] It is necessary to point out that later Hotta[80] still showed a possibility for the reaction through abstraction of the hydrogen atom in the oxidation of a mixture of ordinary and deuterated benzene. However, this direction of the reaction is realized only at high temperatures and to a small extent.[48]

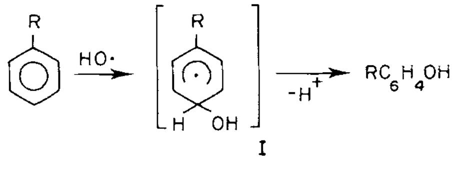
Merts and Waters[52,79] also suggest a chain mechanism of oxidation (Eqn [11]):

$$R\cdot + H_2O_2 \rightarrow ROH + HO\cdot \qquad [11]$$

But its non-applicability to aromatic compounds was shown both by the authors themselves and in later research by Baxendale and Magee in 1953.[56,81] Nevertheless, in 1962 new data were obtained,[74] again with the help of Merz and Waters.

It is important to stress that, when using the Fenton reagent, iron salts can be considered coreagents, and not catalysts, because they are used in amounts comparable with benzene and hydrogen peroxide (besides, this significantly limits the synthetic possibilities of the reaction).

At the beginning of the 1960s it was suggested[82–85] that the hydroxyl radical (HO·) attacks the aromatic ring, forming a new radical C_6H_6OH (radical **I**) (Eqn [12]).



[12]

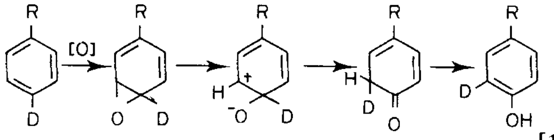
According to various authors[51,86–88] the limiting stage of the process is the generation of hydroxyl radicals in the interaction of iron(II) with hydrogen peroxide. The addition of hydroxyl to the benzene ring goes very quickly at a speed which is close to the speed of diffusion.[54,89] At 25°C, for example, the rate constants of the addition of the hydroxyl radical to benzene, nitrobenzene, chlorobenzene, anisole and phenol are $(3.4–5.1) \times 10^9$ (Ref. 87), $(2.0–2.7) \times 10^9$ (Ref. 90), $(4.0–4.5) \times 10^9$ (Ref. 83), $(4.5–5.2) \times 10^9$ (Ref. 82) and $(6.5–8.0) \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (Refs 91, 92), respectively.

In Refs 32, 54, 59, 61, 62, 93 and 94 the hydroxylation of benzene, fluorobenzene, anisole, some phenols and other compounds by the analogs of Fenton's reagent, copper(II)–hydrogen peroxide and titanium(III)–hydrogen peroxide ($[Ti(III)]_o \approx [H_2O_2]_o$) was investigated by ESR. Titanium(III) as compared to iron(II) can be used at a wider range of pH (0.5–11.0).[95] A mechanism also involving the addition of hydroxyl radical to a benzene ring was suggested.

The existence of the hydroxycyclohexadienyl radical (Radical I, Eqn 12) is obvious today.[49,77,84,94,96–98]. It was proved by pulse radiolysis in combination with flash-absorption spectroscopy;[83] the radical was detected in different conditions by ESR.[61,62,95,99,100] The absorption spectrum of this radical was obtained ($\lambda_{max} = 313$ nm).[90]

However, it should be noted that the adduct of the interaction of the hydroxyl radical with anisole was not detected.[62] Obviously, it is less stable than the one corresponding to benzene.[68]

The data on NIH shift[101] (NIH shift is the migration of hydrogen isotopes to neighboring positions in respect to that in which the hydroxylation occurs) also testify to the radical mechanism of the hydroxylation of aromatic rings by Fenton's reagent (showing small values of NIH shift characteristic of radical processes)[8,31,66,67,102] (Reaction [13]).

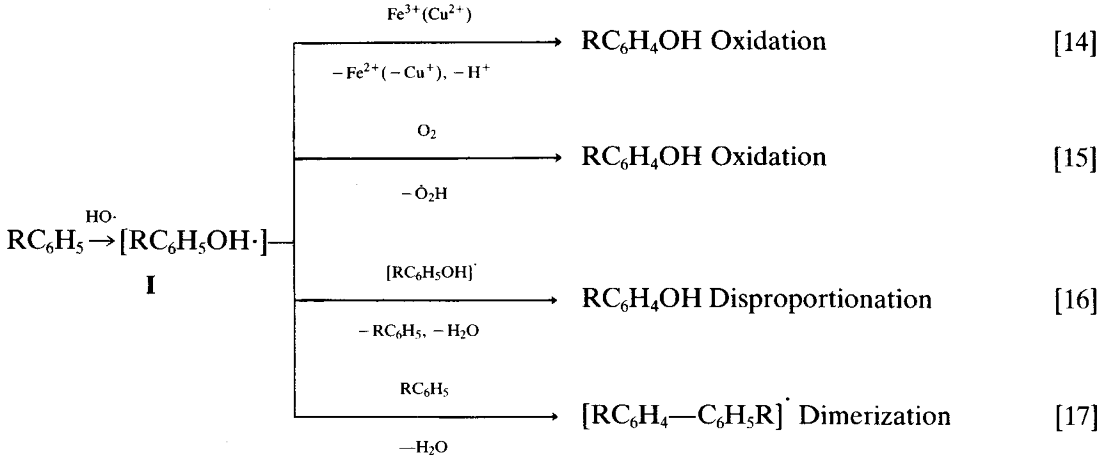


[13]

Thus, the data given above confirm that the first stage of the interaction of hydroxyl radicals with RC_6H_5 (where R is a substituent) is the addition of HO· to the aromatic ring to give a hydroxycyclohexadienyl radical $RC_6H_5\dot{O}H$ (**I**), which can then change in the directions indicated in Scheme 1.

