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Kinetics and mechanism of the oxidation of organic compounds with hydrogen peroxide

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ABSTRACT. The literature data on the kinetics and mechanism of the oxidation of organic compounds of various nature with hydrogen peroxide in aqueous solution have been analysed. A generalised kinetic scheme is described for the radical–chain decomposition of hydrogen peroxide in the presence of organic compounds for which a rate equation for the process has been found by the method of quasi-steady-state concentrations for long chains. Partial expressions have been obtained for the rate of oxidation of various organic compounds with hydrogen peroxide allowing for the nature of the organic compound.

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I. Introduction

Hydrogen peroxide is an available and effective oxidising agent and is widely used as a bleaching agent in the textile,[1] cellulose–paper industries[2] and in other fields.[3–5] Dilute solutions of hydrogen peroxide are used in medicine as an antiseptic and a disinfectant.[6,7] In addition H_2O_2 is used in the preparation of organic peroxides,[8] in the purification of effluent from substances oxidisable under mild conditions such as phenols,[9] and in the delignification of wood pulp.[10]

Hydrogen peroxide is a component of oxidation–reduction systems which are sources of free radicals in the initiation of free radical processes.[11]

Hydrogen peroxide is widely used as an initiator of radical polymerisation processes with unsaturated monomers[12] and also in the grafting of them to cellulose or its derivatives[13] and to water-soluble lignin preparations.[14] The efficiency of graft polymerisation and the extent of grafting are determined to a significant extent by the initiation stage which in fact is the reaction of hydrogen peroxide and its radicals with the initial polymer and with its macroradicals with subsequent interaction of the radicals obtained with the monomer.

Decomposition of hydrogen peroxide by radicals resulting on oxidation of certain oxygen-containing organic compounds (alcohols for example) with oxygen leads to further initiation of oxidation processes and co-oxidation of organic substances.[15]

Hydrogen peroxide often reacts with various types of organic compounds when used as an oxidising agent. Without a study in depth of the chemical mechanism of such practically important processes it is impossible to find optimum conditions for carrying them out, to effect target-directed control of them or to increase their efficiency.

II. Initiation of the oxidation of oxygen-containing organic compounds by hydrogen peroxide

Depending on conditions, the decomposition of hydrogen peroxide in aqueous media proceeds by a radical–chain or ion–molecule mechanism and by a heterogeneous catalytic mechanism on the reactor surface.[16–22] Hydrogen peroxide reacts with organic compounds in aqueous solution predominantly by a radical–chain mechanism which is indicated by the inhibition of such processes by unsaturated monomers and other acceptors of free radicals. Initiation with hydrogen peroxide of the radical–chain oxidation of oxygen-containing organic substances may occur by homolysis of H_2O_2 according to reaction (1) or by the direct interaction of hydrogen peroxide with the organic compound.[15]

$$H_2O_2 \rightarrow 2^{\cdot}OH, \qquad (1)$$

The energy of activation for the homolysis of H_2O_2 according to reaction (1) is close to the energy for the decomposition of the O–O bond in hydrogen peroxide (202 kJ mol^{-1}). In particular the energy of activation for the process in the gas phase at 470–540 °C, when decomposition of unimolecular H_2O_2 predominates, is in the range 170–210 kJ mol^{-1} which is close to the theoretical limit.[23] In an aqueous medium at fairly low temperatures it is significantly less, of the order of 84 kJ mol^{-1}.[21,24]

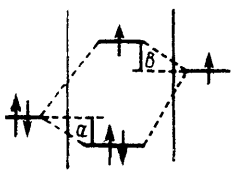
The reduction in the energy of activation may be explained by the formation of a complex of hydrogen peroxide with the solvent. The possibility of complex formation with the participation of hydroxyl-containing compounds has been shown.[24,25] If the H_2O_2 molecule participates in the formation of hydrogen bonds as a proton donor then the H–O and O–O bonds in it will be weakened, as was noted for hydroperoxides.[26]

In organic solvents capable of forming hydrogen bonds with H_2O_2 the decomposition of hydrogen peroxide with the formation of $^{\cdot}OH$ radicals is characterised by a reduced energy of activation

(84–105 kJ mol^{-1}) in comparison with the O–O bond energy in hydrogen peroxide.[27] This is explained by the interaction of H_2O_2 with hetero atoms of the solvent and by the formation of hydrogen bonds which generate favourable conditions for the interaction of electrons from the solvent (Solv) with the unbonded orbital of the radical arising on fission of H_2O_2. This leads to the formation of a complex.

$$\text{Solv...H—O—O—H...Solv} \rightarrow 2(\text{Solv...}^{\cdot}\text{OH}). \quad (2)$$

The energy level diagram for the complex between a hydroxyl radical and the electron-donating solvent is shown in Fig. 1. It is known that the splitting of energy levels on complex formation is greater the closer they are to one another, i.e. in the case in question the energy of complex formation grows with the increase in basicity of the solvent[28] and must increase in the series ketone–alcohol–water.



Solvent Complex Radical

Figure 1. Diagram of the energy levels of a complex between a radical and an electron-donating solvent.[27]

Several physicochemical investigations also show the formation of complexes of hydrogen peroxide with water. Liquidus diagrams for the system hydrogen peroxide–water indicate the presence of two eutectic points for the mixtures of ice–$H_2O_2.2H_2O$ and $H_2O_2.2H_2O$–solid hydrogen peroxide.[29] A deviation was established in such complexes for the atomic concentration (number of atoms per unit volume) from that calculated by the additivity rule.[30] A maximum is observed in the dielectric constant–composition isotherms for this $H_2O_2.2H_2O$ complex.[31]

At low concentrations of hydrogen peroxide in water the decomposition process is described by a kinetic equation which is first order with respect to H_2O_2.[10,25] When investigating the decomposition of concentrated solutions of hydrogen peroxide it was discovered that an increase in the water concentration in the system leads to a growth in the ratio of reaction rate to initial H_2O_2 concentration.[1] The order of the reaction with respect to water found from the data[1] proved to be 1.99 ± 0.41.[22] It was suggested[22] that the decomposition of H_2O_2 in water proceeds through the stage of forming the complex $H_2O_2.2H_2O$.

$$H_2O_2 + 2H_2O \underset{k_{-K}}{\overset{k_K}{\rightleftharpoons}} H_2O_2 \cdot 2H_2O, \quad (3)$$

$$H_2O_2 \cdot 2H_2O \xrightarrow{k_d} 2^{\cdot}OH \cdot H_2O. \quad (4)$$

The concentration of complex at steady-state-concentrations is

$$[H_2O_2 \cdot 2H_2O] = k_K (k_{-K} + k_d)^{-1} [H_2O_2][H_2O]^2. \quad (5)$$

From which it is possible to obtain an expression for the rate of decomposition of H_2O_2

$$w = k_K k_d (k_{-K} + k_d)^{-1} [H_2O_2][H_2O]^2, \quad (6)$$

which corresponds with the experimental data.[1]

The reduction in activation energy to 84 kJ mol^{-1} for the decomposition of hydrogen peroxide in aqueous solution may therefore be explained by the formation of a complex of H_2O_2 with water.

It may be shown that at low concentrations of hydrogen peroxide when $k_K (k_{-K} + k_d)^{-1} [H_2O]^2 \gg 1$, the position of the equilibrium is shifted practically completely to the side of forming the complex, so that $[H_2O_2.2H_2O]_0 = [H_2O_2]_0$ and the rate is practically equal to

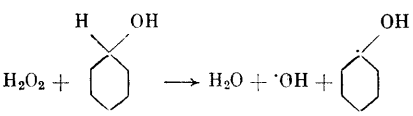
$$w = k_d [H_2O_2], \quad (7)$$

which corresponds with the experimental data.[22]

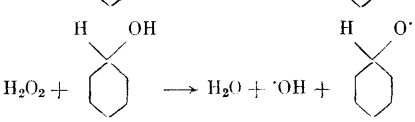
In the opinion of authors,[32] who studied the decomposition of H_2O_2 in cyclohexanol solution at 120–140 °C, the initiation of the oxidation of cyclohexanol with hydrogen peroxide may include the reactions given below:

$$H_2O_2 \rightarrow 2^{\cdot}OH \ (\Delta H = 210 \text{ kJ mol}^{-1}), \quad (8)$$

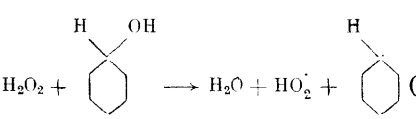
$$2H_2O_2 \rightarrow {}^{\cdot}OH + H_2O + HO_2^{\cdot} \ (\Delta H = 95 \text{ kJ mol}^{-1}), \quad (9)$$



$(\Delta H = 57 \text{ kJ mol}^{-1})$, (10)



$(\Delta H = 141 \text{ kJ mol}^{-1})$, (11)



$(\Delta H = 265 \text{ kJ mol}^{-1})$. (12)

The rate found experimentally for the initiation of the oxidation of cyclohexanol with hydrogen peroxide is described by the expression[32]

$$w_i = k_1 [H_2O_2] + k_2 [H_2O_2]^2, \quad (13)$$

where

$$k_1 = 8.9 \times 10^6 \exp(-98700/RT), \text{ sec}^{-1},$$

$$k_2 = 6.8 \times 10^9 \exp(-122000/RT), \text{ litre mol}^{-1} \text{ sec}^{-1}. \quad (14)$$

The initiation of the oxidation of propan-2-ol with hydrogen peroxide is represented[33] by a reaction of first order with respect to H_2O_2 with rate constant

$$k_1 = 1.1 \times 10^7 \exp(-96600/RT), \text{ sec}^{-1}. \quad (15)$$

Since

$$E_{act} \geqslant \Delta H, \quad (16)$$

for endothermic reactions, the second term in expression (13) may correspond to reaction (9). Consequently the first term in expression (13) may correspond to reactions (8), (10)–(12).

In the opinion of the investigators[32,33] the formation of radicals from H_2O_2 by unimolecular decomposition [reaction (8)] in a non-aqueous medium requires a significant consumption of energy (about 210 kJ mol^{-1}) and must proceed very slowly. The observed

activation energy for the initiation of oxidation of alcohols with hydrogen peroxide is significantly lower and is about 100 kJ mol^{-1}. The latter enabled the authors to propose that this reaction proceeds with the participation of alcohols [reactions (10)–(12)] disposed to form complexes with H_2O_2. However the heat of reaction for (11) and (12) is significantly greater than that of reaction (10) and approaches the heat of reaction for H_2O_2 homolysis. Consequently it was proposed[32] that radicals may be formed only by the bimolecular reaction (10). In addition a hypothesis has also been expressed[32,33] as to the possibility of carrying out a trimolecular reaction through the stage of complex formation.

$$H_2O_2 + 2ROH \rightleftharpoons ROH\ldots\underset{\underset{H}{|}}{O}\!\!-\!\!\underset{\underset{H}{|}}{O}\ldots HOR \longrightarrow 2H_2O + 2RO^{\cdot}. \quad (17)$$

Thermodynamic calculations[32,33] allowing for the stability of the O–H bond in the alcohol, the O–O in H_2O_2 and the H–O in water showed that

$$\Delta H = 2\times 428 + 210 - 2\times 495 = 76 \text{ kJ mol}^{-1}. \quad (17A)$$

It follows that reaction (17) is also energetically more advantageous than reactions (8), (9), (11) and (12) and the size of its heat of reaction relates to the experimentally found activation energy in accordance with expression (16).

In order to determine the reaction order with respect to alcohol for the initiation of oxidation of alcohols with hydrogen peroxide experiments were carried out using dilution of the reaction mixture with an inert solvent (chlorobenzene or decane).[32] However the results obtained, as calculated by the investigators, did not permit an unequivocal answer to the problem posed, since the dilution of the reaction mixture over wide limits (2–10 times) caused practically no change in reaction rate. This may be explained by the fact that in non-polar solvents, in which the solubility of hydrogen peroxide is insignificant, the latter is in the form of associates with cyclohexanol.

Investigation of the kinetics of the decomposition of hydrogen peroxide in an aqueous solution of phenol[25] at 115–160 °C showed that the initiation reaction rate was

$$w_i = k_1 [H_2O_2] + k_2 [H_2O_2][C_6H_5OH], \quad (18)$$

where

$$k_1 = 7.1\times 10^8 \exp(-99500/RT), \text{ sec}^{-1},$$

$$k_2 = 7.3\times 10^{10} \exp(-111000/RT), \text{ litre mol}^{-1} \text{ sec}^{-1}. \quad (18A)$$

The proportionality of the reaction rate in the first step to the concentrations of both peroxide and of phenol at an excess of the latter enabled the suggestion,[25] that initiation of the reaction of hydrogen peroxide and phenol is predominantly a bimolecular reaction.

