KINETICS AND MECHANISM OF OXIDATION OF SOME ORGANIC MOLECULES

SUMMARY

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Chem
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1. OXIDATION OF MONOHYDRIC PHENOLS BY ALKALINE HEXACYANOFERRATE (III).

The kinetics of oxidation of monohydric phenols (phenol and substituted phenols, vanillin and eugenol) by alkaline hexacyanoferrate (III) has been studied in methanol - water mixtures. The reactions showed a first order dependance on the concentrations of each - substrate, oxidant and alkali.

The rates of these reactions showed a decrease, with increasing proportions of methanol, that is, with a decrease in the dielectric constant of the medium. The role of the solvent has been rationalised on the basis of the dielectric constant, indicating that the reactions under consideration involved ions of the same sign.

The effect of changes in temperature on the rates of the reactions has been studied, and the activation parameters have been evaluated.

The presence of radical intermediates in the rate determining step of the reaction has been detected by esr spectroscopy.

The reaction pathway has been mechanistically visualized as proceeding via the formation of a radical intermediate in the rate determining step. The radical then undergoes further reaction to yield coupled products. The products were characterized by analytical and spectral methods.

2. OXIDATION OF DIHYDRIC PHENOLS BY ALKALINE HEXACYANOFERRATE (III).

The kinetics of oxidation of dihydric phenols (catechol, resorcinol, orcinol and quinol) by alkaline hexacyanoferrate (III), has been investigated in methanol - water mixtures. The reactions showed a first order dependence on the concentrations of each - substrate, oxidant and alkali.

Increasing proportions of methanol resulted in a decrease in the rate of the reaction. Plots of log k_{obs} against the reciprocal of the dielectric constant were linear, with negative slopes. This showed that the reactions under consideration involved ions of the same sign.

The rate of the reaction was enhanced, with an increase in the temperature of the medium. The activation parameters have been evaluated.

The presence of radical intermediates was detected by esr spectroscopy.

The mechanism of the reaction involved the formation of a radical intermediate in the rate determining step. Further oxidation of the radical yielded either the quinone, or resulted in the formation of coupled products. These products were obtained in good yields, and were characterised by analytical and spectral methods.

3. OXIDATION OF TRIHYDRIC PHENOLS BY ALKALINE HEXACYANOFERRATE (III).

The kinetics of oxidation of pyrogallol and phloroglucinol by alkaline hexacyanoferrate (III) has been studied in methanol - water mixtures. The reactions showed a first order dependence on the concentrations of each - substrate, oxidant and alkali.

The rate of the reaction was influenced by a change in the solvent composition of the medium. Plots of log k_{obs} against the reciprocal of dielectric constant were linear, suggesting that the reactions under consideration were of the ion-ion type.

The rate of the reaction was increased, with an increase in the temperature of the reaction medium, and the activation parameters have been evaluated.

The presence of radical intermediates was detected by esr spectroscopy.

The mechanism of the reaction involved the formation of a radical intermediate in the rate determining step. Further oxidation of the radical yielded either the extended quinone, or resulted in the formation of coupled products. These products were characterized by analytical and spectral methods.

4. OXIDATION OF NAPHTHOLS BY ALKALINE HEXACYANOFERRATE (III).

The kinetics of oxidation of α-naphthol and β-naphthol by alkaline hexacyanoferrate (III), has been investigated in methanol - water mixtures. The reactions showed a first order dependence on the concentrations of each - substrate, oxidant and alkali.

The rate of the reaction was found to increase with increasing amounts of methanol, that is, with a decrease in the dielectric constant of the medium.

The rate of the reaction was enhanced, with an increase in the temperature of the medium. The activation parameters have been evaluated.

The presence of radical intermediates has been detected by esr spectroscopy.

The mechanism of phenol coupling involves the formation of a radical intermediate in the rate determining step of the reaction. The radical intermediate undergoes rapid and irrversible coupling to give the products. These products have been isolated and characterized by analytical and spectral methods.

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I certify that the thesis entitled "KINETICS AND MECHANISM OF OXIDATION OF SOME ORGANIC MOLECULES" submitted by Miss Mitra Bhattacharjee for the Degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by her under my supervision. She has been duly registered, and the thesis presented is worthy of being considered for the Award of the Ph.D. Degree. This work has not been submitted for any Degree of any other University.

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CONTENTS

Discussion

INTRODUCTION

Metal ion oxidants can function either as one-equivalent or two-equivalent reagents. One-equivalent oxidants are those which accept a single electron by direct transfer or by interaction with a hydrogen atom. Two-equivalent oxidants can accept two electrons from the substrate.

In one-equivalent redox processes, the change of valency can be brought about by either an inner-sphere or an outer-sphere mechanism (1).

1. Inner-sphere mechanism:

The inner-sphere or bonded mechanism envisages a direct contact between the oxidant and the reductant, and the transition state is characterised by a ligand which is bonded to both metal ions. It can therefore act as a bridge between them for the transfer of an electron. The typical reaction is (2):

$$Cr^{2+}(aq) + (NH_3)_5\ Co^{III}\ Cl^{2+} \longrightarrow$$

$$CrCl^{2+}(aq) + Co^{2+}(aq) + 5\ NH_3$$

The formation of an inner-sphere transition state would lead to considerable distortion of the ions, which may thus assist electron transfer by reducing the energy terms involved. In order that an inner-sphere mechanism can operate, the ligand present should behave in a bidentate manner.

The ligand must possess available pi-orbitals, and one of the reagents involved must have a ligand which can be easily displaced.

2. Outer-sphere mechanism:

Outer-sphere electron exchange reactions constitute the simplest class of electron transfer reactions. In an outer-sphere mechanism, the inner co-ordination shell of both reagents is preserved intact in the transition state. Since the metal-ligand distances will be affected by valency change, some distortion of the inner shells would occur,but no metal-ligand bond would be broken or formed.

The essential steps in these reactions would be:

(a) the approach of two reagent ions, which may be aided or hindered by electrostatic forces;

(b) before electron transfer can occur, two conditions must be obeyed (3), in accordance with the Franck-Condon principle:

(i) the electron transfer must not alter the energy of the system. This electron transfer occurs in a very short time, and the only possible loss or gain of energy would be by radiation. Electron transfer can occur only if the oxidant and reductant have been vibrationally excited to the same total energy. Thus, when the valency states of a reagent are closely similar in bond energy and geometry, the outer-sphere process would be expected to be most facile.

(ii) the overall spin angular momentum should not be altered.

(c) the process of electron transfer itself. If the reagent complexes are sufficiently close and of suitable symmetry, such that there is some interaction between the orbitals involved in electron transfer, then the probability of electron transfer would be essentially unity. The requirement of orbital overlap can be related to the orbitals of the reagents. This would suggest that in octahedral complexes, t_{2g} electrons might be more easily transferred than e_g electrons which are in orbitals directed along the metal-ligand axis.

In order to establish that an outer-sphere or non-bonded electron transfer can occur from an organic compound to a metal oxidant, it is necessary to choose a suitable model system in which the probability of non-bonded mechanism would be a maximum, and that of the competing bonded process a minimum. The oxidant should be so chosen such that it possesses ligands which are slow or difficult to replace. The organic substrate should be so chosen such that it is not likely to displace ligands from a metal ion complex. Examples of such exchange-inert oxidants are the iron (III) tris-o-phenanthroline complex (4), $\mathrm{Ir\,Cl_6}^{2-}$ ion (5), Mn (III) tris-acetylacetone complex (6), ceric ions (7), and hexacyanoferrate (III) ion (8,9).

In the reactions of one-equivalent oxidants with organic substrates, the most frequently encountered oxidation process would seem to correspond to an electron transfer between substrate and oxidant, accompanied by the breaking of a C–H bond and loss of a proton to give a substrate radical, as for example (10):

$$\mathrm{Co\ (III)} + C_6H_5CH_3 \longrightarrow \mathrm{Co\ (II)} + C_6H_5CH_2^{\cdot} + H^+$$

It would therefore be expected that the loss of a proton would be slower than electron transfer, and hence would correspond to the rate determining step.

The presence of radicals may be inferred by their oxidation or reduction of added inorganic ions, or by their ability to cause polymerisation to occur with added monomer, as for example, acrylamide or acrylonitrile. If the radical is present in sufficiently high concentrations, its presence can be detected by electron spin resonance spectroscopy.

Although the radical may undergo many other processes, it is most probable that in the presence of an excess of oxidant, the radical will be oxidised further. Examples are known where the main mechanisms of this step may be:
(a) a non-bonded electron transfer (conversion of a neutral radical to a cation), as for example the oxidation of 2,6-dimethylphenol by hexachloroiridate ion (5), and the oxidation of hydroquinones by ferric ions (11); (b) bonded electron transfer or the transfer of a ligand from the oxidant to the

radical, as for example, the reduction of $IrCl_6^{2-}$ by Cr^{2+} ions(12); (c) redox substitution, in which the radical remains attached to the complex, as for example, the phenylation of the ferricenium complex (13,14); (d) redox addition, where the radical remains attached to the complex, as for example, the reaction of hexacyanoferrate(III) with isobutyraldehyde(15).

Oxidation of organic substrates with potassium hexacyanoferrate (III):

Potassium hexacyanoferrate(III), $K_3Fe(CN)_6$, is essentially a substitution-inert transition metal complex(16). It does not exchange its ligands at a rate fast enough to compete with rapid electron transfer. Therefore, oxidations by hexacyanoferrate(III) ion occurs by means of a non-bonded electron transfer or outer sphere process, whereby an electron is transferred from the substrate to the metal ion through the cyano ligand.

In acidic medium, potassium hexacyanoferrate(III) has been used for the oxidation of sulphur containing compounds (17-25), and very recently, for the oxidation of toluene and substituted toluenes (26-29), diphenylmethane and triphenylmethane (30), unsaturated systems (31-32), and polynuclear systems (33-34).

In neutral medium, potassium hexacyanoferrate(III) has been used for the oxidation of aliphatic amines(35).

In alkaline medium, potassium hexacyanoferrate(III), has been extensively used for the oxidation of various kinds of organic substrates such as aldehydes(36-40), ketones (36-37, 41-46), amines (47-53), alcohols and diols(54-62), sulfur compounds (63-69), acids (70-78), sugars (79-82), hydrazines (83-85), amino acids (86-87), acyloins (88-89), As(III)(90-92), hypophosphite(93-94), hydrocarbons (95), and phenols (96-98).

Oxidation of phenols

The chemical oxidation of phenols is complex, in that:

(a) it usually gives a mixture of products; and

(b) with the same phenol, different oxidants can yield quite different product mixtures.

In the presence of oxidizing agents, phenolic molecules can undergo either carbon-carbon or carbon-oxygen coupling to give a variety of products. Simple phenols can be linked at positions ortho and/or para to the hydroxyl group to yield several possible dimers; these can be further oxidized to produce trimers, polymers and quinonoid-type structures. In more complex polyhydroxy aromatic compounds, coupling of both types may occur —— intramolecular as well as intermolecular coupling. Substitution products and compounds resulting from coupling at benzylic positions may also be observed.

In most synthetically employed phenol coupling reactions, polymers are obtained as the side products; polmerization of phenols via oxidative coupling is an industrial process of great commercial importance.

The choice of a phenol coupling reagent will not only increase the synthetic utility of phenol oxidative coupling reactions, but will also indicate the manner in which various enzymes might catalyze such reactions. This would open up vast possibilities for a further probe into the study of important biological reactions, wherein the key step involves the oxidative coupling of phenols.

The oxidation of phenols by hexacyanoferrate(III) in alkaline medium would give the aryloxy anion. This anion can transfer an electron to hexacyanoferrate(III), resulting in the formation of an aryloxy radical. The radical would then be free to react, and the formation of coupled products is a distinct possibility.

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SCOPE OF THE PRESENT INVESTIGATION

SCOPE OF THE PRESENT INVESTIGATION

The present investigation is a detailed kinetic probe into the oxidation of phenols by potassium hexacyanoferrate(III) in aqueous alkaline medium, at constant ionic strength, using aqueous methanol as solvent. The purpose of this investigation has been to attempt to extend the scope of this extremely efficient and versatile one-electron oxidizing agent, in alkaline medium, and to explore and establish mechanistic pathways of reactions involving the oxidative coupling of phenols. The purpose of the present study was:

(a) to study the kinetics of oxidation of phenols;

(b) to determine the nature of oxidative coupling of phenols by product analysis; and

(c) to demonstrate the usefulness of potassium hexacyanoferrate(III) as a reagent which can bring about the oxidative coupling of phenols.

In the present investigation, the substrates chosen for purposes of oxidation by potassium hexacyanoferrate(III), in alkaline medium, have included:

1. Monohydric phenols (phenol and substituted phenols, vanillin and eugenol).
2. Dihydric phenols (catechol, resorcinol, orcinol and quinol).
3. Trihydric phenols (pyrogallol and phloroglucinol).
4. Polynuclear phenols (α-naphthol and β-naphthol).

All the reactions have been carried out under a nitrogen atmosphere, so as to ensure the absence of any aerial oxidation. For each oxidation reaction, the stoichiometry of the reaction has been determined. The concentrations of the substrate, oxidant and alkali have been varied, and the effects of these variations on the reaction rates have been studied. The solvent composition has been varied in order to study the effect of dielectric constant on the rate of the reaction. Changes in temperature of the reaction medium have been made, and the activation parameters have been evaluated. Changes in the ionic strength of the medium, and the effect of the addition of hexacyanoferrate(II) ions on the reaction rates, have been studied. The presence of radical intermediates has been detected and confirmed by ESR spectroscopy, polymerization reactions, and by the use of both, the IR and visible spectra. For each reaction, the products have been isolated and characterized by analytical and spectral methods. Based on the observed experimental results and on the nature of the products, mechanistic pathways have been proposed for the oxidation of all these phenols by potassium hexacyanoferrate(III) in alkaline medium.

PURIFICATION OF MATERIALS AND PREPARATION OF COMPOUNDS

Conductivity Water:

Conductivity water was prepared by the following method: tap water was distilled first with alkaline potassium permanganate and then redistilled with Merck "Pro Analysi" sulphuric acid from an all-glass vessel. This sample of double distilled water was further distilled from an all-quartz vessel (Sunvic, U.K.). The conductivity water thus prepared was utilised for the preparation of all the solutions used in the kinetic determinations.

Methanol:

Methanol (E. Merck) was distilled before use (bp 65^{o}C).

Sodium hydroxide:

BDH (AR) grade sample was used.

Potassium hexacyanoferrate (III):

BDH (AR) grade sample was used.

Potassium hexacyanoferrate (II):

BDH (AR) grade sample was used.

Sodium perchlorate:

Sodium perchlorate was prepared by neutralising 70% perchloric acid (E. Merck) with sodium hydroxide (BDH, AR grade). The solution was concentrated, when crystals of sodium perchlorate were obtained. The crystals were filtered, and recrystallised from water. The recrystallised product was dried over silica gel under vacuum. This sample of sodium perchlorate was used for the preparation of stock solutions which were employed for maintaining the ionic strength of the medium.

Substrates:

Phenol, eugenol and catechol were SD's samples. Resorcinol was an E. Merck sample. α-naphthol, β-naphthol, quinol, pyrogallol, phloroglucinol, orcinol, p-cresol, m-cresol, o-cresol, vanillin, salicylic acid, p-chlorophenol and m-aminophenol were all BDH samples. ~~p~~o-chlorophenol was a Riedel sample. Guaiacol, p-methoxyphenol, p-hydroxybenzoic acid, m-hydroxybenzoic acid, methyl eugenol, all the disubstituted and trisubstituted phenols were all SISCO samples. All these substrates were purified by distillation or repeated crystallizations until their boiling points or melting points, respectively, were in agreement with literature values. The purity of each of the substrates was checked by spectral analysis.