The preferred way for formation of phenol in the absence of oxygen (e.g. in argon or nitrogen) is the oxidation of radical **I** by iron(III) ions or copper(II) ions (Eqn [14].[49,54,58,63,103] According to most authors,[32,49,54,63] copper(II) ions are more active and less selective oxidants of radical **I** than iron(III) ions. The existence of Reaction [14] is also proved by the experiments of Baxendale and Magee,[56] Merz and Waters,[81] and Walling and Johnson,[49,54] who noticed that increase in the concentration of iron(III) or copper(II) in the solution leads to an increase in the phenol yield. A chain mechanism was suggested (Scheme 2). This mechanism was later disputed.[74]

It is necessary to point out that the reaction mechanism with Fenton's reagent was mainly



$$RC_6H_5 \xrightarrow{HO\cdot} [RC_6H_5OH\cdot] \quad \mathbf{I}$$

$$\mathbf{I} \xrightarrow[-Fe^{2+}(-Cu^{+}),\ -H^{+}]{Fe^{3+}(Cu^{2+})} RC_6H_4OH \text{ Oxidation} \quad [14]$$

$$\mathbf{I} \xrightarrow[-\dot{O}_2H]{O_2} RC_6H_4OH \text{ Oxidation} \quad [15]$$

$$\mathbf{I} \xrightarrow[-RC_6H_5,\ -H_2O]{[RC_6H_5OH]^{\cdot}} RC_6H_4OH \text{ Disproportionation} \quad [16]$$

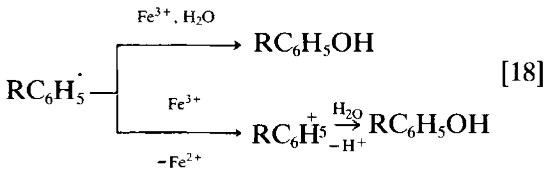
$$\mathbf{I} \xrightarrow[-H_2O]{RC_6H_5} [RC_6H_4\text{—}C_6H_5R]^{\cdot} \text{ Dimerization} \quad [17]$$

Scheme 1

studied for hydroxylations in nitrogen atmospheres.[49,63,77,83] The role of oxygen in this process was neglected. For the first time, Baxendale and Magee[56] (see also Merz and Waters[81]), in making up the material balance of the reaction, pointed out that the presence of oxygen in the system influences the composition of the products of oxidation. Later it was also stressed that the correlation of phenol isomers obtained in aromatic hydroxylations by Fenton's reagent depended on the presence of oxygen in the systems.[54]

In the presence of oxygen the disproportionation of two hydroxycyclohexadienyl radicals (Eqn [16]) is less probable because of their low concentration, steric hindrance and also a high value of the rate constant for interaction of radical **I** with air/oxygen: at 23°C this value is equal to $(5.0 \pm 0.6) \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$.[83] In the presence of oxygen, phenol is obtained according to Eqn [15] through the intermediate peroxy radical (see also Eqn [25]); the biphenyl compounds in this case are not detected in neutral media.[31,52,56,79]

According to several authors[49,54,58,63] the biphenyl yield (Eqn [17]) decreases dramatically with increase in oxygen content in the system, which is explained by a more rapid interaction of radical **I** with oxygen than with RC_6H_5.



$$R\dot{C}_6H_5 \xrightarrow{Fe^{3+},\ H_2O} RC_6H_5OH \quad [18]$$

$$R\dot{C}_6H_5 \xrightarrow[-Fe^{2+}]{Fe^{3+}} R\overset{+}{C}_6H_5 \xrightarrow[-H^{+}]{H_2O} RC_6H_5OH$$

Scheme 2

It was shown[59] that in reactions with labeled oxygen, nearly 5% of oxygen from the gas phase takes part in the formation of phenol. If the hydroxylation of benzene by Fenton's reagent is carried out in an inert gas atmosphere, oxygen from water can also take part in the reaction.

The role of atmospheric oxygen in the hydroxylation of benzene by Fenton's reagent is still a subject of thorough investigation.[96,98,104,105] It was shown[96] that, with the use of gaseous heavy oxygen, oxygen is used in the hydroxylation of benzene even with an excess of hydrogen peroxide in the system. Hydroxyl radicals have been generated by photochemical decomposition of azohydroperoxide in benzene solution in the presence of labeled oxygen, and the latter was found at up to 40% in phenol.[98] The incorporation of ^{18}O into aromatics was not observed[105] in pulse radiolysis of the aqueous solution of benzene, whilst its partial incorporation was noticed when using Fenton's reagent. In all of these cases a high level for incorporation of the oxygen isotope was observed in the presence of the reducing ion (or reagent) in the solution.[96]

As was mentioned above, in the system containing no oxidant (e.g. under pulse radiolysis of the aqueous solution of benzene), biphenyl is the major product. It can be obtained (Eqn [17]) in three ways,[14,49,106] the most probable of which is the slow addition of radical **I** to RC_6H_5 and further fast interaction with another radical (e.g. HO·) or oxidant (e.g. oxygen or iron(III)) to give water, $HO_2^{\cdot}$ and iron(II) + H^+, respectively.[107,108]

Table 1 The composition of hydroxylation products of substituted benzenes by Fenton's reagent[14, 63, 75]

Reaction[a]	Substance PhX	Reactive (PhX/PhH) · K	Phenols (%)		
			ortho	*meta*	*para*
1	$PhCH_3$	—	55.5	15.0	29.5
2	$PhCH_3$	—	71.0	5.0	24.0
3	$PhOCH_3$	6.35	81.0	0.5	18.0
4	$PhOCH_3$	—	84.0	—	16.0
5	$PhOCH_3$	—	88.0	—	12.0
6	PhCl	0.55	42.0	29.0	29.0
7	PhF	—	37.0	18.0	45.0
8	$PhNO_2$	0.4	24.0	30.0	46.0
9	$PhNO_2$	—	24.0	30.0	46.0

[a] Reaction conditions: 1,3, hydroxylation in nitrogen; 2, hydroxylation in air; 4,6–8, Fenton's reagent + ethylenediaminetetra-acetic acid (EDTA); 5, Fenton's reagent + ascorbic acid; 9, hydrogen peroxide + UV irradiation.