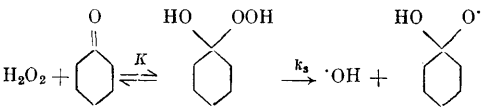
$$H_2O_2 + C_6H_5OH \rightarrow {}^{\cdot}OH + H_2O + C_6H_5O^{\cdot}. \quad (19)$$

It may be proposed that this reaction also includes a complex-forming step.

A thermodynamic calculation of the heat of reaction allowing for the bond stability in phenol (336 kJ mol^{-1}) led[25] to a value of ΔH = 50 kJ mol^{-1}, which according to (16) is in satisfactory agreement with the value of the activation energy found experimentally.

A feature of the decomposition of hydrogen peroxide in alcohols in the presence of ketones, in particular for cyclohexanol in the presence of cyclohexanone,[34] is the ability of the latter to form peroxides and hydroperoxides with H_2O_2 and consequently the initiation of oxidation may be described by the reactions

$$2ROH \ldots H_2O_2 \xrightarrow{k_1} 2RO^{\cdot} + 2H_2O, \quad (20)$$



(21)

The initiation rate of the process in this case is[34]

$$w_i = k_1 [H_2O_2] + k_3 [R(OOH)OH]. \quad (22)$$

The authors[34] noted that the rate of the unimolecular decomposition of the resulting hydroperoxide significntly exceeds the decomposition rate of hydrogen peroxide. Considering that the concentration of cyclohexanone hydroperoxide is proportional to the concentration of both hydrogen peroxide and of cyclohexanone

$$[R(OOH)OH] = K [H_2O_2] [R{=}O], \quad (23)$$

and the experimentally found overall initiation rate is proportional to the concentration of active oxygen, then the apparent rate constant for initiation may be described by

$$k_i = \frac{w_i}{[H_2O_2] + [R(OOH)OH]} = \frac{k_1 + k_3 K [R{=}O]}{1 + K [R{=}O]} \quad (24)$$

This permitted experimental determination of the rate constants of the individual reactions

$$k_1 = 8.9\times 10^6 \exp(-98700/RT), \text{ s}^{-1},$$

$$k_3 = 2.2\times 10^4 \exp(-68000/RT), \text{ s}^{-1}, \quad (24A)$$

and the equilibrium constant

$$K = 2.2\times 10^{-5} \exp(28100/RT), \text{ litre mol}^{-1}. \quad (24B)$$

The formation of acetone hydroperoxide on reaction of hydrogen peroxide with acetone has been observed.[35] At an acetone:H_2O_2 ratio <0.07 the hydroperoxides $(CH_3)_2C(OH)OOH$ and $(CH_3)_2C(OOH)_2$ were mainly formed but a further increase of this ratio as a result of interaction of hydroperoxides led to the appearance of peroxide $HOOC(CH_3)_2OOC(CH_3)_2OOH$ as a product.

Aliphatic acids are also inclined to form hydroperoxides. The reaction forming peroxyacids from hydrogen peroxide and acids is first order with respect to both components.[36–39] It is necessary to record that the reaction is reversible. For example the rate constant for the direct reaction of H_2O_2 with formic acid at 20 °C is 2.1 × 10^{-4} litre mol^{-1} s^{-1} and for the reverse 2.4 × 10^{-4} litre mol^{-1} s^{-1}.[36]

It has been recorded that sulphuric acid catalyses the formation of peroxyacids.[38] A study of the reaction of hydrogen peroxide with several aliphatic acids showed that the the reaction rate is determined mainly by the length and structure of the hydrocarbon radical of the acid. Comparison of the kinetics of forming mono-, di- and trichloroperoxyacetic acids[39] indicated that the reaction rate constants increased with the increase in the number of chlorine atoms in the acid molecule.

It may be concluded from the above that the activation energy for the decomposition of hydrogen peroxide in the presence of water and of hydroxyl-containing organic compounds may be significantly lower than the energy for fission of the O–O bond in hydrogen peroxide because of the formation of a complex between H_2O_2 and the hydroxyl-containing compound. The reduction of the activation

energy for hydrogen peroxide decomposition in the presence of ketones is explained by the formation of organic peroxides and hydroperoxides.

III. Interaction of hydroxyl radicals with organic substances

On oxidation of organic substances with hydrogen peroxide by a radical mechanism an important role is played by their reaction with hydroxyl radicals. Reaction may occur either through addition of ·OH radicals at a multiple bond or by direct abstraction of a labile hydrogen atom from the organic substance with the formation of a molecule of water or as a result of 'adhesion' of the hydroxyl radical to the aromatic ring. In particular the initiation by ·OH radicals of the polymerisation of unsaturated monomers has been fairly well studied. This includes the addition of hydroxyl radicals to substances containing double bonds.[12]

The addition of hydroxyl radical to benzene and some of its derivatives is also possible,[40–43] as a result of which hydroxy derivatives of cyclohexadiene are formed. The course of hydroxylation of benzene, its halogen derivatives and phenol was shown in a study[40] of the IR spectra of the radicals obtained in aqueous organic media under the action of a pulse of electrons.

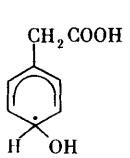
The reaction of benzene and its derivatives with hydroxyl radicals occurs by addition of the latter to the aromatic ring with a rate constant of 4.3×10^9 litre mol^{-1} s^{-1} (at 23 °C). In the presence of oxygen of the air, the nascent radicals add oxygen with the formation of peroxy radicals which in turn decompose into phenol or its derivatives and $HO_2^{\cdot}$ radicals.[40]

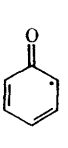
In view of the high reactivity of ·OH radicals displayed on direct addition of them to the aromatic ring of benzene and its derivatives, the rate constants of these reactions may be expected to be close to one another.[41] In reality the rate constants for the addition of hydroxyl radicals to benzene, toluene and benzoic acid at 25 °C lie within a fairly narrow range (2.1 to 3.3) $\times 10^9$ litre mol^{-1} s^{-1}.

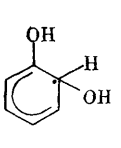
Rate constants for the addition of hydroxyl radicals to several benzene derivatives have been measured[42] and it was shown that they are reduced on going from amino and hydroxy substituted derivatives to nitro and sulphonate derivatives.

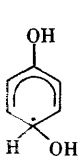
The interaction of hydroxyl radicals with phenylacetic acid[44] leads, according to ESR data, to the formation of radical (I). In acidic medium (I) decomposes with the formation of carbon dioxide, water and the benzyl radical.

The addition of hydroxyl radicals to phenol leads to the formation of various products depending on the solution pH.[43] Radicals (II) are formed in acid solution at pH ≈ 1. An increase of pH to 3.9–7 leads to the appearance of hydroxycyclodienyl radicals (III) and (IV) which are ionised in alkaline solution.

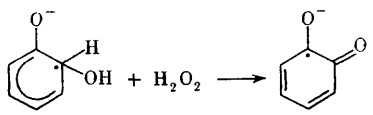

(I)


(II)

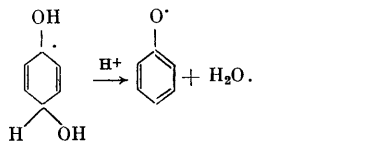

(III)


(IV)

Under the action of hydrogen peroxide the latter are oxidised by the following reaction.[43]

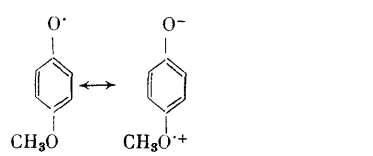

(25)

It was proposed[43] that on interaction of phenol with ·OH radicals in acid media, phenoxyl radicals arise as a result of the elimination of water from the resulting hydroxy-cyclodienyl radicals by the following reaction.

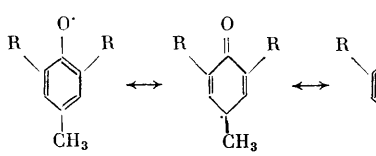

(26)

A broad review of the methods of preparation, structure and isomerisation of phenoxyl radicals resulting on reaction of phenol and its derivatives with hydroxyl radicals has appeared.[45] It was shown that the electron density in phenoxyl radicals is distributed over the aromatic ring and substituent atoms. In phenoxyl radicals the carbon atoms of the ring and the substituent atoms in the *ortho* and *para* positions may be reaction centres in addition to the phenoxyl oxygen.

Study of the ESR spectra of several phenoxyl radicals has enabled their hyperfine structure to be analysed and splitting constants have been found for ring protons and nuclear substituents. Methoxyl and some other similar groups reduce the splitting constants for the ring protons particularly in the *ortho* position to a far greater extent than alkyl groups. This implies that a significant portion of the electron density of such radicals is located on the two oxygen atoms.


(27)

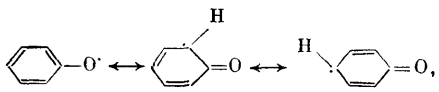
Introduction of a deuterium isotopic label into the hydroxyl group[47] and into the *p*-methyl group of ionol[48] enabled rearrangement of phenoxyl radicals containing a methyl group in the *para* position to benzyl radicals (R = t-C_4H_9) to be demonstrated with rearrangement of hydrogen from the *p*-methyl group to oxygen.


(28)

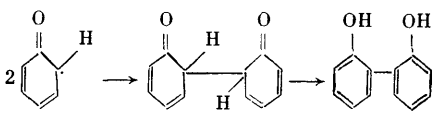
The possibility of such a rearrangement was also confirmed by ESR spectroscopic investigations of the kinetics of the consumption of *p*-alkylphenoxyl radicals.[45]

The dimerisation of phenoxyl radicals on oxidative oligomerisation of phenol is also accompanied by migration of a proton.[49] According to IR spectroscopic data phenolic structural units linked by C–C bonds in the *ortho* and *para* positions are found in the resulting oligomer. The process occurs stepwise by dimerisation of

phenoxyl radicals with subsequent enolisation according to the following scheme.

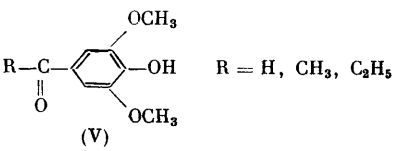


(29)



(30)

Compounds of type (V)



(V)

give stable phenoxyl radicals with an average half-life of about 5 h. In the case of vanillin and its derivatives no ESR signals or only weak ESR signals were observed.[50] The stability of phenoxyl radicals of the syringyl series is explained, in the opinion of the authors,[50] by the presence of two *ortho* substituents and a CO group in the *para* position (in vanillin there is only one *o*-methoxy group). Stable phenoxyl radicals are slowly converted into red products, probably *o*-quinones.

Hammett's rule, which describes the relationship of reaction rate constants to the type of substituent (Figs. 2 and 3), is obeyed in addition reactions of hydroxyl radicals to various derivatives of benzene and benzoate ion. The size of the reaction constant ρ is close to −0.4 which shows the electrophilic character of the ·OH radical in these reactions.[42]

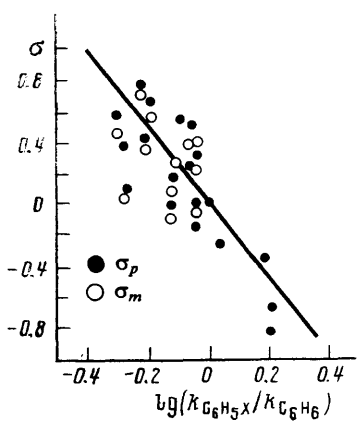


Figure 2. Relationship between the logarithm of the relative rate constant for the reaction of hydroxyl radical and a substituted benzene and the Hammett constant for the substituent.[42]

The reaction of ·OH with aldehydes has been investigated.[51] The interaction of hydroxyl radicals with acrolein and methacrolein occurs by addition of ·OH at the double bond, while reaction with crotonaldehyde includes abstraction of a hydrogen atom from the methyl group.

The kinetics of the consumption of hydroxymethyl radicals formed by reaction of methanol with ·OH radicals obtained by photolysis of hydrogen peroxide has been studied by ESR.[52] The following scheme was proposed for the process:

$$H_2O_2 \xrightarrow{h\nu} 2{}^{\cdot}OH, \quad (31)$$

$${}^{\cdot}OH + CH_3OH \rightarrow {}^{\cdot}CH_2OH + H_2O, \quad (32)$$

$$2{}^{\cdot}OH \rightarrow H_2O_2, \quad (33)$$

$${}^{\cdot}OH + {}^{\cdot}CH_2OH \rightarrow CH_2(OH)_2, \quad (34)$$

$$2{}^{\cdot}CH_2OH \rightarrow HOCH_2CH_2OH. \quad (35)$$

The rate constant for reaction (35), equal to 3.5×10^8 litre mol^{-1} s^{-1} was measured by flash photolysis and recording of the kinetics of the decrease in the ESR signal.[53] The rate constants for reactions (33) and (34) were found to be 1.5×10^8 and 2.8×10^8 litre mol^{-1} s^{-1} respectively (at 213 K). The rate constant for reaction (32) was 8.4×10^8 litre mol^{-1} s^{-1}.