All ir spectra were recorded on an IR-297 (Perkin Elmer) spectrophotometer, uv spectra on an UV-26 (Beckman) spectrophotometer, nmr spectra on an EM-390 (Varian) 90 MHz NMR spectrometer, and esr spectra on an E-4 (Varian) EPR spectrometer.

The boiling points, melting points and the spectral data obtained for each of the substrates used, are summarised in Table I.

TABLE 1

Substrate (1)	Boiling Points or Melting Points(^{o}C) (2)	uv(nm) A=Alcohol M=Methanol (3)
Phenol	43 (mp)	210,270(A)
p-nitrophenol	115 (mp)	224 (A)
O-aminophenol	174 (mp)	232 (A)
m-aminophenol	123 (mp)	286 (A)
o-chlorophenol	175 (bp)	278 (A)
p-chlorophenol	217 (bp)	283 (A)
o-cresol	190 (bp)	273 (A)
m-cresol	201 (bp)	275 (A)
p-cresol	203 (bp)	280 (A)

(1)	(2)	(3)
o-methoxyphenol	204 (bp)	230 (A)
p-methoxyphenol	58 (mp)	225 (M)
o-carboxyphenol	159 (mp)	251 (A)
m-carboxyphenol	201 (mp)	236 (A)
p-carboxyphenol	214 (mp)	232 (A)
2, 4-dichlorophenol	210 (bp)	292 (M)
2, 3-dimethylphenol	75 (mp)	273 (M)
2, 5-dimethylphenol	73 (mp)	276 (M)
2, 6-dimethylphenol	49 (mp)	272 (M)
3, 4-dimethylphenol	66 (mp)	270 (M)
2, 4-dinitrophenol	115 (mp)	254 (M)
2,4,5-trichlorophenol	68 (mp)	296 (M)
2,4,6-trichlorophenol	70 (mp)	252 (A)
Vanillin	80 (mp)	279 (A)
Eugenol	253 (bp)	281 (A)
Catechol	105 (mp)	278 (A)
Resorcinol	110 (mp)	276 (A)
Orcinol	107 (mp)	281 (M)
Quinol	173 (mp)	294 (A)
Pyrogallol	133 (mp)	267 (M)
Phloroglucinol	216 (mp)	270 (M)
α-naphthol	94 (mp)	220 (A)
β-naphthol	123 (mp)	228 (A)

Kinetic method:

All the standard flasks and reaction vessels were of pyrex glass with well-ground stoppers. The reaction vessels used were stoppered conical flasks which were painted black on the outside to prevent any photochemical change. All the glass apparatus used were tested for loss of solvent, and the loss was found to be negligible. The standard flasks, reaction vessels and the pipettes used were standardised, using conductivity water, and the correction was found out and applied.

An electrically operated thermostatic water-bath was used. It was provided with sufficient thermal lagging, suitable heaters and stirrers with proper cooling arrangements for continuous work. Xylene-filled regulator, working in conjunction with an electronic relay, was used to maintain the required temperatures accurately, with fluctuations of not more than ± 0.1°C. The temperatures were recorded by means of an accurate sensitive thermometer, reading to tenths of a degree. The bath-liquid was water, covered with a layer of liquid paraffin to minimise evaporation of water and loss of heat due to radiation.

Spectrophotometers:

For absorption measurements, the spectrophotometers used were (a) Digital spectrophotometer type 106, MK II model (systronics), and (b) UV-26 (Beckman) UV-Visible spectrophotometer.

(a) The MK II model (systronics) spectrophotometer was a single beam spectrophotometer having a grating of 600 lines/mm, and a wavelength range from 340 nm to 960 nm. The nominal spectral slit width was 20 nm, constant over the entire range. The full scale deflection could be obtained over the wavelength range of 340 nm to 600 nm. By the addition of a red filter and interchanging of the phototube, the range could be extended to 960 nm. In order to ensure maximum sensitivity of the instrument, and to minimise the errors in measurements of optical density due to fluctuations in voltage, the spectrophotometer was connected to the mains through an external voltage-stabiliser. This was in addition to the in-built voltage-stabiliser within the instrument itself. The light source was a 15 watt tungsten lamp operated by a regulated power supply. The instrument was calibrated, as specified in the instruction manual, over the range of concentrations of K_2CrO_4 in KOH solutions, so as to verify Beer's law at 370 nm.

(b) The UV-26 (Beckman) UV-Visible spectrophotometer was a single monochromator, having a filter-grating of 1200 lines/mm, and a wavelength range from 190 to 900 nm.

This spectrophotometer had a thermostatic control arrangement and the absorbance value was displayed directly on the digital display and on the recorder. Photometric linearity was checked over the range of concentrations of K_2CrO_4 in KOH solutions, as specified in the instruction manual, so as to verify Beer's law at 370 nm.

Absorption cells:

The absorption cells were of 'Corning' glass and of 8 ml capacity for the spectrophotometer 106 MK II model (Systronics). Quartz cells of 5 ml capacity were used for spectral determinations with the UV-26 spectrophotometer (Beckman). All the cells used were thoroughly cleaned by aqueous ethanol and acetone, and dried before they were used for the spectral measurements. After the transfer of the solution to the cell, care was taken to see that no solution adhered to the outer surface of the cell. During the measurements, the cells were covered.

Solutions of hexacyanoferrate (III) in methanol-water mixtures (60-40 to 75-25 %, v/v) were prepared. The absorbance of each of these solutions was scanned over the range of wavelengths from 350 nm to 700 nm. The maximum absorption in each case was located at 420 nm (Fig.1). At this wavelength of 420 nm, the absorption

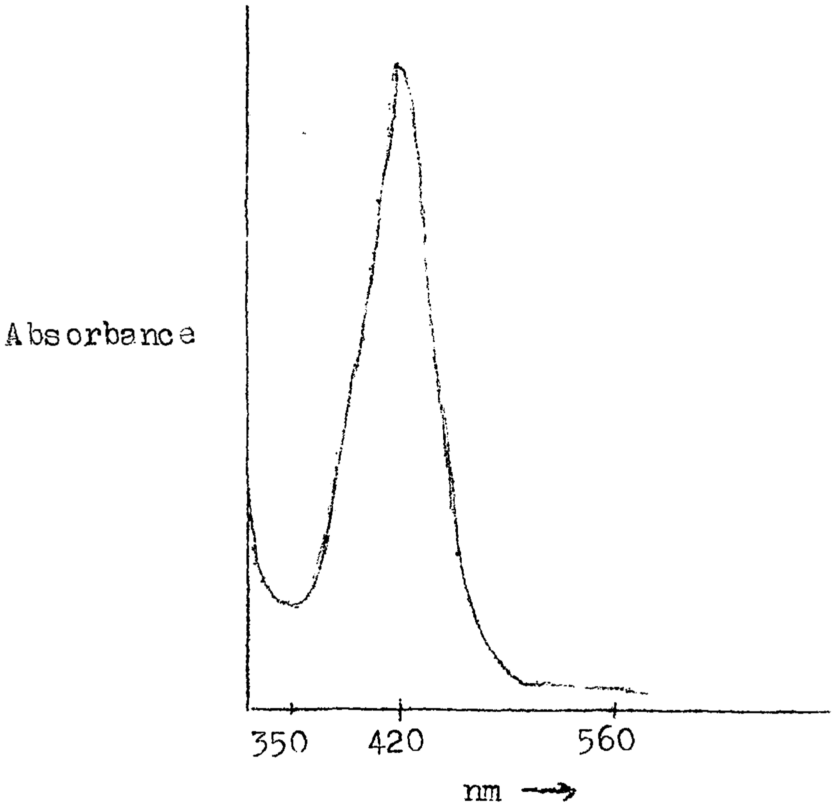


Fig. 1 - Plot of absorbance against wavelength (nm)

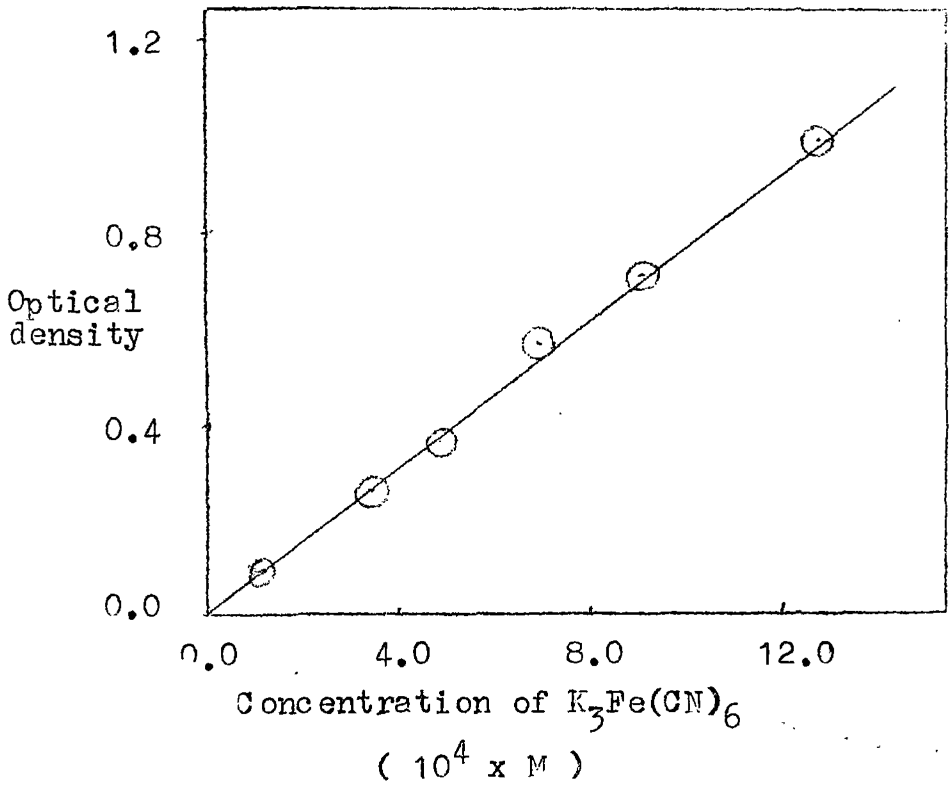


Fig. 2 - Verification of Beer-Lambert's Law. Plot of concentration versus optical density at 420nm .

due to $Fe(CN)_6^{3-}$ has been observed to be a maximum (1), the absorption due to $Fe(CN)_6^{4-}$ being negligible (2).

At 420 nm, Beer's law was obeyed over the range of concentrations of solutions used. A typical graph of the optical density against the concentration of $Fe(CN)_6^{3-}$ is shown (Fig.2).

In this investigation, all the optical density measurements were carried out at a wavelength of 420 nm.

Rate measurements

A known amount of the substrate was weighed accurately into a 10 ml standard flask and made up with the requisite quantities of methanol and water, so as to make the required molar solution. Potassium hexacyanoferrate (III) was accurately weighed out into a 10 ml standard flask, and dissolved in a small volume of water. The requisite amount of sodium hydroxide solution, whose strength had been determined, was added to maintain the required alkalinity. Sodium perchlorate was added so as to maintain a constant ionic strength of the medium. The solution was then made up in methanol and water. Sufficient time was allowed to compensate for any change of heat during dilution. The two reactant solutions were separately thermostated at the required temperature for 3 hours, under a nitrogen atmosphere. The solutions were then mixed in equal volumes. The reaction mixture was homogeneous throughout the duration of the reaction.

The progress of the reaction was followed by observing the disappearance of hexacyanoferrate (III). Readings were taken at regular intervals of time, by noting the decrease in optical density at 420 nm, spectrophotometrically.

All the kinetic experiments were carried out in duplicate or in triplicate, and the rate constants which were determined were found to be reproducible to within ± 1.5%.

Calculations:

(a) Rate constants:

For all the kinetic determinations, pseudo-first order reaction conditions have been used, wherein the concentration of the substrate has been taken in a very large excess over that of the concentration of the oxidant.

The pseudo-first order rate constant, k_{obs}, expressed as sec^{-1}, were calculated from the equation (3):

$$k_{obs} = \frac{2.303}{t} \log \frac{D_o}{D_t} \qquad \ldots\ldots\ldots \qquad (1)$$

where D_o was the initial optical density of the reaction mixture, and D_t was the optical density at time, t.

The logarithmic plots of optical densities against time were linear, and extrapolation to zero time gave the values of D_o .

The values of the second order rate constant , k_2 , expressed in M^{-1} s^{-1} , were computed by dividing the pseudo-first order rate constant (k_{obs}, s^{-1}) by the concentration of the substrate (M).

All values of rate constants were the average of two or more experiments, with agreement being within ± 1.5%.

(b) Thermodynamic activation parameters:

These parameters were determined from a study of the effect of temperature on the rate of the reaction.

The various parameters have been calculated as follows:

(i) Activation energy (E)

From the linear plot of log k_{obs} against the reciprocal of temperature (T),

$$\text{slope} = -\frac{E}{2.303\ R}$$

$$E = -\text{slope} \times 2.303\ R\ (\text{kJ mol}^{-1})$$

(ii) Frequency factor (A)

$$k_{obs} = A\ e^{-E/RT}$$

$$\log A = \log k_{obs} + \frac{E}{2.303\ \ RT}$$

(iii) Enthalpy of Activation ($\Delta H^{\neq}$)

$$\Delta H^{\neq} = E - RT$$

(iv) Entropy of Activation ($\Delta S^{\neq}$)

$$k_{obs} = \frac{kT}{h}\ e^{\Delta S^{\neq}/R}\ e^{-\Delta H/RT}$$

$$\Delta S^{\neq} = 2.303\ R \quad \log k_{obs} + \frac{\Delta H^{\neq}}{2.303\ RT} - \log \frac{kT}{h}.$$

where k is the Boltzmann constant, and h is the Planck's constant.

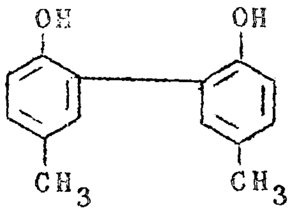
Stoichiometry:

Reaction mixtures containing the substrate and an excess of hexacyanoferrate (III), taken in a known solvent composition of methanol and water, containing the requisite amounts of sodium hydroxide and sodium perchlorate, were allowed to react to completion at a particular temperature. The hexacyanoferrate (III) which was left, was analysed spectrophotometrically at 420 nm. The individual stoichiometric equations are shown along with the reactions of each of the substrates with the oxidant.

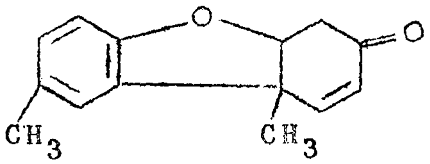
Product analysis:

(a) Products obtained from the oxidation of p-cresol

Stoichiometric amounts of p-cresol in 50% methanol (v/v), and $K_3Fe(CN)_6$ in 50% methanol (v/v), 0.5M NaOH and 0.5M $NaClO_4$, were mixed, and refluxed at $50^{\circ}C$ for 6h, under nitrogen. The reaction mixture was cooled, filtered, and the solvent removed. The filtrate was washed with ether, the ether layer separated, and the solution concentrated. TLC analysis gave three spots. Separation on a silica gel column, using varying proportions of hexane and chloroform (100:0 to 70:30, %, v/v) for elution, yielded three products. The first product, 1 , obtained in about 70% yield, was characterized as 2:2'-dihydroxy-5:5'-dimethyldiphenyl (mp and uv analyses), in agreement with literature data (4-5). The second product, 2 , obtained in 10-15% yield, was characterized as the ketone (5) The third product, 3 , obtained in 5-10% yield, was probably a trimer, and was not characterized.