It should be stressed that the rate of the benzene oxidation can be inhibited at high concentrations of iron ions[109, 110] because at 25 °C ($k_2(Fe^{2+} + HO\cdot) = 2.6 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$,[50] and $k(HO\cdot + C_6H_6)/k_2 = 3.2$.[11]

Important information about the nature of the species attacking the aromatic ring can be derived from the isomer distribution of the reaction products, and from the activity of the interaction of benzene and its substituents with the hydroxylating species.[112] Substituted benzenes[75] can be ordered as follows:

$$PhOCH_3 : PhH : PhCl : PhNO_2 = 6.35 : 1 : 0.55 : 0.14 \qquad [19]$$

It is interesting to note that under irradiation of the reaction mixture and pulse radiolysis of water (numerous experiments showed that $HO\cdot$ and $HO_2^{\cdot}$ radicals are generated exclusively in the given systems; see for example Refs 21, 24, 113–116), this order is preserved, though the yield of the hydroxylaton products is small compared with the catalytic systems.[63]

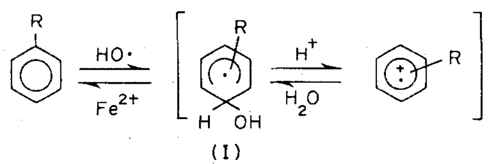
Hydroxyl radicals are considered to possess electrophilic properties.[17, 49, 54, 55, 57, 63, 65, 91, 100, 117–121] The electophilic nature of the hydroxyl radical is also proved by the isomer distribution of products from the hydroxylation of substituted benzenes (Table 1). Electron-acceptor substituents in aromatic rings decrease the rate of the reaction and increase the yield of *meta* isomers, while electron-donor substituents enhance the rate of radical hydroxylation and direct hydroxyl groups mainly to *ortho* and *para* positions.[55, 75, 122] The same effect has been observed for condensed aromatic compounds, e.g. naphthalene.[123] Besides, in the catalysis with copper(II) ions the yield of *meta* isomers is higher than when iron-containing catalysts are used.[54] However, it is necessary to point out that the nature of the isomer distribution of phenols is influenced by the conditions of the reaction.[124]

The negative value ρ in the Hammett equation[125] in the reaction of hydroxyl radicals, obtained by radiolysis of aqueous solutions of a number of substituted benzenes [−0.32 (Ref. 120); −0.41 (Ref. 91)], is also consistent with the electrophilic nature of hydroxyl radicals. The absolute value of ρ increases from a lesser to a more polar transition state with a stronger separation of charges.[123, 126]

The influence of the polarity of the substituents in free-radical processes has been thoroughly examined in a review article.[127]

Radical **I** (Eqn [20]) can undergo acid-catalyzed fragmentation, with pH in this case exerting a profound influence on the composition of the products of oxidation.[62, 77, 128] Thus, when studying [99, 129] the ESR spectra of radicals formed by pulse radiolysis of phenols and aniline aqueous solutions, at pH 1.0 the spectrum of the phenoxyl radical (PhO·, $\lambda_{max} = 400$ nm) was observed. The spectrum of *p*-benzoquinone was observed at pH 7.0; and radicals of the **I** type were detected at a pH from 1.0 to 6.5.

It was suggested[63, 77, 130] that in acid media, when there is a lack of oxidant, the reaction goes through a reversible acid-catalyzed dehydration and leads to the formation of a radical cation, which, in turn can reversibly reduce itself (Eqn [20]):

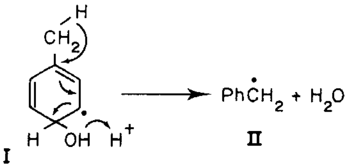


(I)

[20]

An analogous scheme involving intermediate formation of a π-complex was also suggested by Hamilton.[131] However, the radical cations in the hydroxylation of aromatic hydrocarbons were not detected,[123] and their existence for benzene and its derivatives is not thermodynamically advantageous.[49, 54, 132] Small values of NIH shift also testify to the fact that radical (not cation or radical cation) intermediates are more readily formed under these conditions.[31,133] Moreover, acid-catalyzed dehydration in the presence of such active oxidants of radical **I** as copper(II), iron(III), or oxygen, etc., is inhibited. It should be noted that such a mechanism (Eqn [20]) can be realized in the case of condensed hydrocarbons,[134,135] which are good donors of electrons due to low ionization energies.

It is interesting to point out that a change of pH preserves the distribution of isomer products, but the ratio of phenol and biphenyl derivatives changes.[63] For example, in the oxidation of toluene by Fenton's reagent[54,61] in acid media (pH 1.3), bibenzyl prevails among the reaction products in the absence of oxygen. But at pH 3.6 mostly cresols prevail, especially in the presence of copper(II). Most authors[31,54,62,129] consider that the formation of bibenzyl occurs because of the transformation of the corresponding cyclohexadienyl radical (**I**) into a benzyl radical (**II**) catalyzed by acid (Eqn [21]).



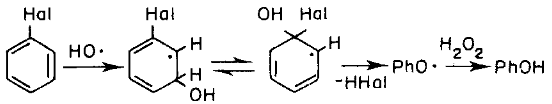
[21]

In the case of phenol[112,129,136] and phenylacetic acid[54,76] the fragmentation of radicals in acid media also takes place.

Acid-catalyzed fragmentation of radicals of the type **I** was detected by ESR spectroscopy in the oxidation by the Fenton's reagent analog titanium(III)–hydrogen peroxide.[61,62,94] At pH>1 the addition of hydroxyl radical to the aromatic ring was observed, and the spectrum of the phenoxy radical PhO· was noticed in more acid media.

Data on the hydroxylation of toluene by hydrogen peroxide under UV-irradiation[63] (the yield of cresols increases with pH), and data on the pulse radiolysis of phenol in an aqueous medium,[129] lead us to the assumption that the change in the composition of products is not connected with the nature of the metal ions used, and the fragmentation of cyclohexadienyl radicals catalyzed by acid is of a universal character. The use of labeled oxygen[86,87,132,137] supports this conclusion.