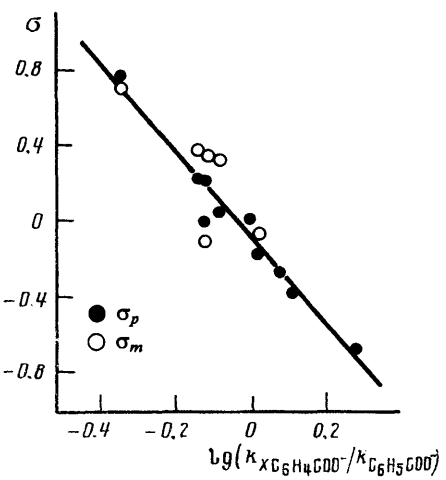


Figure 3. Relationship between the logarithm of the relative rate constant for the reaction of hydroxyl radical and a substituted benzoate ion and the Hammett constant for the substituent.[42]

The structure of the radicals resulting from the reaction of organic acids and ethers with hydroxyl radicals has also been investigated by ESR.[54] In the reaction between ·OH radicals and aliphatic acids and their halogen and hydroxy derivatives, removal of a hydrogen atom is mainly observed with the formation of a radical with the unpaired electron on the carbon atom in the α-position to the carboxyl group. However in the case of formic and malonic acids removal of a hydrogen atom from the carboxyl group occurs. The reaction is accompanied by decarboxylation in the latter case. Acids containing double bonds, such as maleic and methacrylic, add hydroxyl radicals at the multiple bond with the formation of a radical with an unpaired electron on the adjoining carbon atom. When reacting ethers with hydroxyl radicals, radicals are mainly formed with an unpaired electron on the α-carbon atom in relation to oxygen.

Analysis of the reaction between alcohols and ·OH radicals[55] showed that reaction (36) only occurred to a small extent. Process (37) predominates (more than 90%) for methanol, ethanol and propan-2-ol. Reaction (38) is also possible for *n*-propanol, *n*-butanol and isobutanol.

$$R_2CH{-}CH(R'){-}OH + {}^{\cdot}OH \begin{cases} \longrightarrow R_2\dot{C}H{-}CH(R'){-}O^{\cdot} & (36) \\ \longrightarrow R_2CH{-}\dot{C}(R'){-}OH & (37) \\ \longrightarrow R_2\dot{C}{-}CH(R'){-}OH & (38) \end{cases}$$

Several rate constants have been found for the removal of a hydrogen atom from aliphatic compounds by hydroxyl radicals.[56] When reacting ·OH radicals with aliphatic acids the reaction rate constant increases with the increase in the number of hydrogen atoms in the acid molecule. This constant may be calculated by the additivity rule for partial activities of hydrogen atoms in various positions in relation to the carboxyl group. The contributions to the reaction rate constant of H atoms in the α-position to the carboxyl group of CH_3COO^-, RCH_2COO^- and R_2CHCOO^-, are 0.14×10^8, 1.75×10^8 and 5.3×10^8 litre mol^{-1} s^{-1} (per atom) respectively and the contributions of H atoms of CH_3R, RCH_2R and R_2CHR groups in other positions are 0.36×10^8, 3.0×10^8 and 8.4×10^8 litre mol^{-1} s^{-1} (per atom) respectively. It is necessary to note that cyclic carboxyl-containing compounds are less reactive than the corresponding acyclic compounds.

Alcohols possess greater reactivity than acids when reaction with ·OH radicals, however the character of the relationship of reaction rate constant to hydrocarbon chain length is preserved.[56] The partial contributions of the activity of hydrogen atoms in the α-positions of CH_3OH, RCH_2OH and R_2CHOH groups are 1.8×10^8, 5.0×10^8 and 8.8×10^8 litre mol^{-1} s^{-1} respectively. An increase in the number of hydroxyl groups in the alcohol molecule leads to a reduction in reaction rate which is explained by hydration of the alcohol.

The reaction rate constants measured for the reaction of hydroxyl radicals with ethers[56] were, in contrast to the constants given in study,[57] somewhat lower than the reaction rate constants for the corresponding alcohols.[56] The partial activities of hydrogen atoms in the α-position of CH_3OR, RCH_2OR, $(RO)_2CH_2$, $(RO)_2CHR$ and $ROCR_2CH_2OH$ groups are 0.6×10^8, 1.4×10^8, 0.5×10^8, 0.9×10^8 and 1.65×10^8 litre mol^{-1} s^{-1} respectively. A good correlation was also recorded between the rate constants for the reaction of hydroxyl radicals with the aliphatic compounds investigated and the Hammett constants for substituents. The value for the ρ factor was −0.96, i.e. the ·OH radical attacks the aliphatic compound as an electrophilic reagent.

The reaction of aliphatic compounds of various classes with ·OH radicals obtained on radiolysis of water by ^{60}Co has been studied and a series of rate constants for these reactions has been found.[57] In particular it was established that the additivity rule for the contributions of CH_2 groups of the compounds investigated to the reaction rate constant was fulfilled only for a fairly small group of substances containing up to 4–6 carbon atoms. On further increasing the hydrocarbon chain length the growth in reaction rate constant slowed (Fig. 4). A significant increase in rate constant was also recorded for the reaction of hydroxyl radicals with amines and carboxylic acids depending on the increase in pH, the greatest values being achieved in the region of the pK_a of the acid. Evidently this confirms that carboxylate radicals (and not radicals with an unpaired electron on adjacent carbon atoms) are formed predominantly by the reaction of hydroxyl radicals according to the reaction

$$RCOO^- + {}^{\cdot}OH = RCOO^{\cdot} + OH^-, \quad (39)$$

and the one-electron oxidation of the carboxylate ion of a salt to the corresponding carboxyl radical occurs more readily than removal of a hydrogen atom from the carboxyl group of the corresponding carboxylic acid.

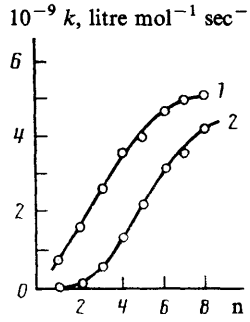


Figure 4. Relationship of the rate constants for the reaction of hydroxyl radicals with *1*, aliphatic alcohols and *2*, dicarboxylic acids to the number of atoms in the hydrocarbon chain.[57]

IV. Decomposition of hydrogen peroxide in the presence of oxygen-containing aliphatic compounds

Study of the kinetics of the oxidation of organic compounds with hydrogen peroxide using ESR showed that decomposition of hydrogen peroxide by radicals of organic compounds is observed in addition to the formation of radicals of organic substances by reaction with hydroxyl radicals (see section III) and recombination of the radicals under specific conditions.

Two types of radicals (VI) and (VII) were detected when investigating the kinetics of oxidation of dimethoxymethane with the system hydrogen peroxide–titanium(III) using ESR spectroscopy.[58]

$$Ti(III) + H_2O_2 \rightarrow Ti(IV) + OH^- + {}^{\cdot}OH, \quad (40)$$

$${}^{\cdot}OH + CH_3OCH_2OCH_3 \rightarrow \underset{(VI)}{{}^{\cdot}CH_2OCH_2OCH_3} + H_2O, \quad (41)$$

$${}^{\cdot}OH + CH_3OCH_2OCH_3 \rightarrow \underset{(VII)}{CH_3O\dot{C}HOCH_3} + H_2O. \quad (42)$$

The change of radical concentration with time showed that the order of the reaction with respect to radicals was close to $^3/_2$. Rate constants for the consumption of radicals (VI) and (VII) calculated from the Arrhenius equation were respectively

$$k_1 = 4 \times 10^{14} \exp(-61800/RT) \text{ litre}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}, \quad (43)$$

$$k_2 = 1 \times 10^{14} \exp(-54300/RT) \text{ litre}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}. \quad (44)$$

The rate of consumption of radicals did not depend on the initial titanium(III) concentration and was proportional to the initial H_2O_2 concentration in the first stages. Gas chromatographic analysis of the reaction products showed the presence of formaldehyde, formic

acid and methanol. Dimers of dimethoxymethane were not detected, on the basis of which the authors came to the conclusion that chain termination by radicals (VI) and (VII) does not occur in practice.[58]

It was also established by ESR spectroscopy that the decomposition of radicals (VI) and (VII) did not play an appreciable role. Based on the data, a kinetic scheme for the process was proposed which included reactions (40)–(42) and provided for the decomposition of H_2O_2 by reactions (45) and (46) and possible chain termination with the participation of radicals (VI), (VII) and ·OH.

$$\cdot CH_2OCH_2OCH_3 + H_2O_2 \rightarrow HOCH_2OCH_2OCH_3 + \cdot OH, \quad (45)$$

$$CH_3O\dot{C}HOCH_3 + H_2O_2 \rightarrow CH_3OCH(OH)OCH_3 + \cdot OH, \quad (46)$$

$$\cdot CH_2OCH_2OCH_3 + \cdot OH \rightarrow HOCH_2OCH_2OCH_3, \quad (47)$$

$$CH_3O\dot{C}HOCH_3 + \cdot OH \rightarrow CH_3OCH(OH)OCH_3. \quad (48)$$

However the orders found for the reactions are not substantiated by an analysis of the given kinetic scheme.[58]

The oxidation of propan-2-ol by the H_2O_2–Ti(III) system has been investigated.[59] The formation of radicals of two types, viz. $(CH_3)_2\dot{C}OH$ (VIII) and $\cdot CH_2CH(CH_3)OH$ (IX), was shown by ESR spectroscopy. With an excess of hydrogen peroxide in the system the kinetic relationships of the change of radical concentration with time are linearised by a first order equation or an order of $^3/_2$ with respect to radicals. The order with respect to hydrogen peroxide for radicals (VIII) and (IX) proved to be 1.1 and 1.2 respectively. The investigators proposed that consumption of these radicals occurs in reactions causing decomposition of peroxide.

$$\underset{(VIII)}{(CH_3)_2\dot{C}OH} + H_2O_2 \rightarrow (CH_3)_2CO + \cdot OH + H_2O, \quad (49)$$

$$\underset{(IX)}{\cdot CH_2CH(CH_3)OH} + H_2O_2 \rightarrow CH_2{=}C(CH_3)OH + \cdot OH + H_2O. \quad (50)$$

The product of the second reaction is the enol form of acetone. The heats of reaction for (49) and (50) (ΔH) are –205 and –165 kJ mol^{-1} and the energy of activation 48.1 and 48.5 kJ mol^{-1}.

At low hydrogen peroxide concentrations, consumption of alcohol radicals occurs according to a second order equation which indicates the bimolecular termination of these radicals. However the authors considered that the radicals resulting from reactions (49) and (50) have relatively low reactivity in relation to the substrate, consequently the radical–chain process does not play an appreciable role. There remains the unclarified reasons for the different reactivity of ·OH radicals formed by reactions (49) and (50) and by reaction (40) of titanium(III) with H_2O_2.

It has been noted[60] that at a low rate of initiation, corresponding to a low titanium(III) concentration, the concentration of radicals (IX) exceeds the concentration of radicals (VIII) and at a high initiation rate, corresponding to a high titanium(III) concentration, the reverse relationship is observed in the initial stages. It was proposed that radicals (VIII) participate in a radical–chain process occurring at low rates of initiation and the chain length increases with the growth in concentration of hydrogen peroxide. Evidently this indicates that only radicals (VIII) may cause additional decomposition of hydrogen peroxide.

The change in concentration of radicals as a function of reactant concentration in the oxidation of propan-2-ol by hydrogen peroxide has been described.[61] This process was initiated by oxidation–reduction systems containing H_2O_2 and a metal of variable valency, such as vanadium(IV), titanium(III), chromium(II) or iron(II). On increasing the hydrogen peroxide concentration in the system the concentration of propan-2-ol radicals passed through a maximum (Fig. 5), while an increase in the variable valency metal concentration led to a significant drop in the concentration of radical (VIII) and practically no change in the concentration of radical (IX). The change of concentration of alcohol radicals obtained on radiolysis of H_2O_2 as a function of the initial reactant concentrations indicated that decomposition of H_2O_2 by radicals (VIII) may be possible at various ranges of reactant concentration. A mechanism for the process was proposed, analogous to that described previously, the only difference being that chain termination by alcohol radicals predominates over termination of the latter by reaction with ·OH radicals. It was shown that chain length in the hydrogen peroxide decomposition process grows according to the increase of hydrogen peroxide concentration.