(1)



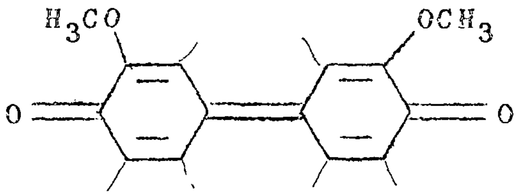
(2)

TRIMER

(3)

(b) Products obtained from the oxidation of guaiacol

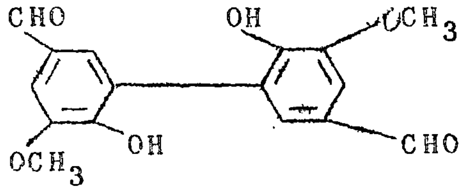
Guaiacol (2.0g) in 70% methanol(v/v), was mixed with 11.0g of $K_3Fe(CN)_6$ containing NaOH(0.05M), 70% methanol (v/v) and $NaClO_4$ (0.5M), and the mixture refluxed at 60°C for 3h under nitrogen. After cooling and filtration, the solvent was removed to give a red residue (0.072 g). The insoluble portion of the mixture was washed with chloroform, and after removal of the chloroform, a red residue (1.615 g) was obtained. The melting points of both these residues, was 245°C. IR analysis of both these residues, in chloroform, showed them to be identical with 3:3-dimethoxydiphenoquinone, 4 . A sharp band at $1640cm^{-1}$ was obtained, corresponding to the carbonyl stretching of the C=O groups in two rings of an extended quinonoid structure(6). The nmr spectrum of the product sample, in chloroform (internal standard TMS, sweep width 10 ppm) gave the OCH_3 peak at 6.1τ, and four doublets in the vinylic proton region at 3.20τ, 3.10τ, 2.30τ and 2.20τ. The structure of the product was confirmed to be 4.



(4)

(c) Products obtained from the oxidation of vanillin

Stoichiometric amounts of substrate and oxidant solutions in 70% methanol (v/v), NaOH(0.5M) and $NaClO_4$ (0.5M), were mixed at 35°C, and maintained under nitrogen for 24h. The reaction mixture was cooled, filtered and concentrated. The residue was extracted with ether, and the ether extract concentrated after drying over anhydrous $MgSO_4$. TLC analysis of the residue, using benzene as the developer, gave two spots. Separation on a silica gel column, using mixtures of hexane and chloroform in varying proportions (100:0 to 70:30, v/v) for elution, gave two products. The first product was obtained in 80% yield (mp 245°C). IR bands indicated: (a) the biphenyl (aromatic) structure (7); (b) phenolic absorptions at 3600, 1350 and 1200 cm^{-1}; (c) aldehydic absorptions at 3085, 2840, 2760 and 1700 cm^{-1}; (d) $\nu(OCH_3)$ band at 1020 cm^{-1}. The structure of this product was confirmed as divanillin, 5. The second product was a polymeric material, and was not analyzed.



(5)

(d) Product obtained from the oxidation of catechol

Stoichiometric amounts of the substrate and oxidant solutions in 70% methanol (v/v), NaOH(0.5M) and $NaClO_4$(0.5M), were allowed to react at 30°C for 24h, under a nitrogen atmosphere. The mixture was filtered. The filtrate was taken in ether, the ether layer separated, washed with water, and then evaporated. The solid residue which remained was analyzed for the product as follows:

(i) The product sample was reddish in colour;

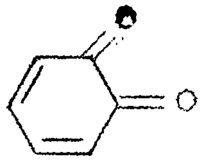
(ii) the melting point of the sample was 61°C;

(iii) on treatment with an alkaline solution of ethylenediamine, a deep red coloured solution was obtained, characteristic of o-benzoquinone (8). The formation of this colour with ethylenediamine is specific for quinone and quinone forming materials, except for anthraquinones and amino-substituted quinones (8);

(iv) IR analysis gave two sharp bands at 1680 cm^{-1} and 1660 cm^{-1}, corresponding to the presence of two carbonyl groups in the same ring, characteristic of o-benzoquinone (9). An absorption band of medium intensity between 1680 cm^{-1} and 1700 cm^{-1}, which was well separated from the main bands, was also obtained. This band had been earlier characterized as a typical band for o-quinone (10-11);

(v) The electronic spectrum of the product in ether gave three bands. The first band of strongest intensity was at 254 nm, the second band of medium intensity was at 368 nm, and the third band of weak intensity was observed in the visible region at 587 nm. These absorptions have been attributed to singlet-singlet $\pi-\pi^*$, $\pi-\pi^*$, and $n-\pi^*$ transitions, respectively, characteristic of o-benzoquinone(12). No absorption band was observed at 420nm, indicating that the product sample did not interfere with the kinetic measurements carried out at 420 nm.

Hence, the product of the oxidation reaction was confirmed to be o-benzoquinone, 6 (yield ~ 80%).



(6)

(e) Products obtained from the oxidation of resorcinol and orcinol

Stoichiometric amounts of the substrate and oxidant solutions, taken in 70% methanol (v/v), NaOH(0.05M), $NaClO_4$(0.5M), were mixed and allowed to stand at 30°C for 24h, under a nitrogen atmosphere. After cooling and filtration, the solvent was removed. The filtrate was extracted with ether, and the ether layer separated and concentrated.

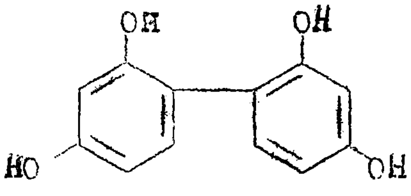
(i) Product from the oxidation of resorcinol

Spotting on TLC plates gave a single spot. The solid residue which was obtained in about 80% yield, was analyzed for the product (mp 310°C; mp of the crystalline tetramethyl derivative was 108°C). IR analysis gave a sharp band at 3350 cm^{-1}, and other bands which were superimposable on the spectrum of 3,3',5,5'-tetrahydroxybiphenyl, 7 (13). UV analysis of the sample in methanol gave the first band of strong intensity at 255 nm, and the second of lower intensity at 290 nm. These bands were probably due to $\pi-\pi^*$ transitions.

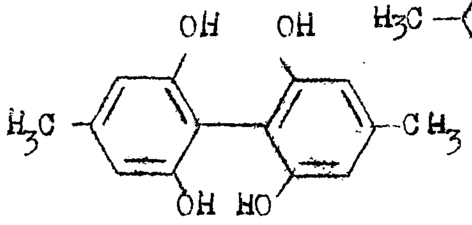
(ii) Product from the oxidation of orcinol

Spotting on TLC plates gave three spots. Separation on a silica gel column, using varying proportions(100:0 to 70:30,v/v) of hexane and chloroform for elution, gave three products. The first product, obtained in 70% yield, was characterized by mp (188°C), and by IR analysis (absorption bands at 3150, 3020, 1610, 1500, 1380, 1240, 1180, 840 cm^{-1}), and assigned the structure, 8 . The other products, each obtained in 10-15% yields, were polymeric materials, and were not analyzed. Compound 8 , in alkaline medium, was converted by aerial oxidation to 9 (14), obtained as yellowish-brown plates when recrystallized from ethanol (yield ~50%), and characterized by mp(230°C), and by

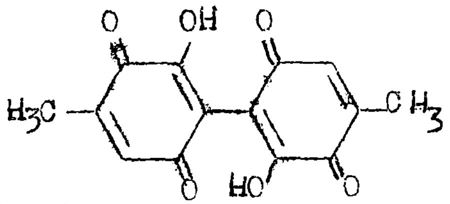
IR analysis.



(7)



(8)



(9)

(f) <u>Product obtained from the oxidation of quinol</u>

Stoichiometric amounts of substrate and oxidant solutions in 70% methanol(v/v), NaOH(0.5M) and $NaClO_4$(0.5M), were allowed to react at 30^{o}C for 24h, under a nitrogen atmosphere. The mixture was filtered. The filtrate was taken up in ether, the ether layer was separated, washed with water, and then evaporated at room temperature. The solid residue which remained was analyzed for the product as follows:

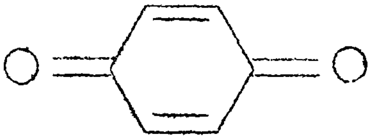
(i) the melting point of the sample was 116^{o}C;

(ii) on treatment with an alkaline solution of ethylenediamine, a deep yellow coloured solution was obtained, characteristic of p-benzoquinone (8);

(iii) IR analysis gave two sharp bands at 1670cm^{-1} and 1655cm^{-1}, corresponding to the presence of two carbonyl groups in the same ring, characteristic of p-benzoquinone (15-16). Pronounced shoulders on the lower frequency side of the main band have been observed between 1640 and 1650 cm^{-1} . This spectrum was compared with that of an authentic sample of p-benzoquinone, and found to be identical (15-16);

(iv) The electronic spectrum of the product sample in CCl_4 gave three bands. The first band of strongest intensity was at 245 nm, the second band of medium intensity was at 288 nm, and the third band of weak intensity was observed in the visible region at 440 nm. These absorptions have been attributed to singlet-singlet $\pi-\pi^*$, $\pi-\pi^*$, and $n-\pi^*$ transitions, respectively, characteristic of p-benzoquinone (17-19). No absorption band was observed at 420 nm, indicating that the product sample did not interfere with the kinetic measurements carried out at 420 nm.

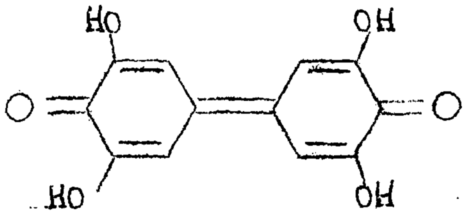
Hence, the product of the oxidation reaction was confirmed to be p-benzoquinone 10 (yield ~ 80%).



(10)

(g) Products obtained from the oxidation of pyrogallol.

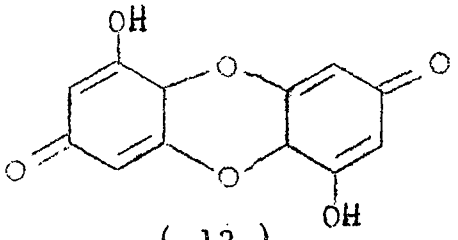
Pyrogallol (2.0g) in 70% methanol (v/v), was mixed with 11.0g of $K_3Fe(CN)_6$ containing NaOH(0.05M), 70% methanol (v/v) and $NaClO_4$ (0.5M), and the mixture refluxed at 60°C for 3h under nitrogen. After cooling and filtration, the solvent was removed to give a red residue (0.065g). The insoluble portion of the mixture was washed with chloroform, and after removal of the chloroform, a red residue (1.585g) was obtained. The melting points of both these residues was 240°C. IR analysis of both these residues, in chloroform, showed them to be identical with 3:3′:5:5′-tetrahydroxy-4:4′-diphenoquinone, <u>11</u>. A sharp band at 1640cm^{-1} was obtained, corresponding to the carbonyl stretching of the C=O groups in two rings of an extended quinonoid structure (6). The nmr spectrum of the product sample, in chloroform (internal standard TMS, sweep width 10ppm) gave the OH peak at 3.90τ, and four doublets in the vinylic proton region at 3.19τ, 3.10τ, 2.31τ and 2.20τ. The structure of the product was confirmed to be <u>11</u>.



(<u>11</u>)

(h) <u>Products obtained from the oxidation of phloroglucinol</u>

Stoichiometric amounts of substrate and oxidant solutions, taken in NaOH(0.05M), methanol(70%, v/v) and $NaClO_4$ (ionic strength adjusted to 0.5M) were mixed at 30^oC and maintained under a nitrogen atmosphere for 24h. After cooling and filtration, the solvent was removed. The residue was extracted with ether, dried over anhydrous Na_2SO_4 , and the ether extract concentrated. TLC analysis of the residue, using benzene as the developer, gave 2 spots. Separation on a silica gel column, using varying proportions of hexane and chloroform (100:0 to 70:30,%,v/v) for elution, yielded two products. The first product, obtained in 80-85% yield, was characterized by mp(250^oC). IR data [2960, 2910(ν_{OH}; H-bonded); 1640,1620($\nu_{C=O}$); 1480, 1380,1210(ν_{C-O}); 1130(ν_{as} for six membered rings as in 1,4-dioxan); 1030 and 920(ν_{C-O})] cm^{-1}, and PMR data in CCl_4 [τ 2.5(OH) and 5.0(tertiary protons)]. It was assigned the structure, 12, based on these data. This product, 12, provides an example of C-O bond coupling, as has been observed, in vivo, in the formation of dehydrodigallic and valonic acids(20). The second product was a polymeric material, and was not analyzed.



(12)

(i) Products obtained from the oxidation of naphthols

Stoichiometric amounts of the naphthols and the oxidant solutions in NaOH(0.05M), 70% methanol (v/v), and $NaClO_4$(0.5M), were mixed and refluxed at 60°C for 3h, under a nitrogen atmosphere. After cooling and filtration, the solvent was removed. The filtrate was washed with ether, and the ether layer separated. This was evaporated, and the solid residue which remained was analyzed for the product.

(i) Oxidation products of α-naphthol

Spotting on TLC plates gave three spots. Separation on a silica gel column, using varying proportions (100:0 to 70:30, v/v) of hexane and chloroform for elution, gave three products in yields varying from 25-30% each. These products, structures **13**-**15**, were characterized by IR analysis, and were observed to be identical to the products which were obtained from the ferric chloride oxidation of α-naphthol(21-22), wherein all three possible carbon-carbon coupled products had been characterized.

(ii) Oxidation products of β-naphthol

Spoting on TLC plates gave three spots. Separation on a silica gel column, using varying proportions of hexane and chloroform (100:0 to 70:30, v/v), for elution, gave the major product in about 80% yield (mp 239°C). This product was characterized by IR analysis (absorption bands at 3040, 1630, 1600, 1500, 1460 cm^{-1} , and other bands which were characteristic of dinaphthylene dioxide) and assigned the structure, 16 . Compound 16 had been characterized in an earlier investigation(23). The other products were probably some quinol ethers, and these were not analyzed. The significance of compound 16 was that the coupling occurred through the two oxygen atoms to yield a carbon-carbon coupled product. The oxidation of β-naphthol by hexacyanoferrate (III) had been earlier shown to yield carbon-oxygen coupled products(24-25).

Tests for Radical formation:

All the oxidation reactions investigated were observed to proceed via radical intermediates formed in the rate determining step of these reactions. The presence of these radical intermediates was confirmed by the following tests:

(a) Reduction of inorganic ions, $R\cdot + M^{(n+1)+} \longrightarrow R^{+} + M^{n+}$. Mercuric chloride was easily reduced by these radicals to insoluble mercurous chloride, which was relatively inert towards reoxidation by the oxidant, M^{n+}.

(b) Polymerisation of an added olefinic monomer, such as acrylonitrile or acrylamide.

Acrylamide and the substrate were placed in the lower part of a Thunberg tube (26), with the oxidant solution placed in the upper portion of the tube. The system was evacuated, filled with dry nitrogen, and then sealed. The two solutions were mixed and allowed to stand at the reaction temperature. After 30 minutes, there was the formation of a white opalescence, indicating the formation of a polymer.

ESR measurements

The presence of radical intermediates formed in the rate determining steps of these reactions was detected and confirmed by esr measurements.