The fragmentation described above explains the formation of phenol in the oxidation of such compounds as chlorobenzene[120] and fluorobenzene[69,132] by Fenton's reagent (Eqn [22]).



[22]

where Hal = F, Cl.

However, increase of biphenyl ratios ([PhPh]//[PhOH]) among the products of the reaction under UV-irradiation of the system benzene–hydrogen peroxide with increase of pH[63] cannot be explained by acid fragmentation, because for this it is necessary to assume that in acid media most phenol is obtained via disproportionation, which is unlikely (see Eqn [16]) and would lead to a decrease in the yield of the products of hydroxylation of an aromatic nucleus.

If the acid-catalyzed fragmentation of radicals of the type **I** does not depend on the metal ions used in a system such as Fenton's, then these and other ions can be of substantial importance in oxidation. The addition of copper(II) to the classical Fenton system, as was mentioned above, increases the yield of phenols in the oxidaton of aromatic hydrocarbons, while the addition of fluoride ions decreases it.[54,57,63,119] The conclusion is drawn that copper(II) effectively oxidized organic radicals (see Eqn [14]), and fluoride ions connect iron(III) ions {and also oxidizing radicals of the type **I** to phenol} in a rather stable complex.[29] It is assumed elsewhere[54,103] that the reactions are conducted through copper-containing organic intermediates in the presence of copper ions.

The catalytic activity of iron chlorides and copper chlorides is weaker than the activity of their sulfates,[138,139] which is explained by the reaction:

$$Cl^- + HO\cdot \rightarrow Cl^\cdot + HO^- \qquad [23]$$

The rate constant of the reaction is $1.8 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$ at 25 °C and pH 2.0 and it grows with decrease of pH.[50] It is also known that the rate constant of interaction of hydroxyl radical with a benzene ring under these conditions is $4.3 \times 10^9\ dm^3 mol^{-1}\ s^{-1}$. Therefore, increase in temperature and decrease of pH can lead to competition between the two reactions in Eqns [23] and [12].

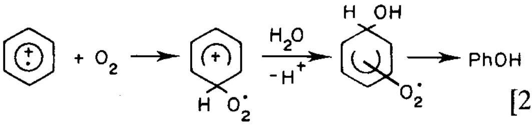
As has been shown,[31] hydroxylation of benzene, toluene and anisole by hydrogen peroxide in a solution of the substrate gives insignificant yields of products (the reaction was conducted both in heterogeneous and homogeneous benzene–acetonitrile systems). The replacement of iron(II) sulfate or iron(III) nitrate by its acetylacetonate analog and the addition of a phase-transfer catalyst to the solution did not give any noticeable positive effects. The authors explained the results obtained not by the absence of hydroxyl radicals in the system, but by their extinction after interaction with an acetylacetonate ligand or with the phase-transfer catalyst. However, this explanation seems disputable, as the concentration of the catalyst in the system is small and they would successfully compete for hydroxyl radicals in the system where a solvent is a substrate. Moreover, increase of activity of rathenium-containing catalysts was observed[140] in the presence of dodecyldimethylammonium bromide when alkylaromatic compounds were oxidized by hydrogen peroxide in substrate solutions under phase-transfer conditions. Yet in this case the oxidation only occured in the side chain.

A study of hydroxylation of trimethoxybenzenes by hydrogen peroxide in the presence of potassium hexacyanoferrate in acetic acid[78] brought the authors to an assumption, that the active species is either the hydroxyl radical, generated in the system, or peracetic acid. However, the oxidation is not only effective in the acid media, but also in acetonitrile and acetone, in which the formation of peracetic acid is unlikely.

Thus, general scheme for hydroxylation by Fenton's reagent can be presented as follows (Scheme 3, Eqn [24]).[96]

Most authors[83,96,98,105] attribute the appearance of labeled oxygen in phenol to the formation of a peroxy radical (Scheme 3, radical **III**), which can give phenol by liberating $HO_2^{\cdot}$ for further regeneration of hydrogen peroxide[141,142] (Scheme 3, route c_1, also called Dorfman's mechanism, is mainly characteristic for aqueous media). It is interesting to note that the rate of disproportionation of the $HO_2^{\cdot}$ radical decreases with increase of the polarity of the media.[143,144]

The high conversion of hydrogen peroxide, and at the same time low yields of the products of hydroxylation, can also be explained by the deactivation of the hydroxyl radical (Scheme 3, route c_5) and route c_4 through intermediate formation of radical cations,[96,104] which can interact with oxygen[145-147] (a parallel route of transformation of radical **I** into **III**, Eqn [25]).



[25]

However, as was pointed out,[123] the formation of a radical cation of benzene is disputable.

Another route of the transformation of peroxy radicals (Scheme 3, **III**) can be their disproportionation to give diol intermediates which are immediately dehydrated to give phenol[98] (route c_3 is typical for non-aqueous media). Almost quantitative introduction of the oxygen isotope into benzoquinone[96,104] proved that the latter is formed from radical **III** exclusively, and not by further oxidation of phenol.

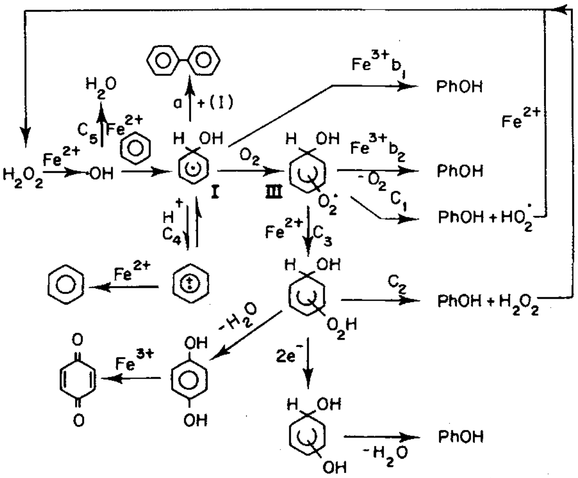
The direct oxidation of radical (Scheme 3, route b_1) is equivalent to step b_2 (see Scheme 3).