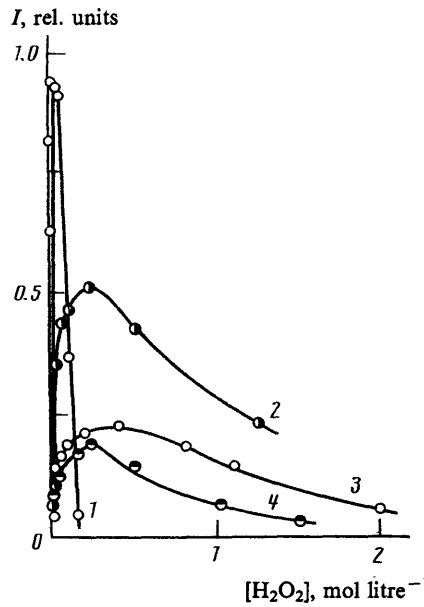


Figure 5. Relative intensity of the ESR signal for radicals formed in reactions of hydrogen peroxide with propan-2-ol in the presence of *1*, titanium(III) at pH 1, *2*, vanadium(IV) at pH 3, *3*, iron(II) at pH 1 and *4*, at pH 3. Concentrations of propan-2-ol and metal were 2.5 mol litre^{-1}.[61]

Investigation of the influence of the concentration of $HO_2^{\cdot}$ radicals on the concentration of alcohol radicals in this system showed[61] that perhydroxyl radicals show no appreciable influence on the content of other radicals. Consequently the authors considered hydroxyl radicals to be the main reactive species.

The mechanism of the interaction of hydrogen peroxide with alcohols has been investigated with initiation of the process by radiolysis of H_2O_2.[62] The concentration of propan-2-ol radicals in the system was found by ESR spectroscopy. With an increase in hydrogen peroxide concentration the overall content of radicals in the system was practically unchanged, while the ratio of the concentrations of radicals (IX) and (VIII) was increased. An

increase in the rate of initiation by increasing the radiation intensity led to growth of both these parameters. On increasing the propan-2-ol concentration the concentration of radical (IX) and the overall concentration of radicals passed through maxima even at low alcohol content while the concentration of radical (VIII) grew constantly. The authors considered[62] that the oxidation of propan-2-ol proceeded by a radical–chain mechanism, comprising decomposition of peroxide according to reaction (53) and termination with the participation of radicals (VIII) and (IX) (54)–(56).

$$^{\cdot}OH + (CH_3)_2CH{-}OH \xrightarrow{k_s} H_2O + (CH_3)_2\dot{C}{-}OH, \quad (51)$$

$$^{\cdot}OH + (CH_3)_2CH{-}OH \xrightarrow{k_{s1}} H_2O + {}^{\cdot}CH_2CH(OH)CH_3, \quad (52)$$

$$(CH_3)_2\dot{C}{-}OH + H_2O_2 \xrightarrow{k_{in}} {}^{\cdot}OH + H_2O + (CH_3)_2CO, \quad (53)$$

$$2(CH_3)_2\dot{C}{-}OH \xrightarrow{k_t} \quad (54)$$

$$(CH_3)_2\dot{C}{-}OH + {}^{\cdot}CH_2CH(OH)CH_3 \xrightarrow{k_t} \text{chain termination.} \quad (55)$$

$$2{}^{\cdot}CH_2CH(OH)CH_3 \xrightarrow{k_t} \quad (56)$$

It was claimed that in view of the high initiation rate the chain length was not large, the concentrations of radicals (VIII) and (IX) were comparable and chain termination by all radicals is possible. An expression for the ratio of the concentrations of the radicals in the system was derived on the basis of the given scheme.[62]

$$[IX]/[VIII] = k_{s1}k_{in}\,(k_s + k_{s1})^{-1}(2k_t w_i)^{-1/2}[H_2O_2] \quad (57)$$

(w_i is the initiation rate) which was confirmed by the experimental data (Fig. 6).

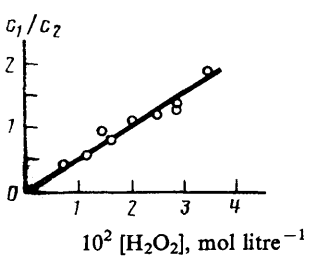


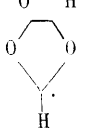
Figure 6. Dependence of the relative concentrations of $^{\cdot}CH_2CH.(OH)CH_3$ (c_1) and $(CH_3)_2\dot{C}OH$ (c_2) radicals on hydrogen peroxide concentration during photolysis of the latter in an aqueous solution of 0.68 mol litre^{-1} acetone and 0.65 mol litre^{-1} propan-2-ol at 30 °C.[62]

Indirect confirmation of the lack of participation of radical (IX) in the decomposition of H_2O_2 is the observation that t-butyl alcohol does not cause decomposition.

An analogous mechanism has been proposed to describe the reaction of hydrogen peroxide with other oxygen-containing compounds (methanol, ethanol, tetrahydrofuran, dioxan, diethyl ether, etc.). Some rate constants for the decomposition of peroxide are given in Table 1.

When initiating the reaction of hydrogen peroxide with alcohols with the H_2O_2–titanium(III) system radical decomposition of peroxide was observed only at high concentrations of it and the chain length was not very large.[63] This is evidently linked with the high rate of the reaction between H_2O_2 and titanium(III). Similar results have been obtained elsewhere.[64]

Table 1. Rate constants for the decomposition of hydrogen peroxide by various radicals at 20 °C.

Radical	$10^{-4}k$, litre mol^{-1} s^{-1}	Refs.
$^{\cdot}CH_2OH$	35	[62]
	5	[63]
	4	[66]
	2.3	[67]
	4	[68]
$CH_3\dot{C}HOH$	18	[64]
	15	[69]
$(CH_3)_2\dot{C}OH$	51	[62]
	50	[63]
$^{\cdot}CO_2^-$	70	[70]
	3	[67]
	6	[67]
$CH_3\dot{C}HOCH_2CH_3$	5.5	[67]
$^{\cdot}CH(OCH_3)_2$	110	[67]

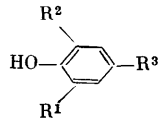
The decomposition of hydrogen peroxide may therefore take place under the action of radicals in which an unpaired electron is present on the α-carbon atom of oxygen-containing compounds. The chain length in this process may vary within wide limits depending on the initiation rate.

The rate constant for the decomposition of hydrogen peroxide by radicals of organic compounds may be increased by reducing the oxidation–reduction potential of the latter. This is observed in their interaction with benzoyl peroxide.[65]

V. Oxidation of phenolic compounds with hydrogen peroxide

Interest in this question is linked with the need to clarify the mechanism of action of phenolic antioxidants, the mechanism of the initiation by hydrogen peroxide of graft polymerisation of monomers to natural polyphenolic compounds such as lignin and its derivatives,[14] and also the chemical mechanism of the delignification of wood by hydrogen peroxide.[10] Lignin macromolecules of coniferous wood contain structural units of 4-hydroxy-3-methoxyphenylpropane (guaiacylpropane) and there are also 4-hydroxy-3,5-dimethoxyphenylpropane (syringylpropane) structures in wood lignins from deciduous species.[71] Consequently phenolic compounds

may serve as the simplest models of the guaiacyl and syringyl structures of lignin units.



$R^1 = H,\ OCH_3;\ R^2 = OCH_3;$
$R^3 = H,\ CH_2OH,\ CHO$ etc.

(X)

The kinetics of the oxidation of guaiacol (X, $R^1 = OCH_3$, $R^2 = R^3 = H$) with hydrogen peroxide at pH 4.0 in an inert atmosphere have been investigated.[22] Guaiacol markedly accelerates the decomposition of H_2O_2, the order of the reaction with respect to the latter is close to 1 and with respect to guaiacol to $^1/_2$, the effective energy of activation being 90 kJ mol^{-1}. Monomer (acrylamide) slows the reaction rate to the rate of decomposition of H_2O_2 in water, which indicates a radical–chain mechanism for the process and its initiation by homolysis of hydrogen peroxide.

To substantiate the results obtained, a kinetic scheme was proposed[22] for the peroxide oxidation of guaiacol and other phenols which provides for the formation of phenoxyl radicals, their subsequent isomerisation into aryl radicals and the decomposition of H_2O_2 under the action of the latter.

$$H_2O_2 \cdot 2H_2O \xrightarrow{k_d^t} 2{}^{\bullet}OH + 2H_2O, \quad (58)$$

$$^{\bullet}OH + Ar{-}OH \xrightarrow{k_s} Ar{-}O^{\bullet} + H_2O, \quad (59)$$

$$Ar{-}O^{\bullet} \xrightarrow{k_r} {}^{\bullet}Ar{-}OH, \quad (60)$$

$$^{\bullet}Ar{-}OH + H_2O_2 \xrightarrow{k_{in}} {}^{\bullet}OH + Ar', \quad (61)$$

$$^{\bullet}Ar{-}OH + {}^{\bullet}OH \xrightarrow{k_{12}} \text{chain termination}, \quad (62)$$

where Ar′ is the oxidation product of the phenolic compound. Eqn. (63) for the consumption of H_2O_2 is obtained from this scheme using quasi-steady-state concentrations.

$$w = k_d \{^1/_2 + (^1/_4 + k_s k_{in} (k_d k_{12})^{-1}[Ph])^{1/2}\}[H_2O_2], \quad (63)$$

where [Ph] is the concentration of phenolic compound. It may be rearranged into (64) which is in agreement with the experimental data.

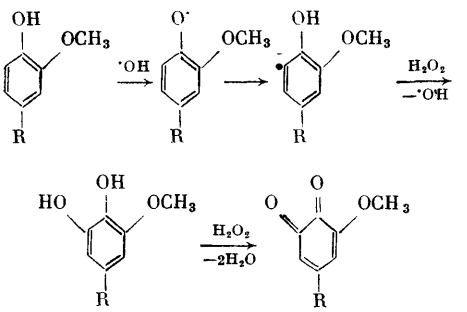
$$w^2/(k_d [H_2O_2]^2) - w/[H_2O_2] = (k_s k_{in}/k_{12})[Ph]. \quad (64)$$

If the rate of decomposition of H_2O_2 by (61) is significantly greater than the rate of its homolysis then Eqn. (63) reduces to expression (65) which corresponds to the order of the reaction found experimentally.[22]

$$w = (k_d k_s k_{in}/k_{12})^{1/2}[Ph]^{1/2}[H_2O_2]. \quad (65)$$

Proposals on the mechanism of initiation by hydrogen peroxide of the grafting of monomers to lignin were also made on the basis of kinetic investigations on the polymerisation of monomers in the presence of phenolic compounds modelling the structural units of lignin.[72–74] A comparison of the influence of guaiacol and veratrole (*o*-dimethoxybenzene),[72] vanillin sulphonate (3-methoxy-4-hydroxybenzyl sulphonate), *p*-hydroxybenzyl sulphonate and veratryl sulphonate (3,4-dimethoxybenzyl sulphonate),[73] guaiacol and 2,6-dimethoxyphenol[74] on the rate of polymerisation of monomers led investigators to the conclusion that the kinetics of the process depend on the presence of a phenolic hydroxyl and a vacancy in the *ortho* position to the phenol in the structure of the model compound.[75]

The kinetic scheme (58)–(62) also provides for homolytic fission of the OH bond of the phenolic compound with subsequent isomerisation of phenoxyl radicals having no substituent in the *ortho* position into aryl radicals capable of inducing chain decomposition of H_2O_2.[76]



(66)

According to this scheme, the accumulation of quinones must correspond to the reduction in the content of phenolic hydroxyls and is not accompanied by demethylation of the starting material. The formation of one mole quinone must consume two moles H_2O_2. However functional analysis of the oxidation products of guaiacol showed,[76] that the reduction in content of phenolic hydroxyls is in good agreement not only with the accumulation of quinone but also with the fall in methoxy group content and the consumption of hydrogen peroxide (Table 2), which contradicts the scheme (66). In the oxidation of guaiacol to quinone an equimolecular (and not double) quantity of H_2O_2 is consumed and the quinone is formed predominantly by demethylation of guaiacol and not as a result of the formation of appropriate bonds in the vacant *ortho* (or *para*) positions to the phenolic hydroxyl as shown in the scheme (66).[76]

Table 2. Relationship between the functional composition (in mmol g^{-1} guaiacol) of the oxidation products of guaiacol and hydrogen peroxide concentration.[76]

$[H_2O_2]$, mmol g^{-1} guaiacol	[OH]	[OCH_3]	[Quinones]	$-\Delta$[OH]	$-\Delta$[OCH_3]
0	8.06	8.06	0	0	0
1.90	6.61	6.51	1.40	1.45	1.55
3.81	4.66	3.96	3.56	3.40	4.10

Footnote. Reaction conditions: guaiacol concentration 161 mmol litre^{-1}, temperature 70 °C, reaction time 1.5 h.