Using the requisite reaction conditions, the radicals were generated in a flow system by mixing the substrate and oxidant, by volume, in an esr sample tube just outside the cavity of the spectrometer. The mixture was placed under high vacuum, in order to expel dissolved oxygen, and the sample tube was placed in the cavity of the spectrometer. The conditions for obtaining the spectrum at room temperature were as follows:

Scan range 4000 G,
field set 3300 G,
modulation amplitude 6.3 G,
microwave frequency 9.45 GHz,
time constant 0.3 sec,
scan time 4min.

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CHAPTER 1

KINETICS OF OXIDATION OF MONOHYDRIC PHENOLS*

The oxidation of monohydric phenols has been studied by several workers, using variety of oxidizing agents.

EARLIER WORK:

Phenol and substituted phenols have been oxidized to coupled products, by a variety of oxidizing agents such as acidic $KMnO_4$(1), LTA(2-3), $PbO_2/HOAc$(4-6), oxygen(7-10), photooxidation (11), autooxidation (12), anodic oxidation(13), $KI/NaHCO_3$(14), peroxydisulfate(15-18), chlorine dioxide(19), $Cl_2/ZnCl_2$ and $SO_2Cl_2/ZnCl_2$(20), enzymatic oxidations(21-22), H_2O_2, $FeSO_4/H^+$(23), Cu(II)-o-toluate(24), Ag-phenolate(25), potassium trans-1,2-diaminecyclohexane tetraacetate manganate (III) (27), $FeCl_3$(28), and by benzoyl peroxide(29).

Phenols and substituted phenols have been converted to quinones by oxidizing agents such as acidic $KMnO_4$(30), LTA(30-31), acid iodate(32-33), acid periodate (34-36), acid bromate(37), peroxydisulfate(38-39), peroxydisulfate catalyzed by silver ions(40-42), V (V) and Cr(VI)(43),

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* S.N. Singh, M. Bhattacharjee and M.K. Mahanti, Bull. Chem. Soc. Japan, 56 , 1855 (1983).

Tl(III) acetate (44), chloramine-T(45), Fe(III)-1, 10-phenanthroline complex (46), Fremy's salt(47-48), phenyl iodosoacetate(49), Hg^{2+} in acid medium(50).

The oxidation of 2,6-dimethylphenol had yielded the diphenoquinone as the major product, when the oxidation was carried out by LTA(2), $FeCl_3$(51-52), CrO_3/HOAc(51-53), acidic dichromate(51), ammonium persulfate(51), peroxydisulfate catalyzed by silver ions(54), peroxydisulfate/Cu(II)-salt(55), Ag_2O(56), MnO_2(52), $MnO_2/PbO_2/Ag_2O$(57), Ag(II)-picolinate(58), $H_2O_2/FeSO_4$, H^+ (23), H_2O_2/Cu-salt(55), acetyl peroxide(59), benzoyl peroxide(29,59), t-butyl peroxide(29), t-butyl hydroperoxide(60), HNO_3(51), Cl_2(51), Br_2(51), ClO_3F/OH^- in both homogeneous and heterogeneous phases (61), Cu(II)-o-toluate(24), 3-Bromocamphor/Cu-metal(62), NaOCl/Cu(II)-salt(55), air in the presence of azobisisobutyronitrile(7), O_2/Cu(I)-salt, pyridine(63), air/CuCl in pyridine(64), O_2/Cu(II)-salt(52, 65-66), O_2/perbenzoic acid (67), O_2/enzyme at pH 4.0 (68), and by 3,5,3′, 5′- tetramethyldiphenoquinone(69).

The oxidation of 2,4,6-trichlorophenol had yielded trimeric products, when oxidized by sodium phenolate/I_2, acetone (70), $CuCl_2$/pyridine(25), and by Ag-phenolate (25,71).

The oxidation of guaiacol had yielded coupled products. For example, the anodic oxidation of guaiacol had resulted in the formation of para-para coupled products (72). Later investigations on the oxidative coupling of guaiacol were carried out using oxidants such as H_2O_2/enzyme (73), Ag_2O(74), O_2/enzyme(74) at pH 4.8, hexacyanoferrate(III) in alkaline medium(74), and by activated MnO_2(75). The oxidation of guaiacol by sodium periodate yielded o-benzoquinone in about 65% yield (76); but with excess of periodate, the quinone was slowly oxidized to cis-cis muconic acid. The same product, o-benzoquinone, was formed when guaiacol was oxidized by periodic acid(77).

The oxidation of vanillin by $FeCl_3$(78), H_2O_2/enzyme (79), $Na_2S_2O_8$/Fe-salt(80), and by O_2/laccase(81), had yielded ortho-ortho coupled products. The oxidation of p-substituted guaiacyl compounds had resulted in the formation of diphenyl compounds, wherein the coupling had occurred at the position ortho to the hydroxyl group(82).

The oxidation of eugenol had yielded ortho-ortho products, when the oxidation was performed by $FeCl_3$(83-85), and by O_2/enzyme(85-87).

Potassium hexacyanoferrate(III) in alkaline medium has been used for the oxidation of p-cresol(88-93), p-methoxyphenol(90), 2:4-di-tertiary butylphenol(94), and p-aminophenol (95).

PRESENT WORK

The kinetics of oxidation of monohydric phenols, by hexacyanoferrate(III) in alkaline medium, has not received much attention. The present work is a detailed kinetic investigation of the oxidation of monohydric phenols (phenols and substituted phenols, vanillin and eugenol) by potassium hexacyanoferrate (III), in alkaline medium, at constant ionic strength, under a nitrogen atmosphere, using aqueous methanol (50%, v/v) as solvent.

Stoichiometry (vide 'Experimental'):

The stoichiometry of the reactions were determined to be:

(a) For Phenol

$$2C_6H_5OH + 2Fe(CN)_6^{3-} + OH^- \longrightarrow 2C_6H_5O + 2Fe(CN)_6^{4-} + H_2O + H^+ .$$

(b) For guaiacol

$$2C_7H_8O_2 + 4Fe(CN)_6^{3-} + OH^- \longrightarrow C_{14}H_{12}O_4 + 4Fe(CN)_6^{4-} + H_2O + 3H^+ .$$

(c) For vanillin

$$2C_8H_8O_3 + 2Fe(CN)_6^{3-} + OH^- \longrightarrow C_{16}H_{14}O_6 + 2Fe(CN)_6^{4-} + H_2O + H^+$$

Effect of substrate, oxidant and alkali

The rates of all these reactions were observed to be dependent on the first powers of the concentrations of substrate, oxidant and alkali (Tables 1-7).

When a constant concentration of substrate (large excess) was used, k_{obs} did not show any appreciable variation with changing concentrations of oxidant, indicating a first order dependence of the rate of the reaction on the concentration of the Oxidant (Tables 3-4).

Table 1 : Effect of substrate

Substrates	$10^4 \times k_{obs}$, s^{-1}, at 40°C for [substrates] at			
	0.005M	0.010M	0.025M	0.050M
Phenol*	2.0	3.6	9.0	18.3
o-cresol*	0.5	1.1	2.6	5.4
m-cresol*	6.6	13.0	33.2	66.2
p-cresol*	70.0	143.0	360.0	716.0
o-chlorophenol	0.5	1.0	2.5	5.2
p-chlorophenol	1.3	2.7	6.5	13.5
o-methoxyphenol^{+} (guaiacol)	10.5	20.9	52.4	105.0
p-methoxyphenol^{+}	120.0	234.0	605.0	1200.0
o-carboxyphenol (salicylic acid)	0.5	1.0	2.6	5.1
m-carboxyphenol	1.0	1.8	4.7	9.3
p-carboxyphenol*	0.4	1.0	1.7	3.6
2,4-dichlorophenol	0.5	1.1	2.6	5.6
2,4,5-trichlorophenol	0.3	0.5	1.3	2.6
2,4,6-trichlorophenol	0.5	0.9	2.6	4.5
Vanillin	1.2	2.3	5.7	11.2
Eugenol (30°C)	180.0	364.0	905.0	-
Methyleugenol$^{\neq\neq}$	1.4	2.3	5.4	11.0

/ $K_3Fe(CN)_6$ / = 1 x 10^{-3}M; / NaOH / = 0.5M ;
MeOH = 50%(v/v); μ = 0.5 M. *At 50°C.
$^{+}$/$K_3Fe(CN)_6$ / = 1x10^{-3}M; /NaOH/ = 0.05M; MeOH = 70%(v/v);
μ = 0.5 M; temp. = 30°C. ; $^{\neq\neq}$ /$K_3Fe(CN)_6$ / = 5 x 10^{-4}M.

Table 2 : Effect of substrate

Substrates	$10^4 \times k_{obs}$, s^{-1}, at 40°C for $[\text{substrates}]$ at		
	0.0001M	0.0005M	0.001M
o-aminophenol	1.5	7.5	15.2
m-aminophenol	0.1	0.6	1.4
2,3-dimethylphenol	0.8	0.4	8.7
2,5-dimethylphenol	1.4	7.0	14.0
2,6-dimethylphenol*	1.0	5.2	10.0
3,4-dimethylphenol	1.1	5.5	11.0

$[K_3Fe(CN)_6] = 1 \times 10^{-3}$ M; $[NaOH] = 0.1$ M;

$[MeOH] = 50\%$ (v/v); $\mu = 0.5$ M.

*At 30°C.

Table 3 : Effect of oxidant

Substrates (0.01M)	$10^4 \times k_{obs}$, s^{-1}, at 40°C for /$K_3Fe(CN)_6$/ at		
	0.0001M	0.0005M	0.001M
Phenol*	3.5	3.8	3.6
o-cresol*	1.2	1.4	1.1
m-cresol*	1.4	1.5	1.3
p-cresol*	146.0	145.0	143.0
o-chlorophenol	1.0	0.9	1.0
p-chlorophenol	2.5	2.7	2.7
o-methoxyphenol+	10.6	11.0	10.5
p-methoxyphenol+	122.0	120.0	120.0
o-carboxyphenol (salicylic acid)	0.9	1.1	1.0
m-carboxyphenol	1.7	1.8	1.8
p-carboxyphenol*	0.7	0.8	0.7
2,4-dichlorophenol	1.0	1.2	1.1
2,4,5-trichlorophenol	0.5	0.6	0.5
2,4,6-trichlorophenol	1.0	0.9	0.9
Vanillin	2.4	2.1	2.3
Eugenol (30°C)	360.0	365.0	364.0
Methyleugenol (7.5×10^{-3}M)	1.5	1.3	1.6

/ NaOH / = 0.5M ; MeOH = 50% (v/v); μ = 0.5 M.

*At 50°C. +/NaOH / = 0.05M ; MeOH = 70% (v/v); μ = 0.5M; temp. = 30°C.

Table 4 : Effect of oxidant

Substrates	$10^4 x k_{obs}$, s^{-1}, at 40°C for $/K_3Fe(CN)_6/$ at (10^3 x M)			
(0.001 M)	0.01 M	0.05M	0.1M	1.0M
O-aminophenol	15.5	15.3	15.2	15.2
m-aminophenol	1.3	1.5	1.4	1.4
2,[illegible]-dimethylphenol	8.7	8.5	8.6	8.7
2,5-dimethylphenol	13.8	14.0	14.2	14.0
2,6-dimethylphenol*	9.9	10.2	10.0	10.0
3,4-dimethylphenol	10.8	11.1	11.0	11.0

/NaOH/ = 0.1M ; MeOH = 50% (v/v); μ = 0.5 M.

*At 30°C.

Table 5 : Effect of NaOH

Substrates	$10^4 \times k_{obs}$, s^{-1}, at 40°C for /NaOH/ at		
(0.01M)	0.10M	0.30M	0.50M
Phenol*	0.7	2.0	3.6
o-cresol*	0.2	0.7	1.1
m-cresol*	0.3	0.9	1.3
p-cresol*	28.0	86.0	143.0
o-chlorophenol	0.2	0.6	1.0
p-chlorophenol	0.5	1.6	2.7
o-carboxyphenol (salicylic acid)	0.2	0.6	1.0
m-carboxyphenol	0.4	1.1	1.8
p-carboxyphenol*	0.1	0.4	0.7
2,4-dichlorophenol	0.2	0.6	1.1
2,4,5-trichlorophenol	0.1	0.3	0.5
2,4,6-trichlorophenol	2.0	5.8	9.8
Vanillin	0.4	1.2	2.3
Eugenol (30°c)	73.0	220.0	364.0
Methyleugenol ≠	0.4	1.0	1.6

/ $K_3Fe(CN)_6$ / = 1 x 10^{-3}M; MeOH = 50% (v/v); μ = 0.5 M.

*At 50°C.

≠/Substrate/ = 7.5 x 10^{-3} M ; /$K_3Fe(CN)_6$ / = 5 x 10^{-4} M.

Table 6 : Effect of NaOH

Substrates (0.005 M)	$10^4 \times k_{obs}$, s^{-1}, at 30°C for /NaOH/ at 0.025M	0.050M	0.10M
o-methoxyphenol (guaiacol)	5.2	10.5	21.0
p-methoxyphenol	61.0	120.0	242.0

/$K_3Fe(CN)_6$ / = 1 x 10^{-3} M; MeOH = 70% (v/v); μ = 0.5 M.

Table 7 : Effect of NaOH

Substrates (0.001M)	$10^4 \times k_{obs}$, s^{-1}, at 40°C for /NaOH/ at 0.01M	0.05M	0.10M
o-aminophenol	1.5	7.4	15.2
m-aminophenol	0.2	0.7	1.4
2,3-dimethylphenol	0.9	4.6	8.7
2,5-dimethylphenol	1.4	7.0	14.0
2,6-dimethylphenol*	1.0	5.0	10.0
3,4-dimethylphenol	1.2	5.6	11.0

/$K_3Fe(CN)_6$ / = 1 x 10^{-3}M; MeOH = 50% (v/v); μ = 0.5M

* At 30°C.

Rate law

Under the present experimental conditions, the rate law could be expressed as:

$$\text{Rate} = -\frac{d[\text{Fe(CN)}_6^{3-}]}{dt} = k_{obs}\,[\text{Substrate}][\text{Fe(CN)}_6^{3-}]\,[\text{OH}^-] \quad \ldots\ldots\ldots \quad (1)$$

The pseudo first order rate constant, k_{obs}, was determined by keeping the concentrations of two out of the three reactants (substrate, oxidant and alkali) constant, and was calculated from the equation (96):

$$k_{obs} = \frac{2.303}{t}\log\frac{D_o}{D_t} \quad \ldots\ldots\ldots \quad (2)$$

where D_o was the initial optical density of the reaction mixture, and D_t was the optical density at time, t (vide 'Experimental' : Calculations).

Solvent influences

The rates of these reactions were influenced by a change in the solvent composition of the medium. The rates of these reactions showed a decrease, with increasing proportions of methanol, that is, with a decrease in the dielectric constant of the medium (Tables 8-10).

Table 8 : Effect of solvent

Substrates (0.01M)	$10^4 \times k_{obs}$, s^{-1}, at 40°C for MeOH(%,v/v) at				
	50%	55%	60%	65%	70%
Phenol*	3.6	2.7	1.8	-	0.8
o-cresol*	1.1	0.9	0.7	-	0.5
m-cresol*	1.3	1.1	0.9	-	0.7
p-cresol*	143.0	116.0	88.0	-	52.0
o-chlorophenol	1.0	0.9	0.7	0.6	-
p-chlorophenol	2.7	2.3	1.8	1.6	-
o-carboxyphenol (salicylic acid)	1.0	0.8	0.7	0.6	-
m-carboxyphenol	1.8	1.4	1.0	0.7	-
p-carboxyphenol*	0.7	0.5	0.3	0.2	-
2,4-dichlorophenol	1.1	0.9	0.6	0.5	-
2,4,5-trichlorophenol	0.5	0.3	0.2	0.1	-
2,4,6-trichlorophenol	0.9	0.7	0.6	0.5	-
Vanillin	2.3	1.8	1.4	-	0.8

/ $K_3Fe(CN)_6$ / = 1 x 10^{-3}M ; / NaOH / = 0.5 M; μ = 0.5 M.