In a number of papers[14,72,148,149] a peroxy radical $HO_2^{\cdot}$ (not hydroxyl radical, HO·) is considered as a species attacking the aromatic ring. This peroxyl radical is less electrophilic than hydroxyl and gives an isomer distribution which is typical for radical substitution processes in the benzene ring. The ERS spectrum for $HO_2^{\cdot}$ is different from that for hydroxyl.

The systems generating $HO_2^{\cdot}$ radicals can be cerium(IV)–hydrogen peroxide and titanium-(III)–hydrogen peroxide (Eqns 26, 27).[150-152]

$$\mathrm{Ce(IV)} + H_2O_2 \rightarrow \mathrm{Ce(III)} + H^+ + HO_2^{\cdot} \quad [26]$$

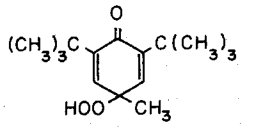
$$\mathrm{Ce(IV)} + HO_2^{\cdot} \rightarrow \mathrm{Ce(III)} + H^+ + O_2 \quad [27]$$



Scheme 3

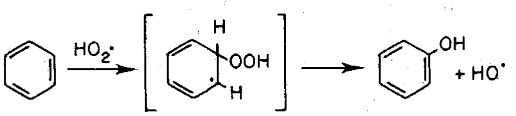
In the Haber–Weiss scheme for iron(II)–hydrogen peroxide, $HO_2^{\bullet}$ radicals can also be formed (see Eqns [3], [4] above).

However, the role of the $HO_2^{\bullet}$ radical in the hydroxylation of the aromatic nucleus is treated differently by different authors. Thus, it was considered that the $HO_2^{\bullet}$ radical is less active compared with hydroxyl[58, 88] whilst elsewhere it was shown[148] that the $HO_2^{\bullet}$ radical can quite effectively attack the benzene ring. To support this supposition, hydroperoxides (**IV**) were obtained in the oxidation of substituted phenols by hydrogen peroxide in the presence of iron(II) and iron(III).



IV

However, the authors pointed out[14] that at high temperatures a part of the substrate can be hydroxylated according to Eqn [28].



[28]

It is interesting to note that the $HO_2^{\bullet}$ radical in appropriate solvents can give a solvated cation of oxygen LO^+, exhibiting high selectivity in the reaction of oxidation of alkanes.[153, 154]

In the Fenton system in alkali media there can exist two more electrophilic particles, which are potentially capable of oxidizing the aromatic ring, viz. the hydroxyl radical in the dissociated form $O^{\dot{-}}$ (Eqn [29]), as well as the superoxide anion radical $O_2^{\dot{-}}$ (Eqns [29a], [29b]).[29, 48, 155, 156]

$$HO^{\bullet} + HO^- \rightleftarrows O^{\dot{-}} + H_2O \qquad [29]$$

$$HO_2^{\bullet} \rightleftarrows H^+ + O_2^{\dot{-}} \qquad [29a]$$

or

$$Fe(II) + O_2 \rightleftarrows Fe(III) + O_2^{\dot{-}} \qquad [29b]$$

However, it was shown[157] that the activity of the hydroxyl radical is substantially higher than the activity of the conjugated base.

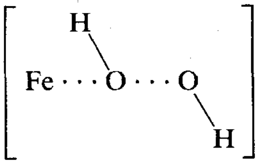
Thus, in the action of Fenton's reagent upon the aromatic ring, the active attacking particle is the hydroxyl radical, formed according to the Haber–Weiss scheme. This is proved by experimental data on the isomer distribution in the oxidation of the aromatic ring, the similarity in the action of the Fenton reagent and hydrogen peroxide–UV irradiation (by analogy with photodecomposition of azohydroperoxide) on the aromatic compounds, the order of reactivity of substituted benzenes, immediate fixation by ESR spectra, low reaction selectivity (unlike enzyme systems), and the initiation by the Fenton system of radical polymerization of acrylonitrile, methyl methacrylate, etc., in aqueous solutions and emulsions.[29, 41, 61, 88, 95, 127, 158]

3 MECHANISMS INVOLVING COMPLEXES

In the 1960s the first papers appeared in which intermediate metal complexes formed in the reaction (not free radicals) were regarded as active particles in hydroxylation. Conventionally, this mechanism can be called the 'complex' mechanism.

The investigation of the titanium(III)–hydrogen peroxide system by an ESR method[159–162] showed that ESR signals do not originate from hydroxyl or $HO_2^{\bullet}$ radicals, but from their complexes, stabilized by compounds of titanium(IV).

In the Baxendale and Magee scheme[56, 81] the possible existence of a complex such as



was also suggested, in which hydroxyl radicals remain bound to metal and act similarly to electrophilic hydroxylating species.

The authors,[74] using ^{18}O-enriched hydrogen peroxide, doubt the participation of free hydroxyl radicals in the hydroxylation of phenol and anthracene even in the presence of the Fenton reagent. Pyrocatechol produced in the reaction contained 95% of heavy oxygen in the newly formed second hydroxyl group. If an $H^{18}O\cdot$ radical from labeled hydrogen peroxide took part in the oxidation, then a light hydroxyl radical would come into pyrocatechol, because it exchanges oxygen with water easily.[163, 164] The authors explain this interesting phenomenon by the formation of hydroperoxide with its subsequent decomposition (Eqn 30):

$$R\cdot + H^{18}O_2^{\bullet} \rightarrow R^{18}O^{18}OH$$

$$\xrightarrow[-Fe(III),\,-^{18}OH^-]{Fe(II)} R^{18}O\cdot \xrightarrow[-Fe(III)]{Fe(II),\,H^+} R^{18}OH \qquad [30]$$

This supposition is doubtful as the stability of the primary hydroperoxides is low. In the case of benzene, for example, its hydroperoxide is not known and all attempts to synthesize it were unsuccessful.[158] Besides, the $HO_2^{\cdot}$ radical, as was pointed out above, is less reactive compared with hydroxyl.