These concepts were confirmed by investigations on the kinetics of the interaction of hydrogen peroxide with phenol, veratrole and syringaldehyde (3,5-dimethoxy-4-hydroxybenzaldehyde), compounds which model the structures with vacant *ortho* and *para* positions relative to a free phenolic hydroxyl and to a hydroxyl included in an ester bond. The investigations showed that of these only syringaldehyde was able to cause decomposition of H_2O_2 (Fig. 7). Consequently in order to carry out the radical–chain decomposition of peroxide the presence of an unsubstituted phenolic hydroxyl

group in the benzene ring is necessary the presence in the ring of other substituents and a vacant position *ortho* or *para* to them is not obligatory.[76]

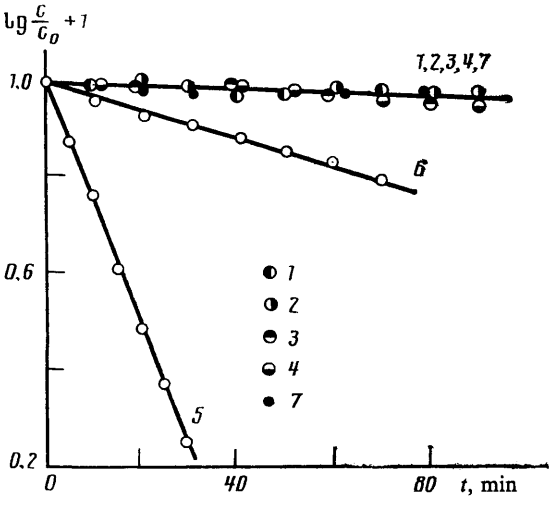
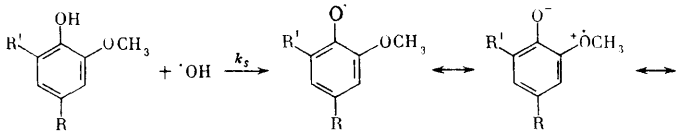


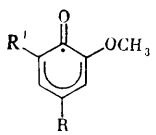
Figure 7. Semilogarithmic plot of the kinetic curves for the consumption of H_2O_2 *1*, in water, in solutions of *2*, veratrole, *3*, phenol, *4*, guaiacol in the presence of acrylamide 0.141 mol litre^{-1}, *5*, guaiacol, *6*, syringic aldehyde, and *7*, syringic aldehyde in the presence of acrylamide 0.282 mol litre^{-1} at pH 4, 70 °C, and initial concentrations of H_2O_2 1.06 mmol litre^{-1} and of phenolic compound 4.03 mmol litre^{-1}.[76]

Allowing for what has been said, the experimental data[22,76] may be described by the kinetic scheme (67)–(70) which includes the decomposition of H_2O_2 by the phenoxyl radical according to reaction (69) since the electron density of its unpaired electron is distributed predominantly between the two oxygen atoms[46] (see section III).

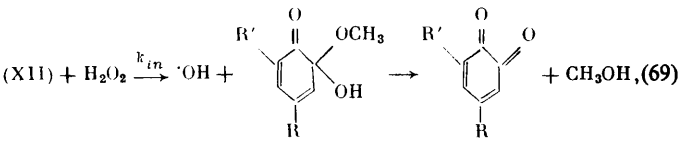
$$H_2O_2 \cdot 2H_2O \xrightarrow{k_d} 2{}^{\cdot}OH + 2H_2O, \qquad (67)$$



(XI) (XII)



(68)



(XII) + ·OH $\xrightarrow{k_{12}}$ chain termination. (70)

Calculations on this scheme using quasi-steady-state concentrations for the interaction of H_2O_2 with guaiacol (XI, R, R′ = H) lead to Eqn. (63) compatible with the kinetic results presented above.

Investigation of the oxidation of vanillin with hydrogen peroxide[77] enables assessment of the effect of carbonyl and methoxy groups in addition to a phenolic hydroxyl in the benzene ring on the kinetics of the process. Vanillin may also serve, as a first approximation, as a model of the guaiacol structural units of lignin with carbonyl groups in the side chain. The rate of consumption of H_2O_2 in the presence of vanillin is greater than the rate of decomposition of peroxide in water under analogous conditions and markedly less than in a solution of guaiacol. Experiments with acrylamide added to the system confirmed the radical–chain mechanism of the reaction. Experiments were also carried out on the oxidation of benzaldehyde and of mixtures of it with guaiacol in order to clarify the influence of substituents in the benzene ring on the kinetics of the process. These showed the ability of aldehyde groups to interact with hydroxyl radicals with the formation of radicals causing no chain decomposition of H_2O_2.

A study of the functional composition of the oxidation products of vanillin with hydrogen peroxide showed[76] that the quantity of quinones formed corresponds approximately to the reduction in the content of hydroxyl and methoxyl groups, carbonyl groups are oxidised to carboxyls, and the consumption of H_2O_2 corresponds to the overall accumulation of quinone and carboxyl groups (Table 3). Vanillic acid was identified in the oxidation products by thin layer chromatography.

This indicates that two reaction centres participate in the oxidation of vanillin, viz. the phenolic hydroxyl and the aldehyde group.

Table 3. Relationship between the functional composition (in mmol g^{-1} vanillin) of the oxidation products of vanillin with hydrogen peroxide and the concentration of the latter.[76]

$[H_2O_2]$, mmol g^{-1} vanillin	[COOH]	[OH]	[OCH_3]	[Quinones]	[COOH]+ [Quinones]	−Δ[OH]	−Δ[OCH_3]
0	0	6.53	6.57	0	0	0	0
1.75	0.93	5.80	6.09	0.72	1.65	0.73	0.48
3.50	2.02	5.44	5.68	1.22	3.24	1.09	1.11
7.00	4.13	4.64	4.26	2.14	6.27	1.89	2.31

Footnote. Reaction conditions: vanillin concentration 63.4 mmol litre^{-1}, temperature 80 °C, reaction time 6 h.

The reaction is first order with respect to hydrogen peroxide since the initial rate of H_2O_2 consumption is proportional to its concentration (Fig. 8). The relationship of the apparent reaction rate constant to vanillin concentration has a complex character. It increases with the growth in concentration of the latter tending to a limiting value (Fig. 9) so that the reaction order with respect to vanillin is changed from $^1/_2$ to zero. The apparent activation energy is 97 kJ mol^{-1}.

The data enable the oxidation of vanillin (XI, R = CHO, R′ = H) with hydrogen peroxide to be described by the kinetic scheme

(67)–(70) supplemented by reaction equations (71) and (72) for the oxidation of vanillin at the aldehyde group.

$$HO{-}C_6H_3(OCH_3){-}CHO + {}^{\cdot}OH \xrightarrow{k_{s1}} \rightarrow HO{-}C_6H_3(OCH_3){-}\dot{C}O + H_2O, \quad (71)$$

$$HO{-}C_6H_3(OCH_3){-}\dot{C}O + {}^{\cdot}OH \xrightarrow{k_{12}} HO{-}C_6H_3(OCH_3){-}COOH. \quad (72)$$

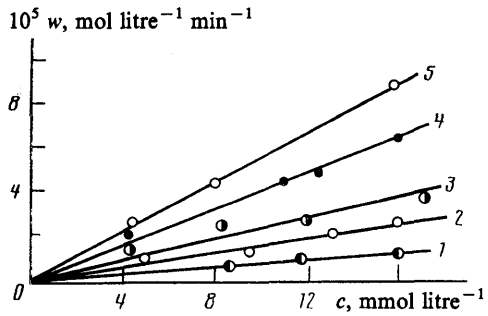


Figure 8. Relationship between the rate of consumption of H_2O_2 during the oxidation of vanillin and the initial concentration of hydrogen peroxide at 70 °C and initial vanillin concentrations of *1*, 0.66, *2*, 3.29, *3*, 6.58, *4*, 32.9, *5*, 65.8 mmol litre^{-1}.

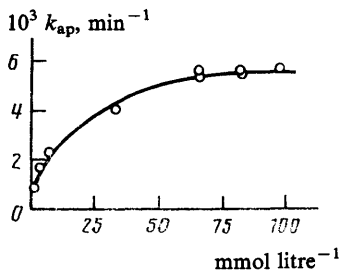


Figure 9. Influence of the initial vanillin concentration during its oxidation by H_2O_2 on the apparent rate constant for the consumption of hydrogen peroxide at 70 °C.

A mathematic model for the kinetics of the process may be obtained from schemes (67)–(72) using quasi-steady-state concentrations.

$$w = k_{ap}[H_2O_2], \quad (73)$$

where w is the rate of H_2O_2 consumption in the oxidation of vanillin.

$$k_{ap} = (2k_{12})^{-1}\{(F^2 + 4k_d k_{in} k_s k_{12}[Ph])^{1/2} - F\},$$
$$F = k_{in}k_{s1}[Ph] - k_d k_{12}. \quad (74)$$

Eqn. (73) is in agrement with the kinetic results given in Fig. 8.

At low vanillin concentrations $k_{in} \gg k_d k_{12}(4k_s[Ph])^{-1}$ and expression (73) simplifies to

$$w = (k_d k_s k_{in}/k_{12})^{1/2}[Ph]^{1/2}[H_2O_2], \quad (75)$$

which is in agrement with the experimentally found partial reaction orders (at vanillin concentrations up to 33 mmol litre^{-1}).

At fairly high vanillin concentrations the relationship (76) may be obtained by expansion of (73) into an exponential series and corresponds to the partial reaction order found by experiment under these conditions.

$$w = k_d(1 + k_s/k_{s1})[H_2O_2]. \quad (76)$$

It is seen from Fig. 9 that the apparent reaction rate constant tends to a limit on increasing the vanillin concentration. It may be shown that the limit of function (74) is determined by the expression

$$\lim_{[Ph]\to\infty} k_{ap} = k_d k_s / k_{s1}. \quad (77)$$

Combinations of rate constants for the individual reactions $k_d k_s/k_{s1}$ and k_s/k_{s1}, equal to 5.56 × 10^{-3} min^{-1} and 12.5 respectivley (at 70 °C), are found from the data given in Fig. 9 using Eqn. (77).

Transformation of relationship (74) leads to the equation

$$(k_{ap} + k_d)/[Ph] = -k_{in}k_{s1}/k_{12} + (k_d k_{in} k_s/k_{12})(1/k_{ap}), \quad (78)$$

which describes the kinetic data well as is evident from Fig. 10. The relationships of the rate constants for the individual reactions are found from the intercept and the slope of the straight line in Fig. 10 and $k_d k_s/k_{s1}$, k_s/k_{s1}, $k_d k_{in} k_s/k_{12}$, $k_{in}k_s/k_{12}$ are 6.38 × 10^{-3} min^{-1}, 14.4 and 1.70 × 10^{-3} litre mol^{-1} min^{-2} and 3.84 litre mol^{-1} min^{-1} respectively at 70 °C. The values obtained from Eqns. (77) and (78) are close to one another. This indicates the adequacy of the mathematical model (73) and (74) describing the kinetic experimental data for the oxidation of vanillin with hydrogen peroxide over a wide range of reactant concentrations.

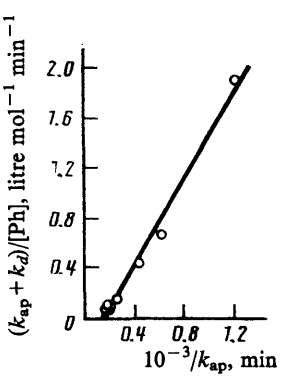


Figure 10. Relationship between the apparent reaction rate constant for the oxidation of vanillin with hydrogen peroxide and vanillin concentration at 70 °C in the coordinates of Eqn. (78).

A feature of the hydrogen peroxide oxidation of vanillyl alcohol (4-hydroxy-3-methoxybenzyl alcohol), modelling the structural units of lignin with benzyl hydroxyls, is the transfer in the initial stage of the reaction centre from the phenolic oxygen of the aromatic ring to

the carbon atom in the α-position.[78] This is indicated by the constant nature of the content of phenolic hydroxyls in the initial stage of the reaction and the correspondence of the quantity of H_2O_2 reacted to the overlall accumulation of carbonyl and carboxyl groups (Table 4) (vanillin was identified as the product of oxidation of vanillyl alcohol by thin layer chromatography).

Table 4. Change of functional composition (in mmol g^{-1} vanillyl alcohol) of the oxidation products of vanillyl alcohol with hydrogen peroxide in relation to the quantity of H_2O_2 reacted.[78]

Quantity of H_2O_2 reacted, mmol $litre^{-1}$ vanillyl alcohol	$[OH_{phenol}]$	$[OCH_3]$	[COOH]	[CHO]
0	6.49	6.47	0	0
0.39	6.49	6.38	0	0.45
0.98	6.49	6.43	0	0.92
1.23	6.57	6.43	0.08	1.01
1.47	6.63	6.46	0.17	1.13

Footnote. Reaction conditions: vanillyl alcohol concentration 66.1 mmol $litre^{-1}$, H_2O_2 concentration 87.5 mmol $litre^{-1}$, temperature 80 °C.