*At 50°C

Table 9 : Effect of solvent

MeOH - H_2O (%, v/v)	o-methoxyphenol (guaiacol)	p-methoxyphenol
	(10^4 x k_{obs}, s^{-1}, at 30°C)	
50-50	-	170.0
60-40	14.1	158.0
65-35	12.9	-
70-30	10.5	120.0
75-25	9.0	-
80-20	-	70.0

/ Substrates / = 5 x 10^{-3}M; / $K_3Fe(CN)_6$ / = 1 x 10^{-3}M;

/ NaOH / = 5 x 10^{-2}M; μ = 0.5 M.

Table 10 : Effect of solvent

Substrates	10^4 x kobs, s^{-1}, at 40^oC for MeOH at (%,v/v)				
(0.001M)	50%	55%	60%	65%	70%
o-aminophenol[+]	1.5	1.1	0.9	0.6	-
m-aminophenol	1.4	1.0	0.7	-	0.5
2,3-dimethylphenol	8.7	7.4	5.1	4.0	-
2,5-dimethylphenol	14.0	-	9.6	7.9	5.3
2,6-dimethylphenol[*]	10.0	8.6	7.2	6.0	-
3,4-dimethylphenol	11.0	-	9.2	8.5	7.9

/ $K_3Fe(CN)_6$ / = 1 x 10^{-3} M; / NaOH / = 0.1 M;

μ = 0.5 M.

[+] / Substrate / = 1 x 10^{-4} M

[*] At 30^oC

The plots of log k_{obs} against the reciprocal of the dielectric constant were linear, with negative slopes (Figs. 1-5). This showed that the reactions under consideration involved ions of the same sign. Using the Scatchard equation (97), the values of r, the distance of approach between the ions, were calculated (Table 11); these values of r were of the right order of magnitude.