Hamilton[69, 165–167] suggested an effective hydroxylating system, iron(III)–pyrocatechol (copper(II)–pyrocatechol), the catalytic qualities of which actively help to oxidize aromatic compounds. The rate of the process is very low without the addition of pyrocatechol, but at high concentrations of pyrocatechol inhibition of oxidation takes place. This is connected with the effective formation of iron-ion complexes with several molecules of pyrocatechol.[168] The hydroxylation is inhibited by ethylenediaminetetraacetic acid,[169] the carboxyl groups of which form stable complexes with iron ions.[170, 171] Hydroquinone also exhibits a catalytic activity, which is smaller than that of pyrocatechol,[166] whilst benzoquinone, phenol and ascorbic acid have either a small effect[172] or no effect at all.[69] (Norman and Smith[173] stated that penols and cresols act as catalysts in a similar system.)

The possible participation of oxygen in hydroxylation with the Hamilton system has been thoroughly studied. In Ref. 165 it is assumed that oxygen does not influence the rate of oxidation and the composition of the products. It is interesting to note that the use of the Hamilton system does not give dimerization products. However, it was established later[174] that phenol yields in the hydroxylation of benzene in the presence of iron(III)–lipophilic catechol are higher in nitrogen than in air.

It is considered[26] that the replacement of iron(II) by iron(III) does not change the activity of the system, because in the presence of hydrogen peroxide iron(II) is quickly oxidized to iron(III). However, as was shown,[29, 109, 175, 176] the initial rate of the catalytic decomposition of hydrogen peroxide (H_2O_2) and, consequently, the effective use of the oxidant depend on the initial state of iron salts and complexes: the rate of hydrogen peroxide decompositon is considerably higher in the presence of iron(II) than in the presence of iron(III).

The distribution of the phonol isomers formed, as well as the kinetics of hydroxylation by Hamilton's reagent, allowed the authors[69, 166] to propose a mechanism, in which the hydroxylating agent is a complex consisting of hydrogen peroxide, iron(II) and pyrocatechol (Scheme 4, Eqn [31]).

Apart from Hamilton, Norman and Smith[173] also drew the same conclusion about the participation of this complex in the reaction. The existence of a similar complex was proposed in Refs 177–181.

The proposed scheme (Scheme 4) includes the formation of intermediates from the oxidized forms of a catalyst; moreover, the latter must be reversibly oxidized in the catalytic cycle and give a fairly stable complex of Type **VI** (Scheme 4). The possibility of the existence of a large number of resonance forms makes **VI** more stable,[182, 183] whilst phenol gives an unstable complex **VI**.[184]

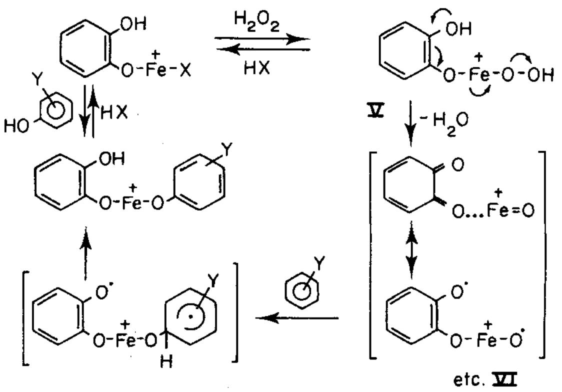
The rate of the whole process shown in Scheme 4 is limited by the formation of complexes **V** and **VI**.[69] Moreover, the latter acts non-selectively like a radical, giving a typical radical attack distribution of isomers. However, this distribution is slightly different from the one obtained for the Fenton system (Table 2).

It is also reported[166] that the hydroxylating species in Hamilton's system is electrophilic to a certain extent.

There are references to this system as one which models some features of the action of reduction–oxidation enzymes.[5, 185–187]

Hamilton's system is most effective in aqueous media, in organic solvents (ether, acetone) the reaction rate decreases.[69, 165]

It is pointed out[57, 119] that in the oxidation of phenol by hydroxyl radicals generated (in the first case) by Fenton's reagent, or by the action of X-rays on water (as a second case) the isomer distribution of products becomes different. Hydroxyl radicals obtained from the iron(II)–hydrogen peroxide system react with phenol to



Scheme 4

give pyrocatechol. After a while the composition of the catalytic system differs substantially from the Fenton's one and, according to the authors, becomes more similar to Hamilton's system.

There is an attempt[188] to describe Hamilton's system, and the phenomena which take place in it, on the basis of a free-radical mechanism: the interaction of pyrocatechol and iron(III) leads to the reduction of iron and the formation of the semiquinone radical as an intermediate product. However, intensive oxidation of the ligand only begins at pH 1.0–1.5, and in Hamilton's system at pH 3.5–4.0 almost all iron ions are in the form of a complex with pyrocatechol.[177] The use of compounds, containing a pyrocatechol fragment, e.g. tiron,[189] which are difficult to oxidize, facilitates the process of hydrogenation. Tiron is 4,5-dihydroxy-m-benzenedisulfonic acid.

Some authors observe that the hydroxylation of aromatic hydrocarbons is more effective when lipophilic (not hydrophilic) dioxybenzenes are used as a catalyst in Hamilton's system.[190–192]

The same effect would be expected when surfactants are used.

The activity of two-component catalytic systems, consisting of transition-metal ions and a number of surfactants, in hydroxylation of benzene by hydrogen peroxide in a homogeneous (water–acetonitrile) and heterophase (water–substrate) systems under mild conditions has been reported.[109, 193–199] A number of polymers, crown ethers, quarternary ammonium and sulfo salts are used as surfactants. Due to optimization of the process the authors[110, 200] obtained high yields of phenol (up to 80% per substrate) in the selective oxidation of benzene to phenol in the presence of ionic surfactants in a hetero system.