The kinetic investigations showed the acceleration of hydrogen peroxide decomposition in aqueous media in the presence of vanillyl alcohol. Acrylamide suppressed the decomposition of peroxide which indicates the radical–chain mechanism of the process. Partial orders of the reaction were 1 with respect to peroxide and $^1/_2$ with respect to vanillyl alcohol. The apparent activation energy was 92 kJ mol^{-1}.

The results obtained are in agreement[78] with the kinetic scheme (79)–(85). In this, attack by the radical initiator of the phenolic hydroxyl and the C–H bond of the alcohol group is proposed, then rearrangement (82) of phenoxyl to benzyl radical, which was confirmed by ESR spectroscopic investigations on the kinetics of the consumption of *p*-alkylphenoxyl radicals (see section III).[45,79]

$$H_2O_2 \cdot 2H_2O \xrightarrow{k_d} 2\,{}^{\cdot}OH + 2H_2O, \tag{79}$$

$$^{\cdot}OH + HO{-}C_6H_3(OCH_3){-}CH_2OH \xrightarrow{k_s} {}^{\cdot}O{-}C_6H_3(OCH_3){-}CH_2OH + H_2O, \tag{80}$$

$$^{\cdot}OH + HO{-}C_6H_3(OCH_3){-}CH_2OH \xrightarrow{k_{s1}} HO{-}C_6H_3(OCH_3){-}\dot{C}HOH + H_2O, \tag{81}$$

$$^{\cdot}O{-}C_6H_3(OCH_3){-}CH_2OH \xrightarrow{k_r} HO{-}C_6H_3(OCH_3){-}\dot{C}HOH, \tag{82}$$

$$HO{-}C_6H_3(OCH_3){-}CHOH + H_2O_2 \xrightarrow{k_{in1}} {}^{\cdot}OH + HO{-}C_6H_3(OCH_3){-}CHO + H_2O, \tag{83}$$

$$^{\cdot}O{-}C_6H_3(OCH_3){-}CH_2OH + {}^{\cdot}OH \xrightarrow{k_{12}} \text{chain termination} \tag{84}$$

$$HO{-}C_6H_3(OCH_3){-}\dot{C}HOH + {}^{\cdot}OH \xrightarrow{k_{13}} \text{chain termination} \tag{85}$$

Using a quasi-steady-state approach for long chains and the condition that

$$k_r\,(k_s + k_{s1})\,k_{13} \gg k_{in1}k_sk_{12}\,[H_2O_2] \tag{86}$$

It follows that

$$w = \{k_dk_{in1}\,(k_s + k_{s1})/k_{13}\}^{1/2}[Ph]^{1/2}[H_2O_2], \tag{87}$$

which is in agreement with the partial reaction orders given above.

The kinetics have also been investigated for the reaction of hydrogen peroxide with the phenolic carboxylic acids (X), containing a phenolic hydroxyl and a carboxylic acid group, viz. ferulic (R^1 = H, R^2 = OCH_3, R^3 = CH=CH–COOH), syringic (R^1 = R^2 = OCH_3, R^3 = COOH), gallic (R^1 = R^2 = OH, R^3 = COOH) and protocatechuic (R^1 = H, R^2 = OH, R^3 = COOH) acids.[80,81]

It was established that the rate of consumption of H_2O_2 in a solution of ferulic acid increases with the increase in acid concentration (in the range 0.05–15.5 mol $litre^{-1}$) and in a solution of gallic acid the reaction rate increases with the increase in concentration of the latter only up to 0.29 mmol $litre^{-1}$ and then remains practically constant. In the presence of a monomer (acrylic acid) a reduction in the rate of the process practically to the rate of homolysis of peroxide in water indicates the radical–chain character of the reaction and its initiation by homolysis of H_2O_2.

From the initial rate of consumption of peroxide in the presence of the phenolic acids mentioned the reaction order found with respect to H_2O_2 was close to 1, with respect to ferulic acid to $^1/_2$, with respect to protocatechuic and syringic acids it was zero and with respect to galic acid it varied from $^1/_2$ (at concentrations up to 0.29 mmol $litre^{-1}$) to zero (at higher concentrations). The apparent activation energies for the oxidation of ferulic and gallic acids were 72 and 79 kJ mol^{-1} respectively. The data obtained[81] are in agreement with the kinetic scheme of (88)–(96) which proposes the formation of carboxyl and aryl radicals in addition to phenoxyl radicals.

$$H_2O_2 \cdot 2H_2O \xrightarrow{k_d} 2\,{}^{\cdot}OH + 2H_2O, \tag{88}$$

$$^{\cdot}OH + HO{-}Ar{-}COOH \xrightarrow{k_s} H_2O + {}^{\cdot}O{-}Ar{-}COOH, \tag{89}$$

$$^{\cdot}OH + HO{-}Ar{-}COOH \xrightarrow{k_{s1}} H_2O + HO{-}Ar{-}COO^{\cdot}, \tag{90}$$

$$^{\cdot}O{-}Ar{-}COOH \xrightarrow{k_r} HO{-}Ar{-}COO^{\cdot}, \tag{91}$$

$$HO{-}Ar{-}COO^{\cdot} \xrightarrow{k_c} CO_2 + HO{-}Ar^{\cdot}, \tag{92}$$

$$^{\cdot}O{-}Ar{-}COOH + H_2O_2 \xrightarrow{k_{in}} {}^{\cdot}OH + \text{products}, \tag{93}$$

$$^{\cdot}O{-}Ar{-}COOH + {}^{\cdot}OH \xrightarrow{k_{12}} \text{chain termination} \tag{94}$$

$$HO{-}Ar{-}COO^{\cdot} + {}^{\cdot}OH \xrightarrow{k_{13}} \text{chain termination} \tag{95}$$

$$HO{-}Ar^{\cdot} + {}^{\cdot}OH \xrightarrow{k_{14}} \text{chain termination} \tag{96}$$

Although oxidation of syringic aldehyde leads to the formation of stable phenoxyl radicals, the oxidation of syringic and sinapic (R_1 = R_2 = OCH_3, R_3 = CH=CH–COOH) acids leads to the observation of only a weak ESR signal[50] since seemingly their phenoxyl radicals are capable of conversion into reactive carboxyl and aryl radicals.[81] These facts point in favour of the occurrence of reactions (91) and (92). The reaction products of (93) are *o*-quinones which was confirmed by their colour reactions with ethylenediamine.

An expression was obtained from the kinetic scheme (88)–(96) for the rate of the radical–chain decomposition of H_2O_2 by the method of quasi-steady-state concentrations.[80,81]

$$w = k_{in}\{(F_1^2/4 + F_2)^{1/2} - F_1/2\}[H_2O_2], \quad (97)$$

$$F_1 = k_r(k_s + k_{s1})[Ph](k_{in}k_{12}[H_2O_2])^{-1} + k_s k_{12}^{-1}[Ph],$$

$$F_2 = k_d(k_s + k_{s1})(k_{in}k_{12})^{-1}[Ph].$$

At low concentrations of the phenolic carboxylic acid the expression (97) is simplified and takes the form of (98),[81] which corresponds to the experimental data given above for the decomposition of hydrogen peroxide in the presence of ferulic and gallic (at concentrations below 0.29 mmol litre^{-1}) acids.

$$w = \{k_{in}k_d(k_s + k_{s1})/k_{12}\}^{1/2}[Ph]^{1/2}[H_2O_2]. \quad (98)$$

At higher concentrations of phenolic carboxylic acids and hydrogen peroxide the Eqn. (97) is transformed into (99).[81] The empirical partial reaction orders given above for the hydrogen peroxide oxidation of protocatechuic, syringic and gallic acids (at concentrations of the latter above 0.29 mmol litre^{-1}) are in agreement with this equation.

$$w = \{k_d(k_s + k_{s1})/k_{s1}\}[H_2O_2]. \quad (99)$$

The oxidation of lignosulphonic acid (LSA) with hydrogen peroxide is first order with respect to H_2O_2 and about $^1/_2$ with respect to LSA. The apparent activation energy (58 kJ mol^{-1}) is significantly less than in the oxidation of model compounds of lignin.[82] The deceleration of the reaction by stable 2,2,6,6-tetramethylpiperidin-1-oxyl radicals indicates its radical–chain mechanism.

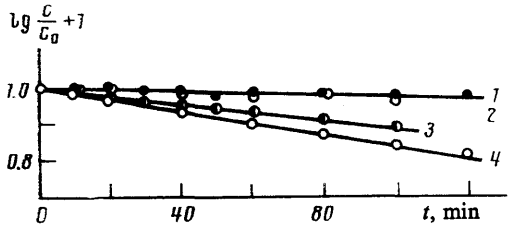


Figure 11. Semilogarithmic plot of the kinetic curves for the consumption of H_2O_2 in *1*, water, in solutions of lignosulphonic acid methylated *2*, with dimethyl sulphate and *3*, with diazomethane and *4*, in a solution of the initial LSA at concentrations of H_2O_2 2.6 mmol litre^{-1} and LSA 4.24 mmol litre^{-1} at 70 °C.[83]

An absorption band in the IR spectrum of LSA oxidised with peroxide appears at 1730 cm^{-1}, characteristic of a carbonyl group.[83] With an increase in the initial H_2O_2 concentration the content of acidic OH^- and carbonyl groups in the reaction products increases significantly, the quantity of quinone groups increases insignificantly and the content of methoxy groups is almost unchanged. This supports the hypothesis that the oxidation of LSA with hydrogen peroxide occurs in the side chain to a significant extent. In order to clarify whether phenolic hydroxyls participate in the oxidation, the kinetics of the interaction of H_2O_2 with lignosulphonic acid were investigated[83] after only the acidic OH groups had been methylated with diazomethane or after all the hydroxyl groups had been methylated with dimethyl sulphate. In the first case the rate of peroxide consumption was somewhat lower than in a solution of the initial unmethylated LSA but in the second case it approached the rate of decomposition of H_2O_2 in water (Fig. 11). This supports the proposal that the decomposition of hydrogen peroxide occurs only partially with the participation of phenoxyl radicals but to a significant extent with the participation of radicals with an unpaired electron in the side chain.

The kinetic scheme of (100)–(106) corresponds to the results obtained. In this it is proposed that the accumulation of carbonyl compounds and quinones occurs by reactions (103) and (104) and of acidic OH groups by secondary oxidation processes.

$$H_2O_2 \cdot 2H_2O \xrightarrow{k_d} 2^{\cdot}OH + 2H_2O, \quad (100)$$

$$^{\cdot}OH + HO{-}C_6H_3(OCH_3){-}R(X)H \xrightarrow{k_s} {}^{\cdot}O{-}\underset{(XIII)}{C_6H_3(OCH_3)}{-}R(X)H + H_2O, \quad (101)$$

$$^{\cdot}OH + HO{-}C_6H_3(OCH_3){-}R(X)H \xrightarrow{k_{s1}} HO{-}\underset{(XIV)}{C_6H_3(OCH_3)}{-}\dot{R}(X) + H_2O, \quad (102)$$

$$(XIII) + H_2O_2 \xrightarrow{k_{in}} {}^{\cdot}OH + O{=}\langle\rangle{-}R(X)H + CH_3OH, \quad (103)$$

$$(XIV) + H_2O_2 \xrightarrow{k_{in1}} {}^{\cdot}OH + HO{-}C_6H_3(OCH_3){-}RO + \text{products}, \quad (104)$$

$$\left.\begin{array}{ll}(XIII) + {}^{\cdot}OH \xrightarrow{k_{12}} & (105)\\ (XIV) + {}^{\cdot}OH \xrightarrow{k_{13}} & (106)\end{array}\right\} \text{chain termination.}$$

An equation was obtained for the rate of consumption of H_2O_2 in LSA solution[83] from this scheme using a kinetic model for unbranched radical–chain processes[84] in a quasi-steady-state approach for long chains.

$$w = (k_s + k_{s1})(k_d k_{in} k_{in1})^{1/2}(k_s k_{in1} k_{12} + k_{s1} k_{in} k_{13})^{-1/2}[LSA]^{1/2}[H_2O_2]. \quad (107)$$

This is in agreement with the reaction orders with respect to LSA and hydrogen peroxide found experimentally.

On reacting hydrogen peroxide with nitrolignin (NL) the reaction order with respect to H_2O_2 was close to 1 and with respect to NL close to $^1/_3$, the apparent energy of activation was 75 kJ mol^{-1}.[24] The marked deceleration of H_2O_2 consumption in a solution of NL under the influence of an unsaturated monomer indicated the radical–chain mechanism of the reaction and the fact that the reaction rate in this case exceeds the rate of peroxide homolysis points in favour of initiation of the process by an associate of nitrolignin with hydrogen peroxide according to reaction (108).