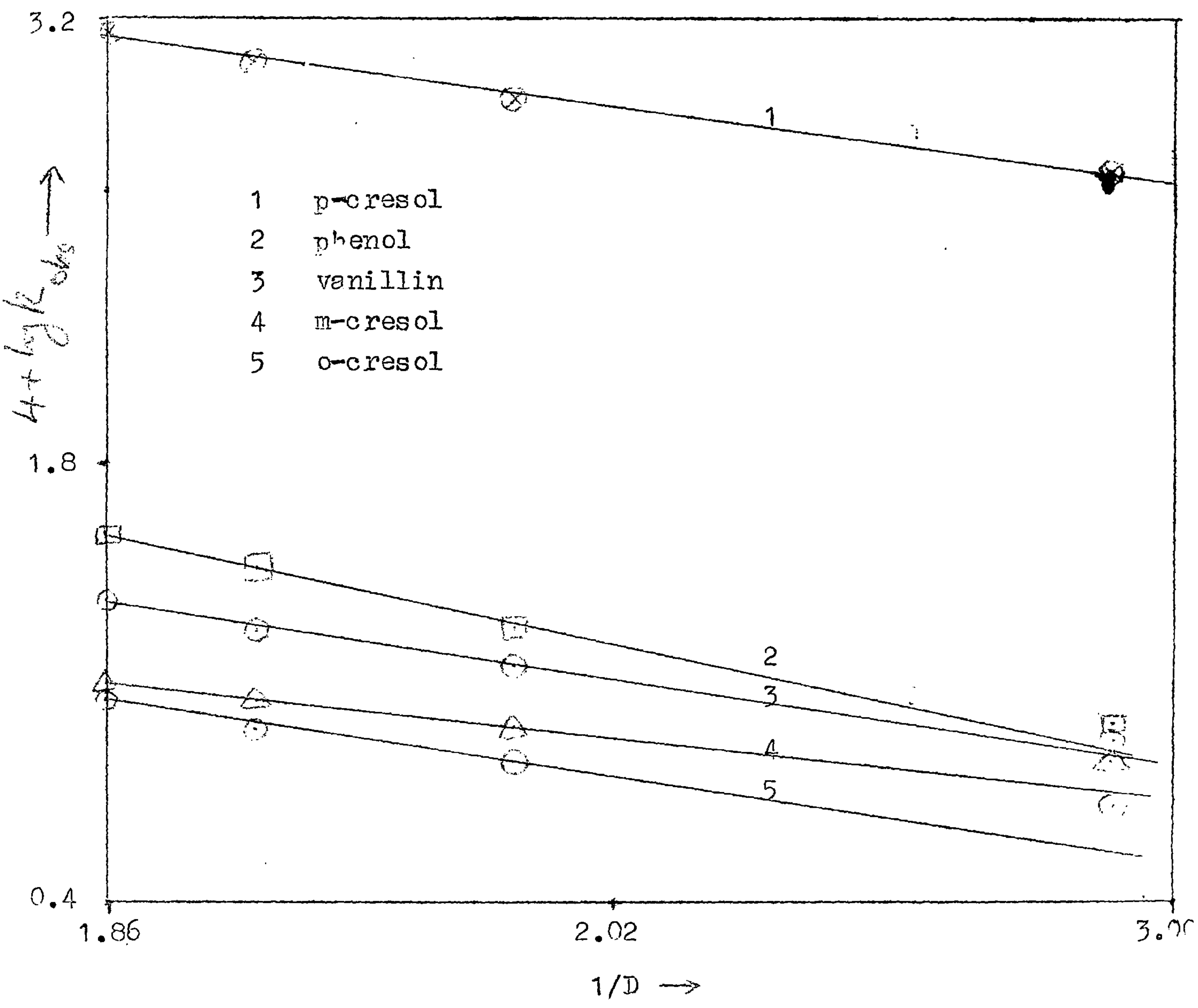


Fig. 1 - Plot of log k_{obs} against 1/D

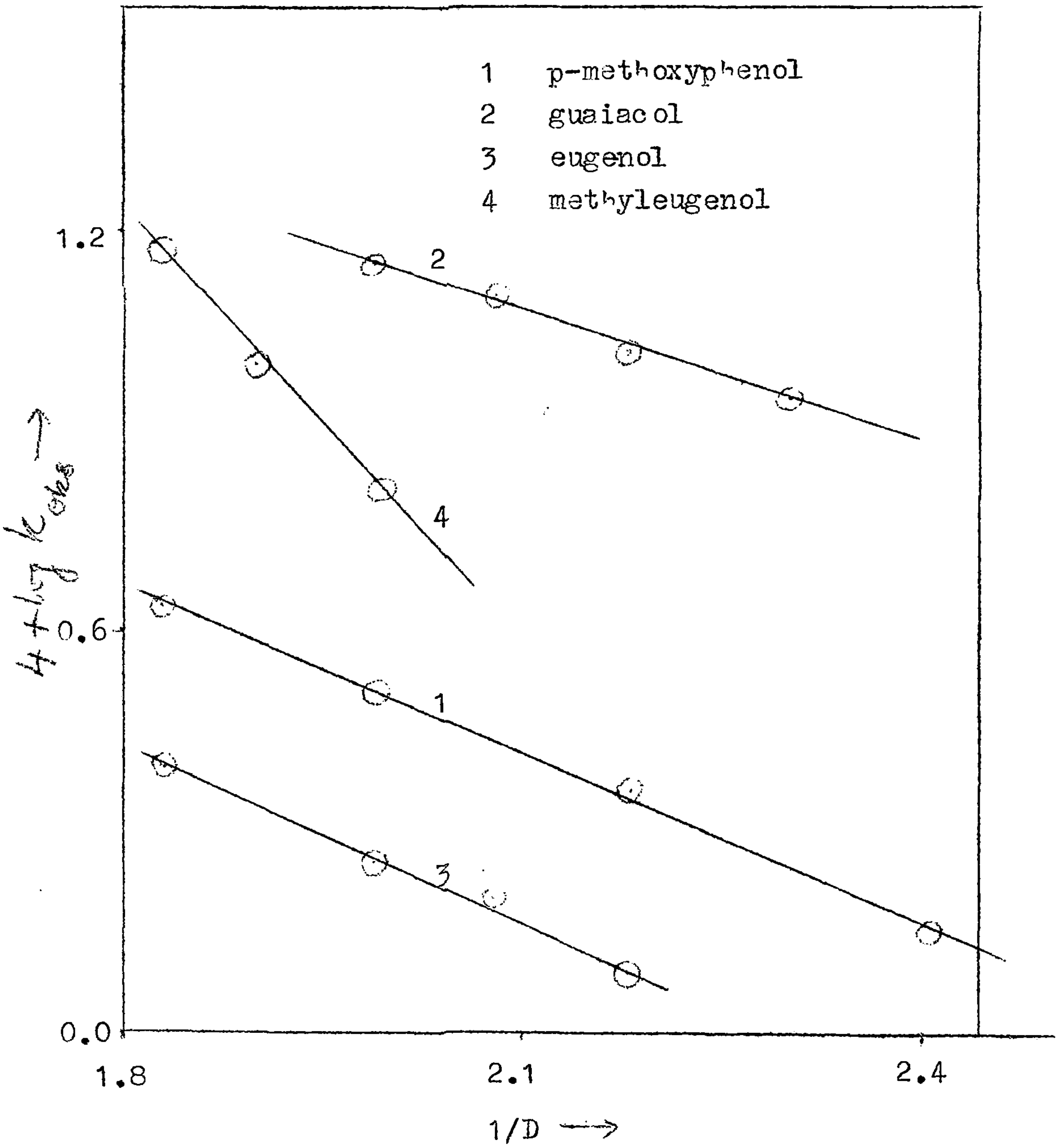


Fig. 2 - Plot of log k_{obs} against 1/D

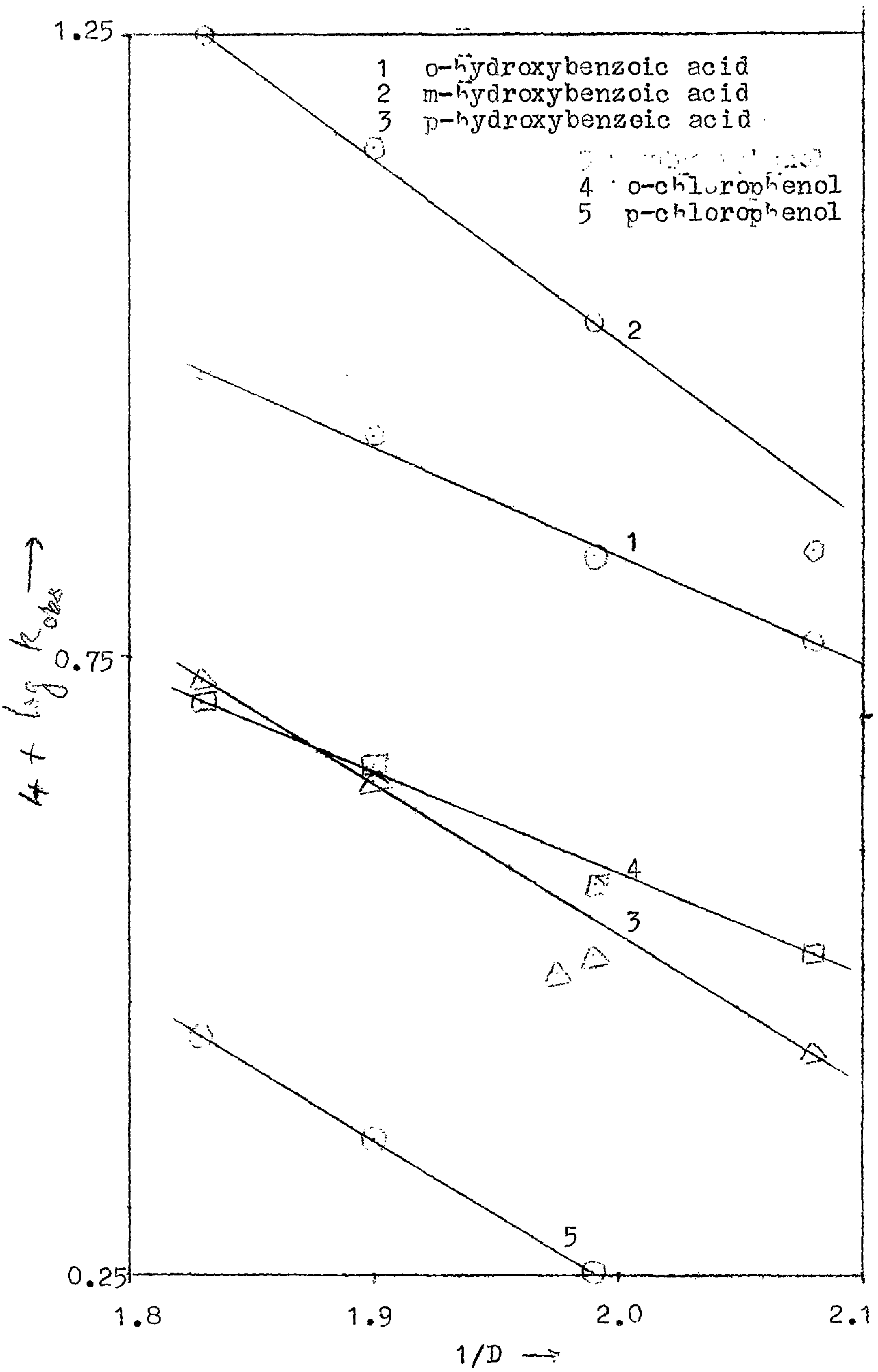


Fig. 3 - Plot of log k_{obs} against 1/D

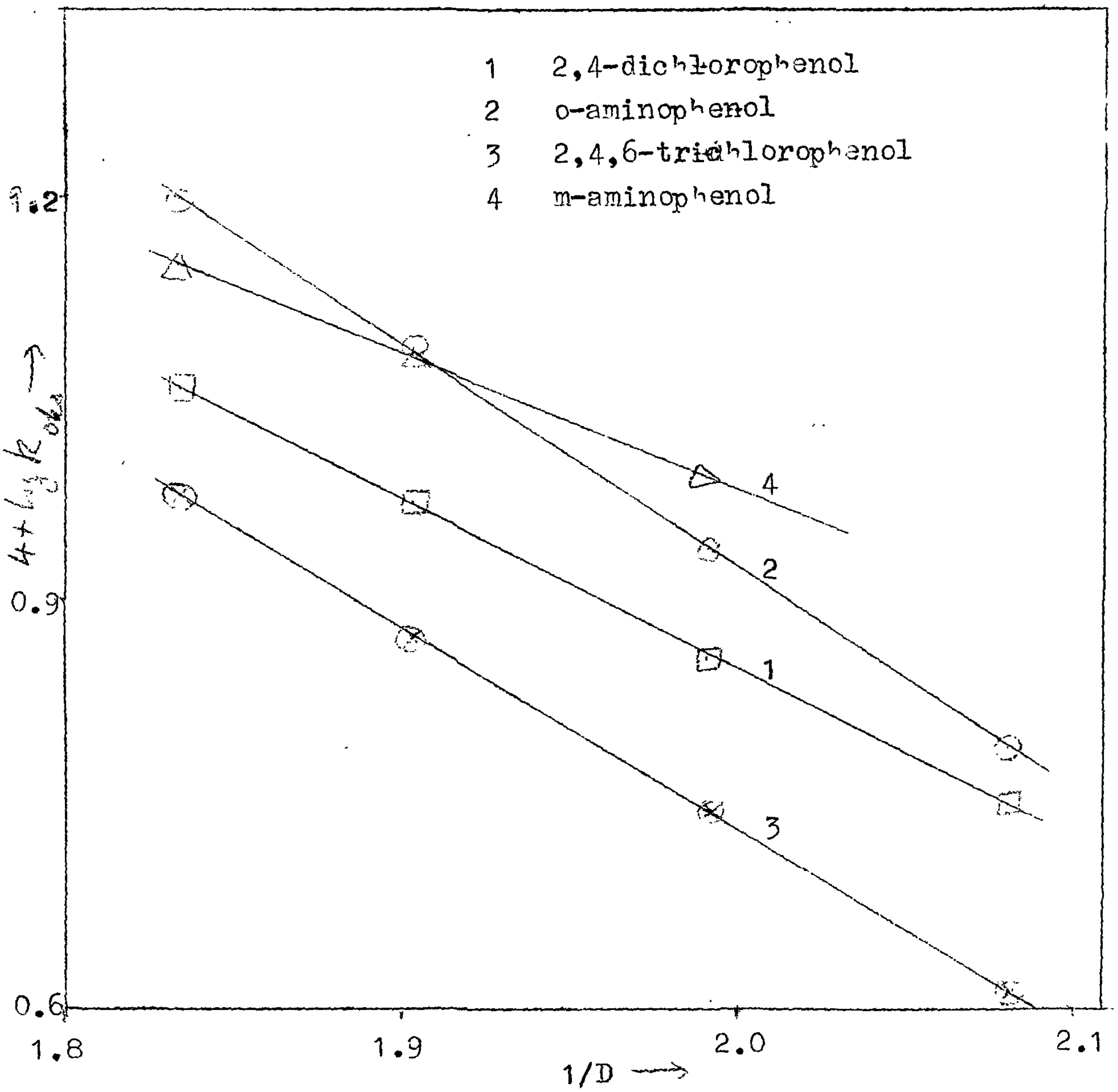


Fig. 4 - Plot of log k_{obs} against 1/D

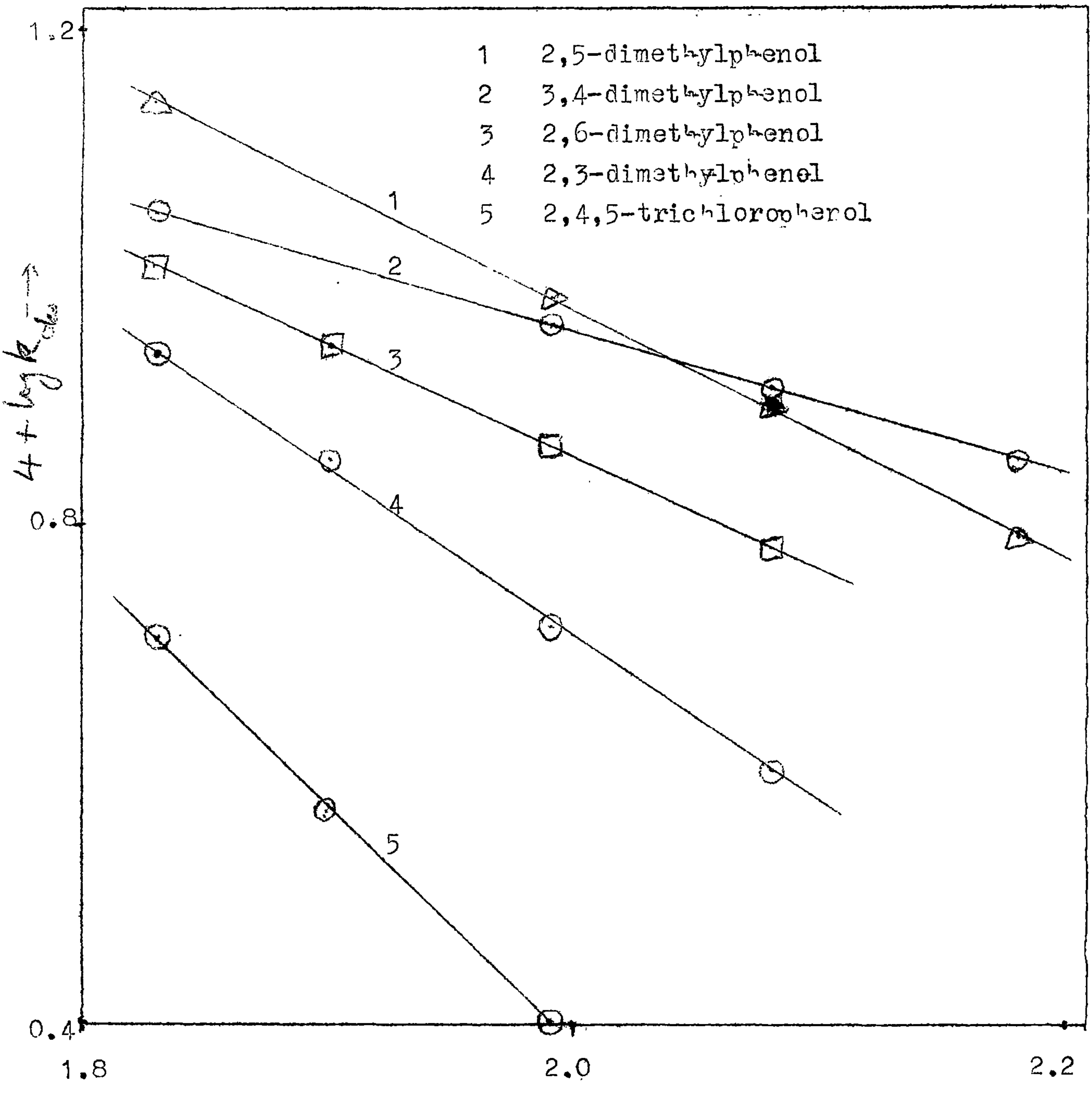


Fig. 5 - Plot of log k_{obs} against 1/D

Table 11 : Values of r

Substrate	r (Å)
Phenol	5.6
o-cresol	5.0
m-cresol	4.6
p-cresol	4.8
o-chlorophenol	6.5
p-chlorophenol	6.8
o-carboxyphenol (salicylic acid)	5.2
m-carboxyphenol	5.0
p-carboxyphenol	5.4
vanillin	4.5
Eugenol	4.2
Methyleugenol	4.0
o-methoxyphenol	3.1
p-methoxyphenol	3.8
o-aminophenol	4.5
m-aminophenol	4.2

In the alkaline fading of bromphenol blue (BPB), in mixtures of ethanol and water (98), it was shown that the plot of log k against the reciprocal of the dielectric constant was linear, with a negative slope, since the reaction was between a univalent negative ion(OH^-) and a divalent negative ion (BPB^{2-}), that is, between ions of the same sign.

Effect of temperature

The rates of these reactions were enhanced, with an increase in temperature (Tables 12-13).

Table 12 : Effect of temperature

Substrates (0.01 M)	$10^4 \times k_{obs}$, s^{-1}, at temperatures($\pm$ 0.1°C)				
	30.0	35.0	40.0	45.0	50.0
Phenol	-	1.8	2.4	2.9	3.6
o-cresol	-	0.6	0.7	0.9	1.1
m-cresol	-	8.0	10.0	11.1	13.0
p-cresol	-	96.0	110.0	122.0	143.0
o-chlorophenol	-	0.8	1.0	1.3	1.6
p-chlorophenol	-	2.2	2.7	3.1	4.0
o-methoxyphenol$^+$ (guaiacol)	10.5	14.3	18.6	20.5	26.8
p-methoxyphenol$^+$	120.0	135.0	146.0	172.0	-
o-carboxyphenol	-	0.8	1.0	1.1	1.3
m-carboxyphenol	-	1.4	1.8	2.1	2.4
p-carboxyphenol	-	0.6	0.7	0.9	1.1
2,4-dichlorophenol	-	0.9	1.1	1.3	1.6
2,4,5-trichlorophenol	0.2	0.4	0.5	0.6	-
2,4,6-trichlorophenol	0.6	0.7	0.9	1.1	-
Vanillin	-	1.7	2.3	3.0	4.6
Eugenol(1.0×10^{-4}M)*	2.4	3.0	3.6	4.2	-
Methyleugenol$^{\neq}$	0.9	1.2	1.5	2.0	-

/ $K_3Fe(CN)_6$ / = 1×10^{-3}M; / NaOH/ = 0.5 M;
MeOH = 50% (v/v); μ = 0.5 M.; */NaOH/ = 0.05M.

$^+$ /Substrates/ = 5×10^{-3}M; / $K_3Fe(CN)_6$ / = 1×10^{-3} M;
/NaOH/ = 0.05M; MeOH = 70% (v/v); μ = 0.5M

$\neq$ /Substrate/ = 7.5×10^{-3} M; /$K_3Fe(CN)_6$ / = 5×10^{-4} M.

Table 13 : Effect of temperature

Substrates (0.001 M)	$10^4 x\ k_{obs}$, s^{-1}, at temperatures ($\pm$ 0.1°C)				
	30.0	35.0	40.0	45.0	50.0
O-aminophenol$^+$	0.8	1.3	1.5	2.0	-
m-aminophenol	-	1.2	1.4	1.6	1.9
2,3-dimethylphenol	-	7.3	8.7	1.0	1.2
2,5-dimethylphenol	-	11.4	14.0	16.3	18.5
2,6-dimethylphenol	10.0	13.2	15.1	-	-
3,4-dimethylphenol	-	9.4	11.0	12.8	16.3

/ $K_3Fe(CN)_6$ / = 1 x 10^{-3} M; / NaOH / = 0.1 M;

MeOH = 50% (v/v); μ = 0.5 M.

$^+$ /substrate/ = 1 x 10^{-4} M.

The plots of log k_{obs} against the reciprocal of temperature were linear (Figs. 6-10). The slopes of these plots were used to calculate the activation energies. The other activation parameters were calculated, and have been shown (Tables 14-15).