Various authors[174, 189, 190, 201] have recently reported an interesting, practical improvement of similar two-component catalytic systems: a heterogeneous catalyst (a complex of iron(III) with substituted catechols, on silica gel, as well as quinones[64] is used for the hydroxylation of benzene by hydrogen peroxide in a two-phase water–substrate system.

The study of the mechanism of benzene hydroxylation by various methods brought the authors[169, 202, 203] to the conclusion that in the presence of ionic surfactants and transition metal ions the reaction proceeds as a micellar catalysed process. The appearance of catalytic amounts of phenol and dioxybenzenes in the system leads to the formation of complexes with different forms of iron and can bring about the further active hydroxylation of the substrate.

A mechanism for the activation of the catalyst in the catalytic oxidation of phenol by hydrogen peroxide has been proposed recently.[73, 204, 205] This mechanism includes the formation of metal complexes first with hydrogen peroxide, then with the initial phenol and the products of its oxidation. The influence of the nature of the substituents, and of additions of metal salts and organic ligands on catalitic activity has been evaluated quantitatively. By analogy the formation of an active complex of hydroquinone with an iron-containing catalyst and hydrogen peroxide has been assumed.[206]

The hydroxylation of a number of phenols by hydrogen peroxide, catalyzed by copper, ruthenium and vanadium complexes, has been studied.[60, 207–210] The acrylonitrile test proved the absence of free radicals in the system.[210] A mechanism is proposed according to which metal ions, phenols and hydrogen peroxide form an active complex, analogous to an iron-containing one (see Scheme 4), which directs the hydroxylation of an aromatic nucleus mainly into an *ortho*

Table 2 Isomer distribution of hydroxylation products of aromatic compounds[75, 165]

		Distribution of isomers (%)					
		Hamilton's system			Fenton's system		
Reaction	Aromatic compound	*ortho*	*meta*	*para*	*ortho*	*meta*	*para*
1	Nitrobenzene	48	26	26	24	30	46
2	Chlorobenzene	45	15	40	42	29	29
3	Anisole	64	3	33	84	0	16

position in the case of copper complexes, and into a *para* position in the case of ruthenium complexes.

4 OXENOID MECHANISM

In 1954 Udenfriend[211,212] showed that aromatic compounds are hydroxylated by hydrogen peroxide (or oxygen) in the presence of iron(II) or iron(III), ascobic acid and/or EDTA at neutral pH. Copper(I) and copper(II) ions are not active in the system, as a rule. However, as is shown in Ref. 172, copper(II) is a more effective catalyst than iron(II).

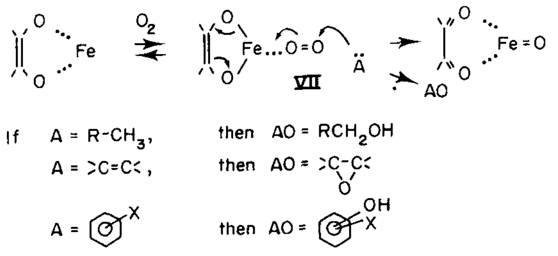
Udenfriend's system is considered to model some aspects of the action of enzymes, which led to further investigations.[9,10,75,213-220]

In the first experiments oxygen was used as an oxidant. Later on Udenfriend's system was reported to work effectively in the presence of hydrogen peroxide.[211]

It is assumed[221,222] that the hydroxylating particle in this system is the hydroxyl radical. However, the fact that besides hydroxylating aromatic compounds Udenfriend's reagent oxidizes aliphatic hydrocarbons and compounds with double bonds, as well as the absence of biphenyl derivatives among the products of oxidation[60] (and their isomer distribution[166,172,217,223]) do not suggest the participation of free radicals in the oxidation process.

It is shown[217,224] that in the presence of oxygen the hydroxylating agent is complex **VII** (Scheme 5) consisting of the ascorbic acid molecules, oxygen and iron(II) which is capable of transferring the singlet oxygen atom from the bound oxygen molecule on to the aromatic substrate, acting like an oxenoid (by analogy with a carbene) species FeO^{2+} (ferryl ion)[60,225] (Scheme 5).

The oxenoid mechanism presupposes the intrusion of the oxygen atom on to the C—H bond without the formation of intermediate free radical or ionic species[8,226] (an oxenoid particle behaves similarly to singlet oxygen). The role of iron ions in this system is to combine with the reducing agent and oxygen, giving the latter electrons in the transition state, which weakens the bonds between the atoms of oxygen in ferryl ion as compared with the molecule of oxygen.[14] At the same time in complex **VII** (Scheme 5) there evidently occurs a transition of the proton of ascorbic acid into the complex with oxygen and a transition of electrons through the iron ion, which leads to the oxidation of complexed ascorbate and the reduction of the oxygen atom, which is not transferred to the substrate. Another oxygen atom, possessing six electrons, is introduced into the substrate. Four-electron reduction of oxygen takes place, which is characteristic for enzyme processes. In the reaction the ascorbic acid, which is the donor of hydrogen, transfers into dehydroascobic acid.



Scheme 5

5-Methylphenazinium acid,[227] thiosalicylic acid,[228] hydrazobenzene[229] and the cathode of an electrochemical cell[3] can be used as reducing agents in similar systems.