According to data from gel permeation chromatography (GPC) the polydispersity (from 2.96 to 10.30) and the mean molecular mass MW (from 3190 to 11470) of nitrolignin are increased by oxidation with hydrogen peroxide. In the opinion of the authors,[24] this occurs as a result of recombination of NL macroradicals by chain termination reactions (112)–(114). The kinetic scheme proposed[24] involves the isomerisation of an aroxyl radical having a vacant *ortho*

position into an aryl radical (criticism of such ideas is given above). The possibility of carrying out the previously considered rearrangement of aroxyl radical into a radical with an unpaired electron in the side chain is disregarded.[78] Allowing for what has been said the kinetic scheme for the oxidation of NL with peroxide may be described by the equations

$$H_2O_2 + HO{-}Ar{-}RH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O_2 \ldots HO{-}Ar{-}RH \xrightarrow{k'} 2{}^{\cdot}OH + HO{-}Ar{-}RH, \quad (108)$$

$${}^{\cdot}OH + HO{-}Ar{-}RH \xrightarrow{k_s} H_2O + {}^{\cdot}O{-}Ar{-}RH, \quad (109)$$

$${}^{\cdot}O{-}Ar{-}RH \xrightarrow{k_r} HO{-}Ar{-}R^{\cdot}, \quad (110)$$

$$HO{-}Ar{-}R^{\cdot} + H_2O_2 \xrightarrow{k_{in}} {}^{\cdot}OH + \text{products}, \quad (111)$$

$$2\,{}^{\cdot}O{-}Ar{-}RH \xrightarrow{k_0} \quad (112)$$

$${}^{\cdot}O{-}Ar{-}RH + HO{-}Ar{-}R^{\cdot} \xrightarrow{\sigma k_0} \text{chain termination} \quad (113)$$

$$2HO{-}Ar{-}R^{\cdot} \xrightarrow{\sigma^2 k_0} \quad (114)$$

It is possible to obtain an equation for the rates of the radical–chain decomposition of H_2O_2 from the given scheme using quasi-steady-state concentrations taking geometric means and corresponding to that given previously.[24]

$$w = \frac{k_{in}k_r(2k/k_0)^{1/2}[NL]^{1/2}[H_2O_2]^{3/2}}{k_{in}[H_2O_2] + \sigma k_r + \sigma(2kk_0[NL][H_2O_2])^{1/2}}, \quad (115)$$

where $k = k_1k'(k_{-1} + k')^{-1}$. Proceeding from the proposed different contributions of radicals with an unpaired electron in the side chain and aroxyl radicals to chain termination, the reaction order with respect to NL and H_2O_2 must be intermediate between 0 and $^1/_2$ and between $^1/_2$ and $^3/_2$ respectively according to expression (115).[24] This is in agreement with the partial reaction orders found empirically, so that in the system investigated radicals with an unpaired electron in the side chain and aroxyl radicals from nitrolignin evidently participate in chain termination. High molecular weight fractions of NL appear as a result and this was confirmed by GPC data.

The oxidation with hydrogen peroxide of water-soluble lignin derivatives and of compounds modelling units of its structure proceeds according to a radical–chain mechanism with the participation of both phenolic hydroxyls and of functional groups in the side chain.

VI. Analysis of the kinetic scheme for radical–chain oxidation of phenolic compounds with hydrogen peroxide

The results of the kinetic investigations considered above enable the conclusion to be drawn that the interaction of hydrogen peroxide with organic substances, particularly phenolic compounds, usually proceeds by a radical–chain mechanism. This is indicated by the acceleration of peroxide decomposition in the presence of organic compounds, the frequently encountered fractional partial reaction orders, the dependence of the form of the rate equation on the relative concentrations of organic compound and peroxide and by the sensitivity of the reaction to the action of small amounts of catalysing or inhibiting substances.

The kinetic schemes given above for the oxidation of phenolic compounds with hydrogen peroxide are in fact partial variants of the general scheme of (116)–(126) which comprises chain initiation by homolysis of peroxide (116), interaction of hydroxyl radicals with the phenolic compound with the formation of phenoxyl radicals (117) and radicals with an unpaired electron in the side chain (118), rearrangement of the former to the latter (119), decomposition of hydrogen peroxide by these radicals (120) and (121) and chain termination with the participation of these radicals and of hydroxyl radicals.

$$H_2O_2 \cdot 2H_2O \xrightarrow{k_d} 2{}^{\cdot}OH + 2H_2O, \quad (116)$$

$${}^{\cdot}OH + HO{-}Ar{-}R(X)H \xrightarrow{k_s} H_2O + {}^{\cdot}O{-}Ar{-}R(X)H, \quad (117)$$

$${}^{\cdot}OH + HO{-}Ar{-}R(X)H \xrightarrow{k_{s1}} H_2O + HO{-}Ar{-}\dot{R}(X), \quad (118)$$

$${}^{\cdot}O{-}Ar{-}R(X)H \xrightarrow{k_r} HO{-}Ar{-}\dot{R}(X), \quad (119)$$

$${}^{\cdot}O{-}Ar{-}R(X)H + H_2O \xrightarrow{k_{in}} {}^{\cdot}OH + \text{products}, \quad (120)$$

$$HO{-}Ar{-}\dot{R}(X) + H_2O_2 \xrightarrow{k_{in\,1}} {}^{\cdot}OH + \text{products}, \quad (121)$$

$${}^{\cdot}O{-}Ar{-}R(X)H + {}^{\cdot}OH \xrightarrow{k_{12}} \quad (122)$$

$$HO{-}Ar{-}\dot{R}(X) + {}^{\cdot}OH \xrightarrow{k_{13}} \quad (123)$$

$$2\,{}^{\cdot}O{-}Ar{-}R(X)H \xrightarrow{k_{22}} \text{chain termination} \quad (124)$$

$${}^{\cdot}O{-}Ar{-}R(X)H + HO{-}Ar{-}\dot{R}(X) \xrightarrow{\sigma k_{22}} \quad (125)$$

$$2\,HO{-}Ar{-}\dot{R}(X) \xrightarrow{\sigma^2 k_{22}} \quad (126)$$

The rate equation for each process depends mainly on the chain length and on the relative contributions of chain propagation reactions (117)–(121). It is expedient in this connection to conduct an analytical calculation of the given kinetic scheme using the quasi-steady-state concentrations under conditions when the chain length is sufficiently large.

1. Analytical calculation of a kinetic scheme with the long-chain approach

A general rate equation for long-chain oxidation of phenolic compounds with hydrogen peroxide has been derived using a kinetic model of the unbranched radical–chain process.[84] It is possible to represent the topology of the kinetic scheme (116)–(126) by the diagram shown in Fig. 12. The total chemical reaction proceeds by three routes, i.e. the first includes reactions (117) and (120), the second reactions (118) and (121) and the third reactions (117), (119) and (121).

The overall rate equation for the consumption of hydrogen peroxide is obtained by summation of the rates for each route.[83]

$$w = (2k_dk_{in\,1})^{1/2}(k_s + k_{s1})\,F_3[Ph]^{1/2}[H_2O_2]/(2F_3F_4 + F_5F_6)^{1/2}, \quad (127)$$

where

$$F_3 = k_r + k_{in}[H_2O_2],\ F_4 = k_{12}k_{in1}k_s[H_2O_2] + k_{13}(k_{s1}F_3 + k_rk_s),$$
$$F_5 = k_{22}k_s[Ph],\ F_6 = k_{in\,1}k_s[H_2O_2] + \sigma(k_{s1}F_3 + k_rk_s). \quad (128)$$

It may be shown that on satisfying the condition

$$[Ph] \gg 2F_3F_4/(k_{22}k_sF_6) \quad (129)$$

chain termination by substrate radicals according to reactions

(124)–(126) predominates. In this case equation (127) is transformed into (130).

$$w = (2k_d k_{in\,1})^{1/2}(k_s + k_{s1})\,(k_{22}k_s)^{-1/2}F_3[H_2O_2]/F_6^{1/2}. \quad (130)$$

However from this expression a first order equation with respect to peroxide, compatible with the experimental data, may be derived when $k_{in} = 0$ and $k_{in1} = 0$ [i.e. reactions (120) and (121) for the chain decomposition of H_2O_2 at any reaction centre do not play an appreciable role], which contradicts the result given in section V.

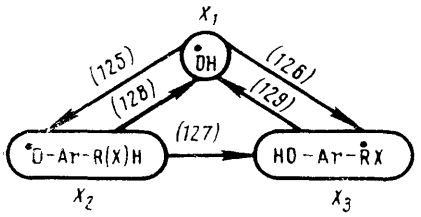


Figure 12. Diagram representing the topology of the kinetic scheme for the oxidation of phenolic compounds with hydrogen peroxide.

At the same time under conditions the reverse of (129) chain termination by hydroxyl radicals [reactions (122) and (123)] must predominate and the reaction rate will be described by Eqn. (131), following from (127).

$$w = (k_d k_{in\,1})^{1/2}\,(k_s + k_{s1})\,F_3\,[Ph]^{1/2}[H_2O_2]/F_4^{1/2}. \quad (131)$$

Partial reaction orders with respect to peroxide and to substrate may be obtained from the equation given and correspond to the results of experiments. This points in favour of the hypothesis on the preference under selected experimental conditions (see section V) for chain termination by reactions (122) and (123). In reality is follows from Eqn. (131) that the reaction order with respect to substrate is $^1/_2$, but with respect to peroxide it may be less, equal to or greater than 1 depending on the peroxide concentration and the values of the rate constants for the individual reactions (117)–(123). Such partial reaction orders were observed on oxidation of lignosulphonic acid, vanillyl alcohol and guaiacol. It may be shown that the rate equations obtained for these processes (see section V) are partial instances of the general dependence (131).

For example $k_r = 0$ in the system lignosulphonic acid–hydrogen peroxide (this is indicated by kinetic data on the oxidation of initial and methylated LSA, see Section V). Under this condition Eqn. (131) is in fact transformed into (107).

It follows from the data given in Section V on the change of functional composition of the products that $k_{in} = 0$ for the oxidation of vanillyl alcohol with hydrogen peroxide. In this case, allowing for the condition (86), Eqn. (131) is simplified to (87).

Finally, on oxidising guaiacol, which has only one reaction centre due to the absence of a side chain, it is possible to set rate constants k_r and k_{s1} to zero. Eqn. (131) is then transformed into (65). This confirms the correctness of Eqn. (131), which may aid (by drawing on results obtained by other methods) an adequate choice for the kinetic scheme and the corresponding expressions for reaction rates.

2. Analysis of a kinetic scheme at an arbitrary chain length

On oxidising certain phenolic compounds (vanillin, phenolic carboxylic acids) with hydrogen peroxide a first order is retained with respect to H_2O_2 while the order with respect to the organic substance may vary depending on the reaction conditions. This is not explained within the framework of the long-chain approach.

It is possible to analyse the kinetic scheme for the process at arbitrary chain length by the method of quasi-steady-state concentrations. However it is impossible to solve the system of nonlinear equations for the quasi-steady-state in explicit form in the present case consequently it was proposed to reduce it from a stationary reaction rate to a kinetic polynomial.[85] Application of such an approach to the kinetic scheme (116)–(123) enables the following polynomial to be obtained in the form represented by the equation:

$$F_7^2F_8 = c_1 + c_2/[H_2O_2] + c_3F_7F_8 + c_4F_7 + c_5[Ph]\,F_7/k_d, \quad (132)$$

where

$$c_1 = k_{in}k_{in\,1}(k_s + k_{s1})^2(k_{12}k_{13})^{-1},\ c_2 = k_r k_{in\,1}(k_s + k_{s1})^2(k_{12}k_{13})^{-1},$$
$$c_3 = -(k_s + k_{s1})\,k_r k_{12}^{-1},\ c_4 = (k_{in}/k_{12} + k_{in\,1}/k_{13})\,(k_s + k_{s1}),$$
$$c_5 = -(k_{in}k_{s1}/k_{12} + k_{in\,1}k_s/k_{13}),$$
$$F_7 = w\,[H_2O_2]^{-1}[Ph]^{-1},\ F_8 = wk_d^{-1}[H_2O_2]^{-1} - 1. \quad (133)$$

The kinetic polynomial (132) may be used in the analysis of the results obtained for discriminating between the kinetic hypotheses and in the choice of a variant of the kinetic scheme (116)–(123) for appropriate experiment. The following partial cases are considered.