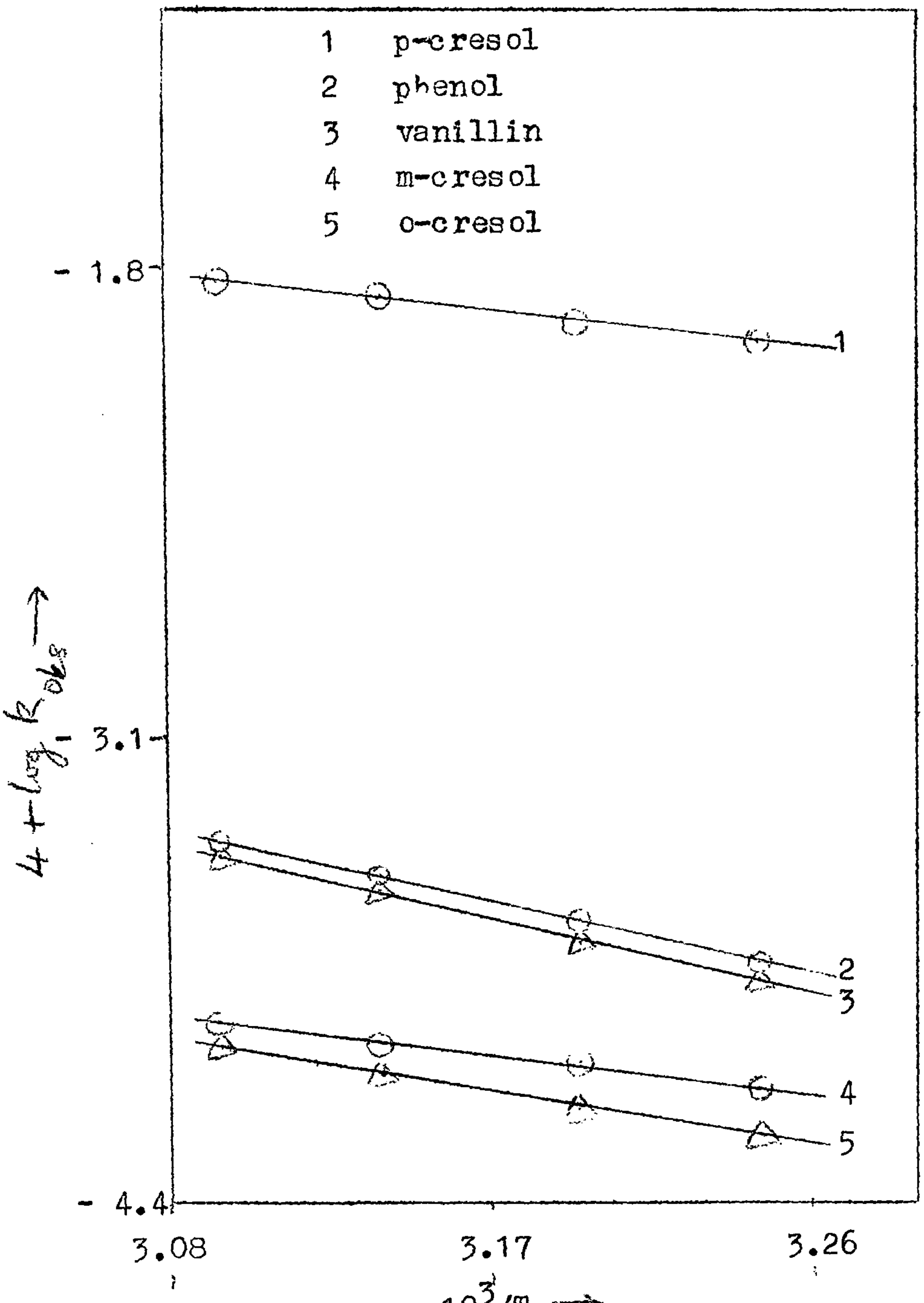


Fig. 6 - Plot of log k_{obs} against 1/T

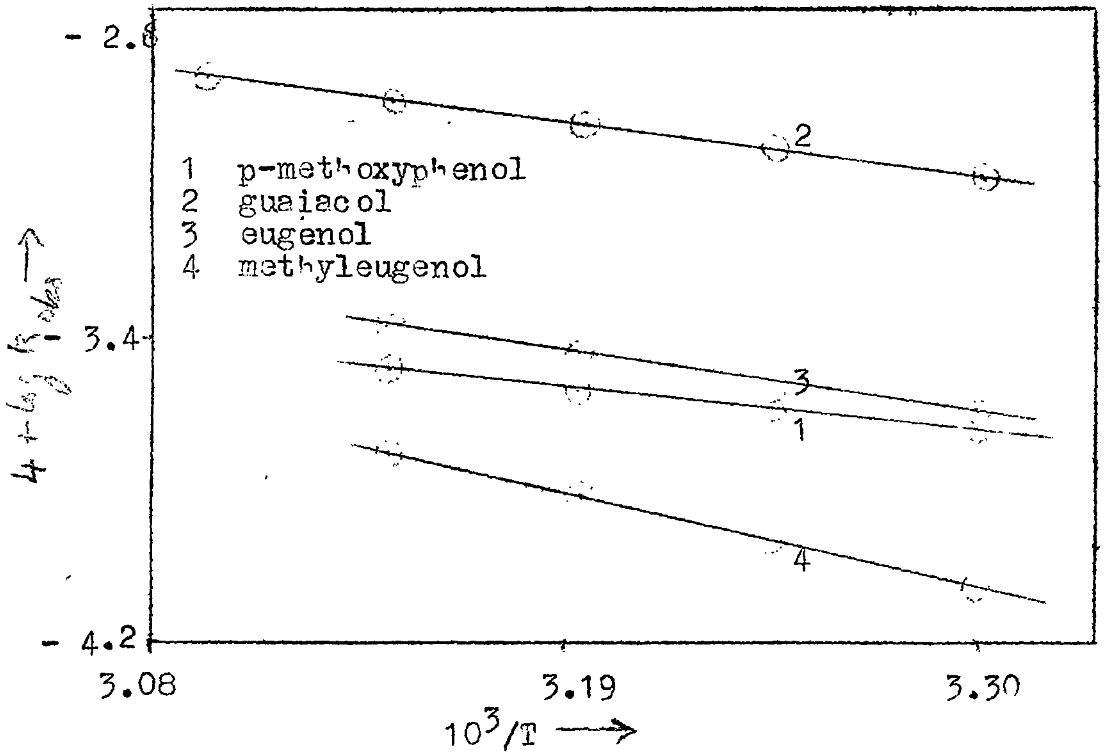


Fig. 7 - Plot of log k_{obs} against 1/T

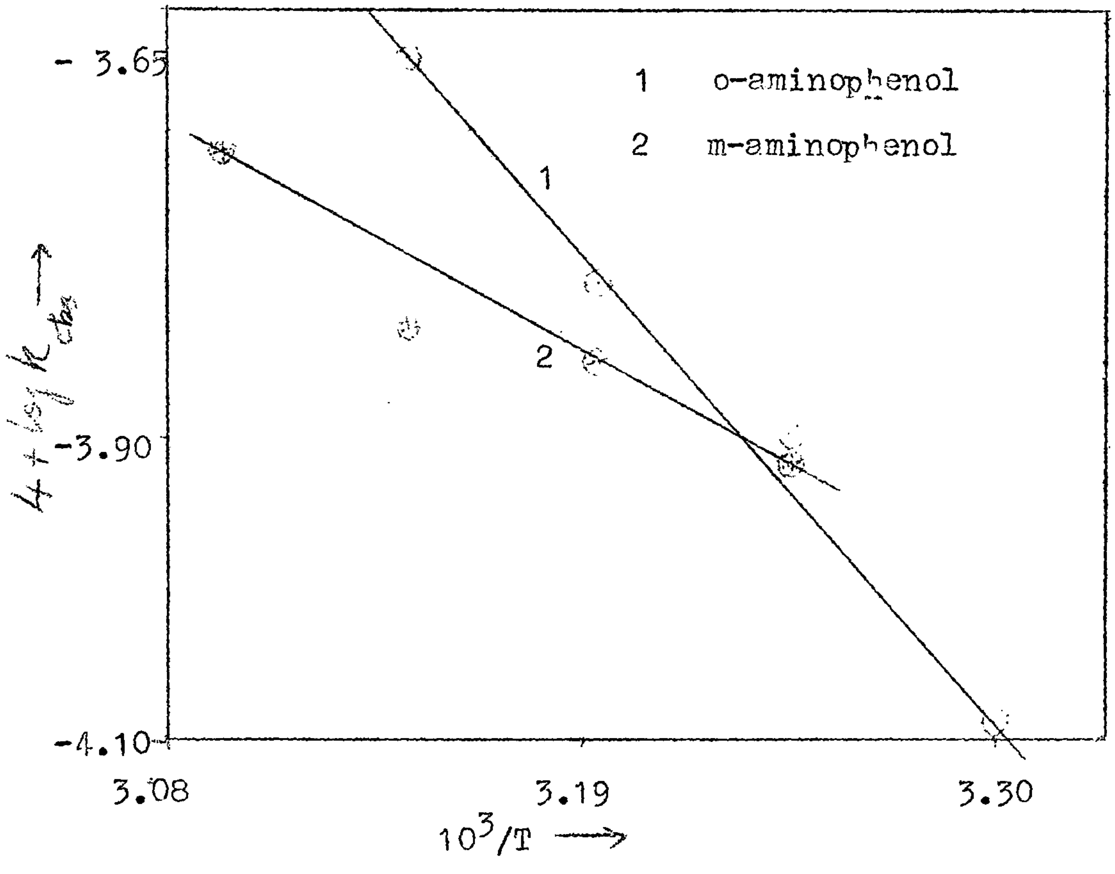


Fig. 8 - Plot of log k_{obs} against 1/T

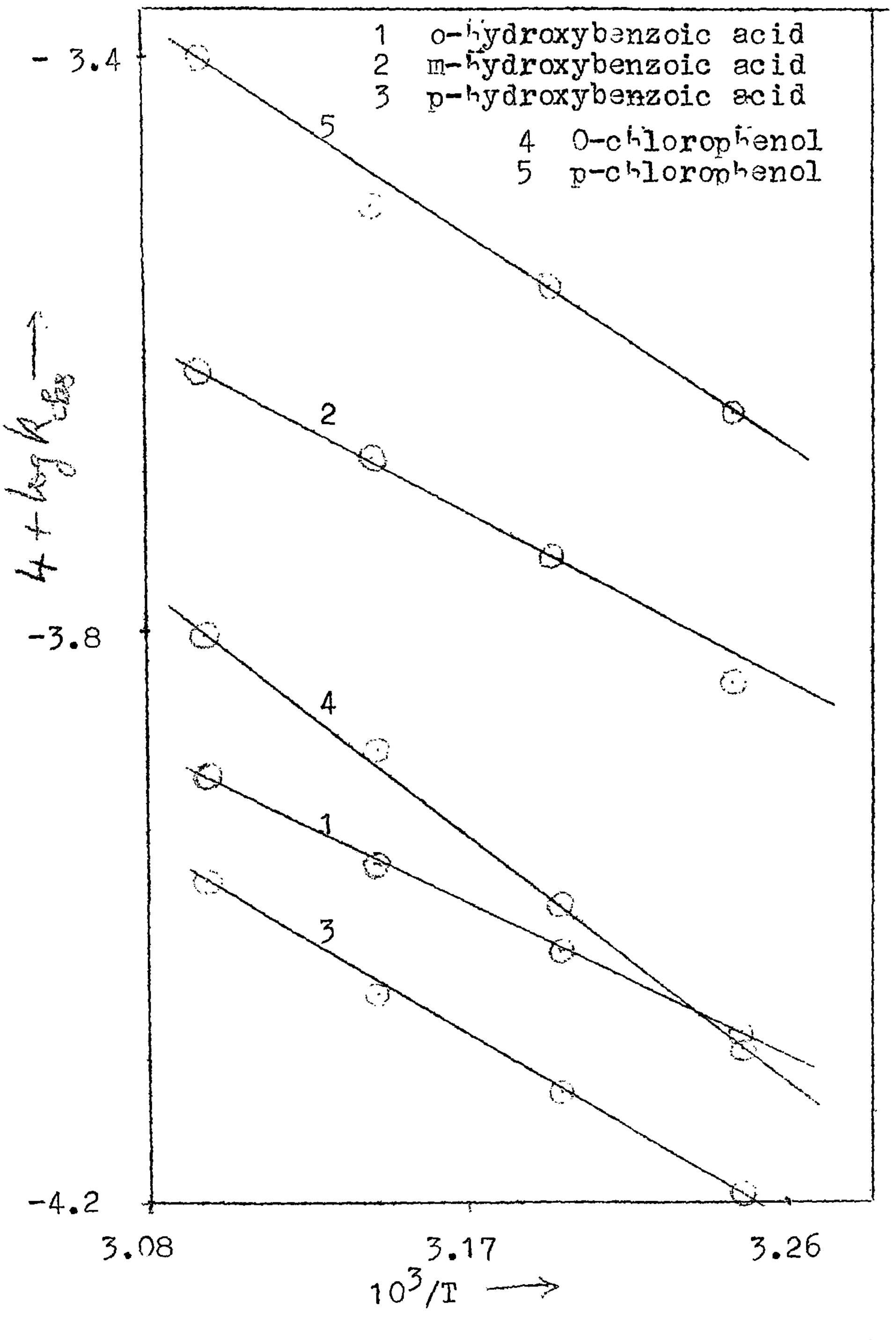


Fig. 9 - Plot of log k_{obs} against 1/T

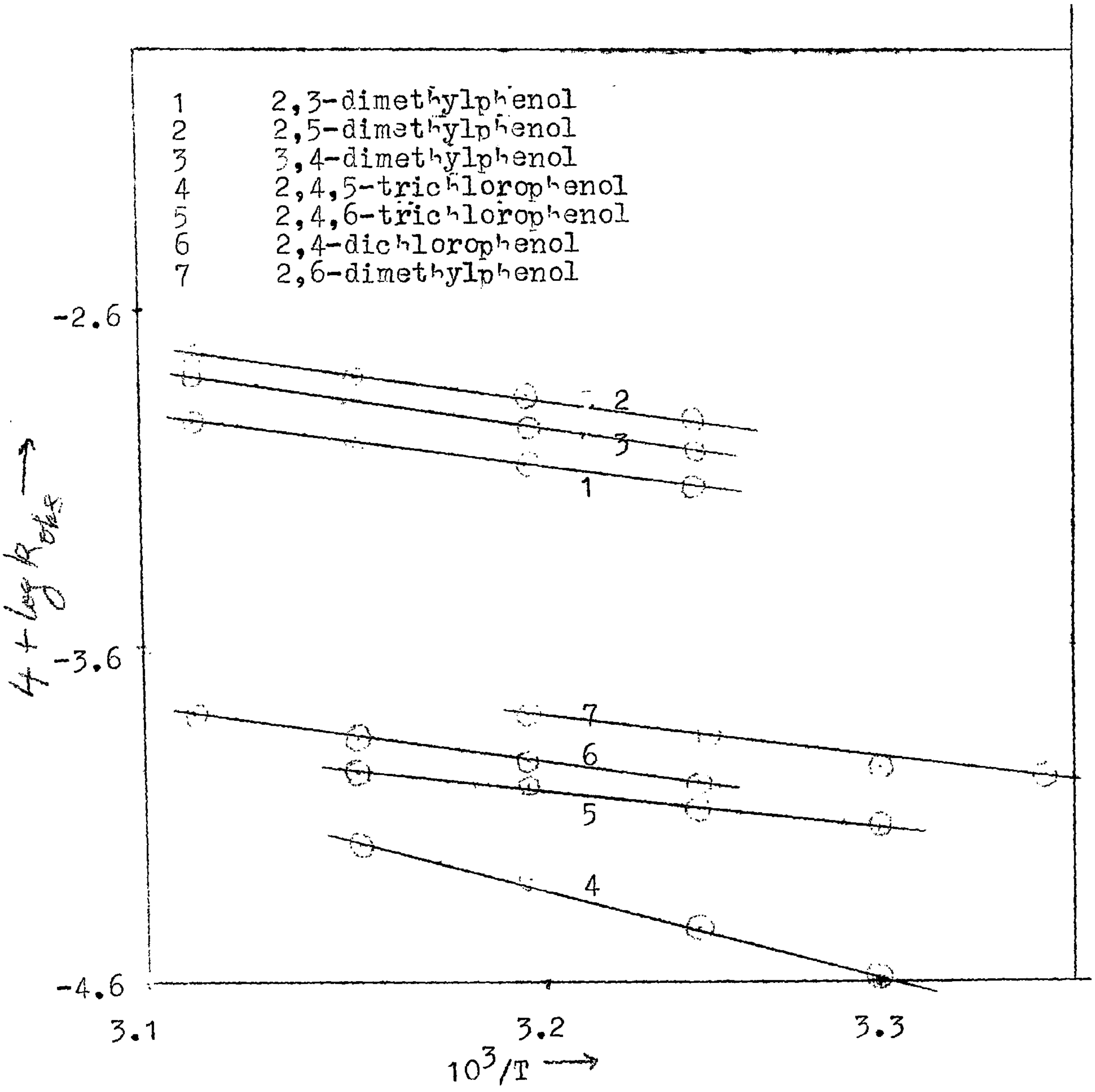


Fig. 10 - Plot of log k_{obs} against 1/T

Table 14 : Activation Parameters

Substrates	E (kJmol^{-1})	A (s^{-1})	$\Delta H^{\neq}$ (kJmol^{-1})	$\Delta S^{\neq}$ (JK^{-1}mol^{-1})
Phenol	25.1±0.8	170±1.6	22.0±0.7	-210±5
o-cresol	32.7±0.9	20±1.0	29.2±0.8	-195±5
m-cresol	28.1±1.1	9±0.5	25.0±1.0	-185±5
p-cresol	20.2±0.9	6±0.5	17.4±0.8	-206±5
o-chlorophenol	35.6±0.7	91±1.0	32.9±1.0	-216±3
p-chlorophenol	33.7±0.6	88±1.0	30.4±0.7	-216±5
o-methoxyphenol (guaiacol)	23.0±0.8	9.5±0.5	20.4±0.8	-120±5
p-methoxyphenol	18.1±0.5	0.3	15.6±0.3	-263±5
o-carboxyphenol (salicylic acid)	23.1±1.2	0.7	20.5±1.1	-256±8
m-carboxyphenol	27.7±1.5	7±0.2	25.1±1.3	-237±7
p-carboxyphenol	28.4±1.3	4±0.2	25.8±1.2	-242±7
2,4-dichlorophenol	26.8±1.2	3±0.2	24.1±1.1	-243±6
2,4,5-trichlorophenol	57.4±1.5	0.7	54.8±1.3	-152±3
2,4,6-trichlorophenol	22.6±1.0	0.5	20.1±1.0	-258±6
Vanillin	40.0±1.3	1.1x10^{3}	37.3±1.0	-196±5
Eugenol	27.5±1.0	14±0.8	25.0±0.7	-231+5
Methyleugenol	39.6±1.1	617±1.8	37.0±0.8	-200±6

Table 15 : Activation Parameters

Substrates	E_a ($kJmol^{-1}$)	A (s^{-1})	$\Delta H^{\neq}$ ($kJmol^{-1}$)	$\Delta S^{\neq}$ ($Jk^{-1}mol^{-1}$)
o-aminophenol	50.7±1.0	5.0×10^4	48.2±0.8	-163±4
m-aminophenol	25.5±0.6	2.5	22.9±0.5	-246±6
2,3-dimethylphenol	25.9±0.6	19.0	23.3±0.6	-229±6
2,5-dimethylphenol	26.5±0.5	36.0	23.8±0.5	-223±6
2,6-dimethylphenol	22.7±0.5	1.0	20.0±0.6	-254±5
3,4-dimethylphenol	30.4±0.6	133.0	27.5±0.5	-213±5

Effect of ionic strength

The variation of ionic strangth by using $NaClO_4$ (0.10M to 0.50M), did not have any effect on the rates of these reactions.

Effect of added $K_4Fe(CN)_6$

The addition of $K_4Fe(CN)_6$ in the concentration range, 1.0×10^{-4}M to 1.0×10^{-3}M, did not have any influence on the rates of these reactions.

Radical intermediates (Vide 'Experimental')

Phenols are known to give rise to stable radicals, which have been detected and characterized (99-100).

In the present investigation involving the oxidation of monohydric phenols by alkaline hexacyanoferrate (III), the esr spectra of the radicals generated in a flow system have confirmed the presence of radical intermediates, thus establishing that the reaction pathway was via the formation of radical intermediates formed in the rate determining step of the reaction.