The existence of the oxenoid species, which is able to transfer the oxygen atom on to the substrate, mostly according to the electrophilic mechanism, was first suggested in 1932 by Bray and Gorin,[230,231] who proposed a mechanism of hydrogen peroxide decompositon as an alternative to a free-radical mechanism (Eqns [33]–[36]).

$$Fe^{2+} + H_2O_2 \rightleftarrows FeO^{2+} + H_2O \qquad [33]$$

$$2Fe^{3+} + H_2O_2 \rightleftarrows Fe^{2+} + FeO^{2+} + H_2O \qquad [34]$$

$$FeO^{2+} + H_2O_2 \rightleftarrows Fe^{2+} + O_2 + H_2O \qquad [35]$$

or

$$FeO^{2+} + H_2O_2 \rightleftarrows HO\cdot + HO_2^{\cdot} + Fe^{2+} \qquad [36]$$

Oxenoid species can interact with the organic substrate (Eqn [37]).

$$FeO^{2+} + PhH \xrightarrow[-H^+]{} PhOFe^+ \xrightarrow{+H^+} PhOH + Fe^{2+} \qquad [37]$$

Later this mechanism was discussed many times[11,232-238] and other ways of oxenoid formation were suggested,[26,44,239] e.g.

$$Fe^{3+} + HO\cdot \rightarrow FeO^{2+} + H^+ \qquad [38]$$

However, its existence was not proved experimentally. To identify the active hydroxylating particle (hydroxyl radical or ferryl ion) has been very difficult so far. Thus, for example, Udenfriend's reagent, as has been mentioned above, acts similarly to an oxenoid particle, and its analog oxygen–$TiCl_3$–acetanilide, according to the authors,[149] generates $HO_2^{\cdot}$ radicals. As for the oxygen–Sn^{2+}–HPO_4^{2-} system, the $HO_2^{\cdot}$ radical cannot be considered an attacking particle, since the reagent does not only hydroxylate the aromatic ring, but also oxidized aliphatic substances.[14]

To define the active hydroxylating species is difficult, because its existence cannot always be interpreted consistently. Besides, the kinetics of both mechanisms are the same, and the presence of ferryl ion in the system does not exclude the presence of hydroxyl radicals, since FeO^{2+} quickly interacts with the molecules of water to give hydroxyl radicals:[29]

$$FeO^{2+} + H_2O \rightleftarrows HO^{\cdot} + Fe(OH)^{2+} \qquad [39]$$

Trapping methods turned out to be futile for the same reason.

However, there is some evidence, in that the stability of the oxenoid particle in non-protic media increase.[17] Thus, extraordinarily high values of the NIH shift observed in the hydroxylation of deuterated chlorobenzene and anisole by Fenton's reagent in acetonitrile[16,66,67] led the authors to the assumption that the oxenoid species take part in the reactions.

Moreover, FeO^{2+} can be present in biological non-aqueous systems and can be an active hydroxylating species in enzyme oxidation[238,240] as well as in the hydroxylation of aliphatic compounds and the epoxidation of olefins.[241–244]

However, oxenoid species are not always present in non-protic media. Thus, the oxidation of aromatic hydrocarbons by hydrogen peroxide in acetonitrile, acetic acid or acetone in the presence of iron(II) and iron(III) proceeds, according to the authors of Refs 16, 31 and 78, through the formation of hydroxyl radicals. But the possibility of the formation of ferryl ion in the systems studied was not rejected completely.[78] Hydrogen peroxide decomposition in a water–acetonitrile medium, catalyzed by iron ions, also led to the formation of a hydroxyl radical.[245]

The formal oxidation state of iron in oxenoid species is +4 [the iron(IV) ion is very stable in ligand substitutions]. The perferryl ion FeO_2^{2+} species is also described.[235,237] Kremer[28,238,245–249] assumed the existence of a FeO^{3+} species on which iron has the oxidation state [Fe(V)] (Eqn [40]).

Kremer and co-workers[249,250] showed that the amount of oxygen released in the catalytic decomposition of hydrogen peroxide, in the presence of an organic substrate and without it, cannot serve as a criterion to distinguish the mechanisms of aromatic nucleus hydroxylation, as was supposed.[251] They also gave an explanation of the results of Walling and Goosen[43] (the influence of the organic substrates upon hydrogen peroxide catalytic decomposition) on the basis of a complex, and not free-radical, scheme which was suggested by the authors themselves (Eqn [40]).

$$Fe^{3+} + HO_2^- \rightleftarrows Fe^{3+}HO_2^-$$

$$\xrightarrow[-OH^-]{} FeO^{3+} \xrightarrow[-O_2,\,-OH^-]{+HO_2^-} Fe^{3+} \qquad [40]$$

It should be also noted that the $Fe^{3+}HO_2^-$ complex (see Eqn [40]) can be subjected to one-electron reduction in acid media, giving the same ferryl ion, as a result:

$$Fe^{3+}HO_2^- + e^- \xrightarrow{H^+} FeO^{2+} + H_2O \qquad [41]$$

It should be mentioned that Chance (cited in Ref. 14) also showed the participation of the complex in which iron formally has the oxidation state +5 [Fe(V)], in the reaction of hydrogen peroxide with catalase.

Benzene oxidation in acetonitrile has recently shown[67,252] that the hydroxylating agent, behaving similarly to hydroxyl or $HO_2^{\cdot}$ radicals, is a complex of iron (ether FeO^{3+} or FeO^{2+}) with an aromatic nucleus. The latter is oxidized to phenol through a cyclohexadienyl cation.

Mimoun *et al.*[60] describes the formation of oxenoid analog–vanadium(V) peroxo complexes which are highly electrophilic, and exhibit high efficiency in aromatic hydroxylation. The NIH shift is 70% in the oxidation of toluene by this reagent. The complexes CuO^+,[253,254] and the dioxo complexes of molybdenum(VI),[255,256] are effective in the hydroxylation of benzene.

It should be noted that, whereas earlier the oxenoid mechanism was considered to be an alternative to the radical one,[230,231] but in the accumulation of data the majority of authors concluded that these two mechanisms complement each other.[14,17,25,257]

5 CONCLUSION

Analysis of the literature data on the mechanisms of catalytic hydroxylation of aromatic compounds by hydrogen peroxide in the liquid phase has shown that at present there are different opinions on the possible mechanisms of this process. The character of the attack on the benzoic ring may be radical, electrophilic or nucleophilic. The reaction can be simultaneously conducted in different ways. This depends on the initial state of the intermediate (ionic or radical), which, in turn, depends on the nature of the metal used, the composition and the nature of the surrounding ligand, the oxidant, the components ratio in the catalytic system, and the conditions of the reaction. All this makes study of catalytic systems for the hydroxylation of aromatic compounds under mild conditions and the mechanism of their activity on important areas for further work.

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