1. If rearrangement of phenoxyl radicals into radicals with an unpaired electron in the side chain (119) is not feasible then substitution of $k_r = 0$ in polynomial (132) leads to the expression

$$F_7^2F_8 = c_1 + \left\{c_4\frac{w}{[H_2O_2]} + \frac{c_5}{k_d}\left(\frac{w}{[H_2O_2]}\right)^2\right\}\frac{1}{[Ph]} \quad (134)$$

In this case the dependence of reaction rate on the concentration of phenolic compound (at constant initial H_2O_2 concentration) must be linear in the coordinates of Eqn. (134) and enables exclusion of Eqn. (119) from the kinetic scheme (Table 5).

2. If $k_r = 0$ and $k_{in1} = 0$ also, i.e. the radicals with an unpaired electron in the side chain do not cause decomposition of hydrogen peroxide (121), then allowing for (133) $c_1 = 0$ and expression (134) reduces to Eqn. (135). It also follows from this that the experimental data in the coordinates of Eqn. (134) must be described by a straight line passing through the origin of coordinates.

$$F_7F_8 = c_4 + (c_5k_d^{-1}[H_2O_2]^{-1})\,w. \quad (135)$$

In this case the relationship between reaction rate and the concentration of the phenolic compound (at constant initial H_2O_2 concentration) must be linear in the coordinates of Eqn. (135). The passing of the straight line of (134) through the origin indicates fulfilment of the conditions $k_r = 0$ and $k_{in1} = 0$ and enables reactions (119) and (121) to be excluded from the overall kinetic scheme (Table 5).

3. If the condition $k_{s1} = 0$ is fulfilled in addition to $k_r = 0$ and $k_{in1} = 0$ then $c_5 = 0$ and Eqn. (135) is transformed into

$$wF_8/[H_2O_2] = (k_{in}k_s/k_{12})\,[Ph]. \quad (136)$$

It also follows from this that the experimental straight lines must be parallel to the abscissa axis in the coordinates of Eqn. (135) and must pass through the origin in the coordinates of Eqn. (134). Linearity of the experimental data in the coordinates of Eqn. (136)

combined with the line of (135) being parallel to the abscissa axis and the line of (134) passing through the origin indicates that the conditions $k_r = 0$, $k_{in1} = 0$ and $k_{s1} = 0$ are fulfilled and reactions (118), (119) and (121) may be excluded from the overall kinetic scheme (Table 5).

Table 5. Discrimination between kinetic hypotheses when oxidising phenolic compounds with hydrogen peroxide in aqueous solution.

Variant number	Determining conditions	Linear relationships	Discriminating reactions
1	$k_r = 0$	(134)	(119)
2	$k_r = 0$, $k_{in\,1} = 0$	(134) *. (135)	(119). (121)
3	$k_r = 0$, $k_{in\,1} = 0$, $k_{s\,1} = 0$	(134) *. (135) **. (136) *	(118). (119). (121)
4	$k_{in\,1} = 0$	(137)	(121)
5	$k_{in} = 0$	(138)	(120)

*The straight line in the coordinates of the given equation passes through the origin.

**The straight line in the coordinates of the given equation is parallel to the abscissa axis.

4. If only the condition $k_{in1} = 0$ is fulfilled then polynomial (132) allowing for (133) reduces to the equation

$$F_7F_8 = c_4 + (c_3/[H_2O_2] + c_5/k_d)\,F_8. \qquad (137)$$

Linearity of the data in the coordinates of Eqn. (137) indicates the fulfilling of the condition $k_{in1} = 0$ and points in favour of excluding reaction (121) from the overall kinetic scheme (Table 5).

5. If there is no decomposition of hydrogen peroxide by phenoxyl radicals, i.e. $k_{in} = 0$, then when $k_{ap} \gg k_d$ the kinetic polynomial (132) is transformed into the linear relationship

$$[Ph]/(k_{ef}^2[H_2O_2]) = (c_6 - c_7) + c_8(k_{ef}/[Ph]),$$

Where

$$c_6 = \{k_{in\,1}/k_{13} + k_r/(k_{12}[H_2O_2])\}\,k_{12}k_{13}\,(k_dk_{in\,1}k_r)^{-1}(k_s + k_{s1})^{-1},$$

$$c_7 = k_{s1}k_{12}\,(k_dk_r)^{-1}(k_s + k_{s1})^{-2},$$

$$c_8 = k_{12}k_{13}\,(k_dk_{in\,1}k_r)^{-1}(k_s + k_{s1})^{-2}. \qquad (138)$$

Linearity of the experimental data in the coordinates of Eqn. (138) indicates that $k_{in} = 0$ and points in favour of the exclusion of reaction (120) from the experimental scheme (Table 5).

The analysis of the kinetic polynomial (132) enables a purpose-directed discrimination to be made between kinetic hypotheses and may facilitate appreciably the choice by experiment of an appropriate variant of the kinetic scheme (116)–(123). Such an approach enables a simplified kinetic scheme of the actual process being investigated to be obtained from the complete scheme (116)–(123) by discarding individual reactions which make little contribution to the kinetics of the process.

What has been said enables the kinetic polynomial (132) to be used for the analysis of the kinetic scheme for the oxidation of phenolic compounds with hydrogen peroxide and may give desirable information on the mechanism of the process under investigation. This is illustrated by some examples.

When oxidising guaiacol with hydrogen peroxide linear relationships are observed for (134), (135) and (136). The straight lines in the coordinates of (134) and (136) pass through the origin of coordinates (Fig. 13, *1*) and (Fig. 14, *3*) and the straight line in coordinates of Eqn. (135) is parallel to the abscissa axis (Fig. 14, *1*). This corresponds to case 3 (Table 5) and indciates that reactions (118), (119) and (121) do not play a significant role in this system. In reality the structure of the guaiacol molecule and the change in its functional composition in the process of peroxide oxidation (see Section V) confirm this conclusion. What has been said enables exclusion of reactions (118), (119) and (121) from the kinetic scheme (116)–(123) and is in agreement with the scheme for the oxidation of guaiacol considered in Section V. When $k_r = 0$, $k_{in1} = 0$ and $k_{s1} = 0$ the general Eqn. (132) reduces to expression (63).

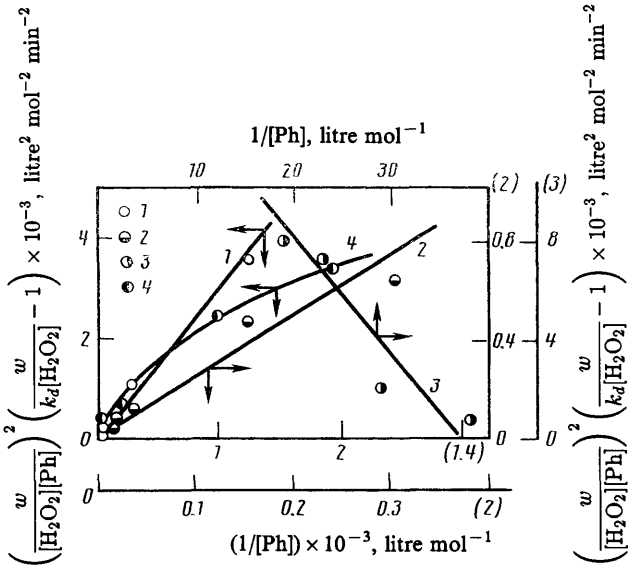


Figure 13. Relationship of the rates of oxidation with hydrogen peroxide of *1*, guaiacol, *2*, vanillin, *3*, LSA and *4*, ferulic acid to the concentration of phenolic compound in the coordinates of Eqn. (134) at 70 °C.[22,76,81]

Similarly when oxidising ferulic acid with hydrogen peroxide the relationship (134) is not linear (Fig. 13, *4*) but relationship (137) is linear (Fig. 15, *1*) which corresponds to case 4 (Table 5). The latter indicates that induced decomposition of H_2O_2 by reaction (121) does not occur in practice in the system being investigated. This enables reaction (121) to be excluded from the kinetic scheme (116)–(123) and is in agreement with the oxidation scheme for phenolic carboxylic acids given in Section V. When $k_{in1} = 0$ the overall Eqn. (132) is transformed into expression (97).

Investigation of the kinetics of the interaction of H_2O_2 with LSA and its methylated derivatives showed that in this system chain decomposition of peroxide by radicals in the side chain and by phenoxyl radicals occurs (see Section V). In this case a linear relationship was observed for (134) while the straight line did not pass through the origin of coordinates (Fig. 13, *3*). This

corresponds to case 1 (Table 5) and indicates that reaction (119) does not play an appreciable role in the system under investigation. What has been stated enables exclusion of reaction (119) from the overall scheme (116)–(123) and is in agreement with the kinetic scheme for the oxidation of LSA considered in Section V.

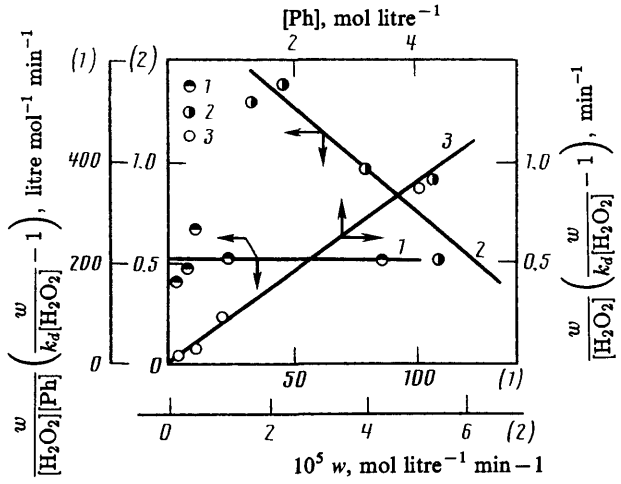


Figure 14. Relationship of the reaction rates of hydrogen peroxide with *1*, *3*, guaiacol and *2*, vanillin to their concentrations in the coordinates of Eqn. (135) *1*, and *2*, and of Eqn. (136) (*3*) at 70 °C and a hydrogen peroxide concentration of 1.06 mmol litre^{-1}.[22,76]

When oxidising vanillin with hydrogen peroxide a linear relationship was observed for (134) and (135). Although the straight line drawn from the experimental data in the coordinates of Eqn. (134) passes through the origin of coordinates, the straight line in coordinates of Eqn. (135) is not parallel to the abscissa axis (Fig. 13, *2*; Fig. 14, *2*) This corresponds to case 2 (Table 5) and indicates that reaction (119) and the decomposition of H_2O_2 by radicals with an unpaired electron on the carbon atom of the carbonyl group (121) do not make significant contributions to the kinetics of the process. These conclusions are confirmed by data on the kinetics for the decomposition of hydrogen peroxide in solutions of benzaldehyde, guaiacol, and mixtures of them (see Section V). Consequently reactions (119) and (121) may be excluded from the overall kinetic scheme in this case which is in agreement with the scheme given in Section V for the oxidation of vanillin. When k_r = 0 and k_{in1} = 0, the general Eqn. (132) reduces to expression (71).

Analysis of the functional composition of the oxidation products of vanillyl alcohol with hydrogen peroxide showed that the content of phenolic hydroxyls and methoxyl groups was practically unchanged in the oxidation process, while the alcohol is oxidised to a carbonyl group (see Section V). This indicates that the decomposition reaction (120) does not make an appreciable contribution to the kinetics of the process. The linearity of relationship (138) (Fig. 15, *2*) confirms this conclusion and enables assignment of this system to case 5 (Table 5). Reaction (120) may therefore be excluded from the overall kinetic scheme (116)–(123) in agreement with the oxidation scheme for vanillyl alcohol represented in Section V. When k_{in} = 0 and allowing for (86) the overall Eqn. (132) is transformed into expression (87).

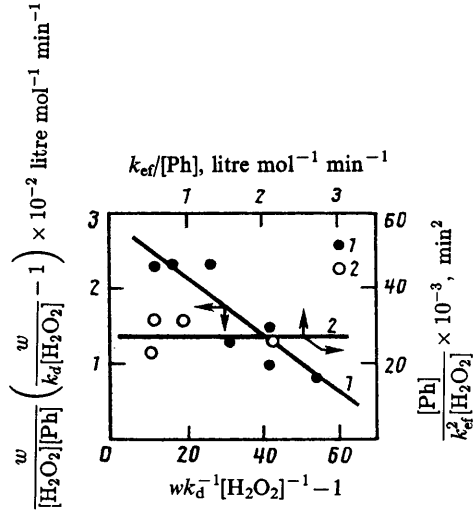


Figure 15. Relationship of the rates of oxidation with hydrogen peroxide of *1*, ferulic acid and *2*, vanillyl alcohol to reactant concentration in the coordinates of *1*, Eqn. (137) and *2*, Eqn. (138) at 70 °C.[78,81]

The rate equations given in Section V for the oxidation of phenolic compounds with hydrogen peroxide are partial cases of the general relationship (132) obtained by analysis of the kinetic scheme (116)–(123). This confirms the correctness of the chosen kinetic schemes to describe the oxidation processes of phenolic compounds with hydrogen peroxide in aqueous medium.

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