(a) From the oxidation of phenol and cresols

The esr spectra of the radicals generated in a flow system from the oxidation of phenol and cresols by alkaline hexacyanoferrate(III), revealed a spectral pattern similar to that reported earlier(101). These results confirmed the formation of a radical intermediate in the rate determining step of the reaction. The radical intermediates formed, showed absorptions in the visible region between 650 nm and 670 nm, and a typical band at 1560 cm^{-1} in the infrared spectrum.

(b) From the oxidation of guaiacol:

The esr spectrum of the radical generated in a flow system from the oxidation of guaiacol by alkaline hexacyanoferrate (III), was obtained as a spectrum consisting of 9 lines, which were rather broad. This spectrum was interpreted in a manner similar to that in an earlier investigation (101). The rate determining step of the reaction involved the formation of a radical intermediate, which could be stabilized by resonance. This radical showed a typical absorption band at 1560 cm^{-1} in the infrared spectrum.

(c) From the oxidation of vanillin:

The esr spectrum of the radical generated in a flow system from the oxidation of vanillin by alkaline hexacyanoferrate (III), gave 6 spectral lines. The splitting due to the hydrogen atoms in positions 3 and 5 were observed. This radical intermediate showed an absorption in the visible region at 650 nm, and gave an absorption band at 1560 cm^{-1} in the infrared spectrum.

In general, phenoxyl radicals have been characterized by their electronic spectra (102-103).

Mechanism

Pummerer et. al (104-105) had postulated a free phenoxy radical as the first intermediate in the reactions of phenol coupling.

In the present investigation, involving the oxidation of monohydric phenols by alkaline hexacyanoferrate (III), the mechanistic pathways have been established on the basis of the formation of radical intermediates (confirmed by esr spectroscopy), and by product analyses (vide 'Experimental' : Product analysis).

(a) Oxidation of phenol and cresols:

The phenoxy radical, 2·, is stabilized by resonance (2a ⟷ 2b ⟷ 2c ⟷ 2d). The reaction of 2b + 2c, followed by the removal of an electron, by hexacyanoferrate (III), from the resultant product, 3, yields I. Similarly, the reaction of 2d with the anion of the cresol, at the ortho position, would afford the coupled radical, 4. The latter is oxidized further by hexacyanoferrate (III), undergoing aromatization, to give 4-aryl-4-methyl cyclohexadienone, 5. Compound 5 undergoes an intramolecular Michael addition reaction, and is converted to the ketone, II. The formation of 5 can also be envisaged as arising from the coupling of the two canonical forms, 2b + 2d. The dual course of the oxidation of p-cresol lends support to the resonance hybrid structure of the phenoxy radical, 2 . The reaction sequence is given in the Scheme.

This reaction sequence finds support from the synthesis of complex natural products such as usnic acid (91) and griseofulvin (106). Significantly, a key step in the biosynthesis of many of these compounds is the oxidative coupling of a phenol.

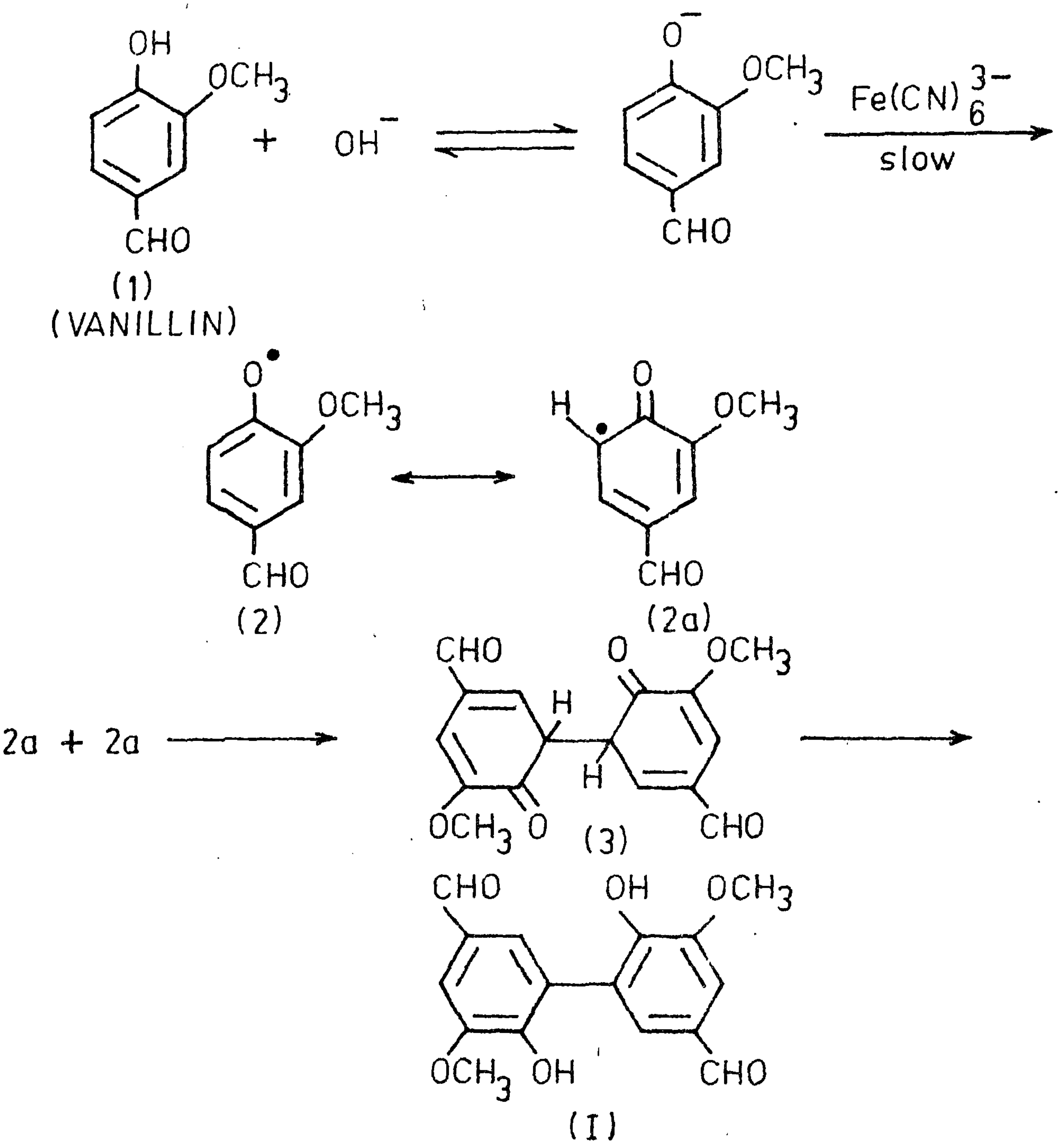
It would be reasonable to assume that the phenoxyl radicals, once formed, would couple at the positions of high spin density. Such coupling would be rapid and irreversible. Support for this hypothesis comes from flash photolysis experiments in which phenoxyl radicals have been generated in solution, and their decay followed spectrophotometrically (107-108).

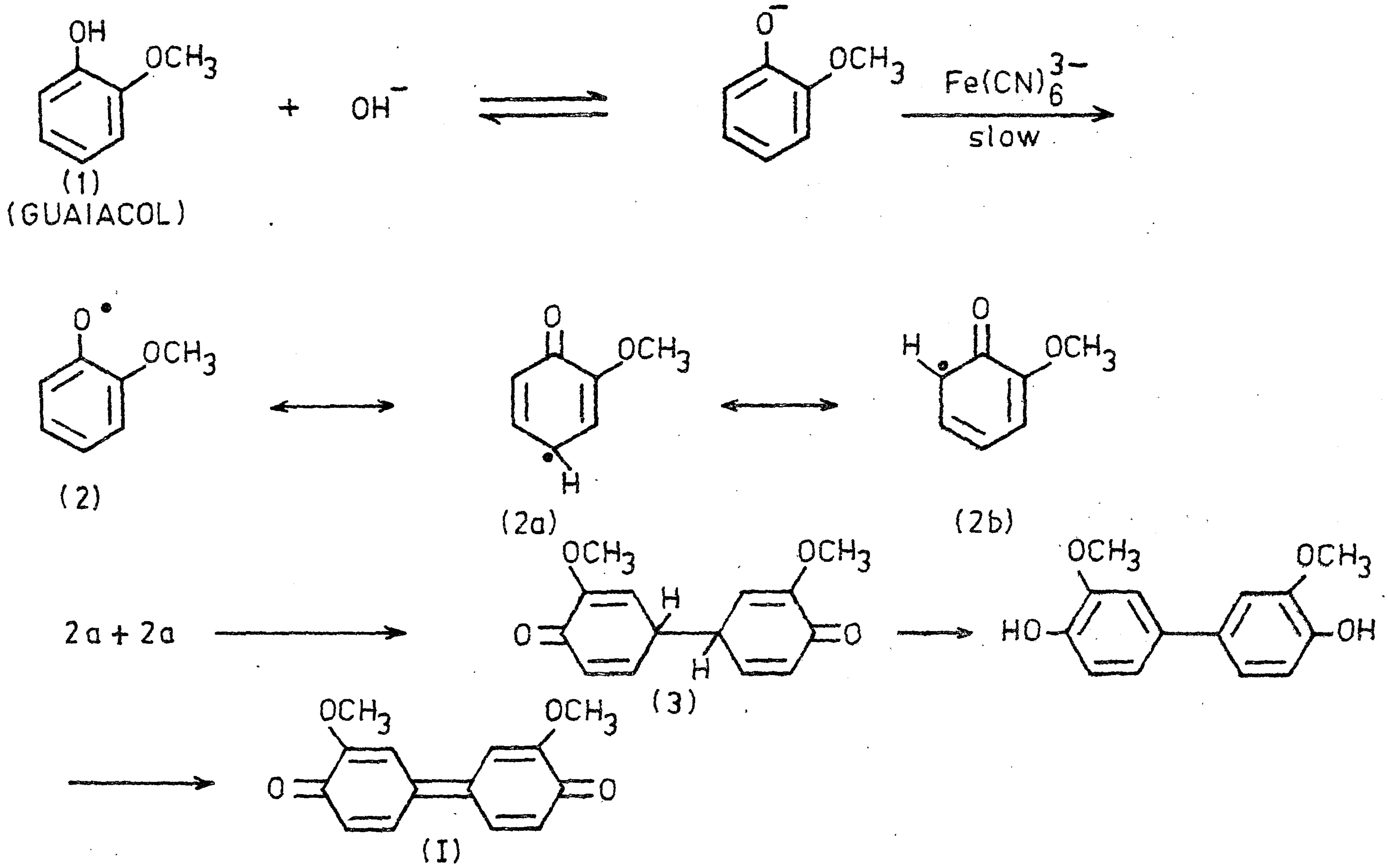
(b) Oxidation of guaiacol:

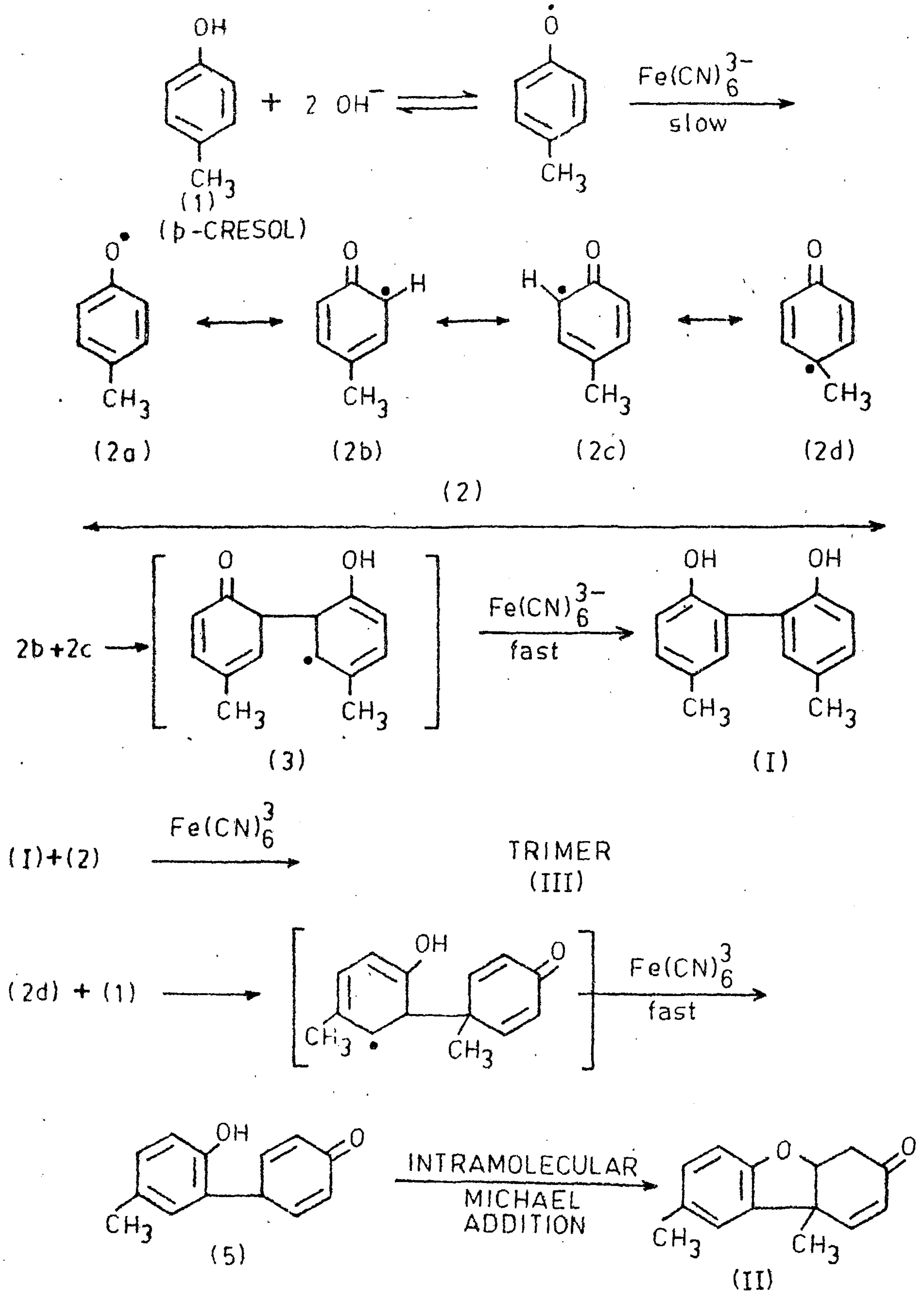
In guaiacol, the observed coupling positions, ortho and para, show that a free phenoxyl radical would be reactive only on the oxygen and on the ortho and para carbon atoms. The resonance structures for the radical would symbolize a high density of the unpaired electron at these positions. Guaiacol, 1 , can be oxidized to the corresponding phenoxyl radical, 2 ⟷ 2a ⟷ 2b . Combination of 2a + 2a would result in the formation of the dimer, 3 , which would undergo tautomerization rapidly in methanol, and would be oxidized further to yield the extended quinone, 4 . No other intermediate product(s) could be recovered. The mechanism is shown in the Scheme.

(c) Oxidation of vanillin

In the case of vanillin, the radical formed would be reactive on the oxygen and in the ortho position, since the para position was blocked. Vanillin, 1 , can be oxidized by hexacyanoferrate (III) to the radical, 2 —— 2a. Combination of 2a + 2a would give the dimer, 3 , which would undergo tautomerization in methanol rapidly to give divanillin, I . The reaction sequence is given in the Scheme.


OH
OCH3
+
OH−
(1)
(VANILLIN)
O−
OCH3
CHO
Fe(CN)6 3−
slow
O•
(2)
H
O
(2a)
2a + 2a
(3)
(I)


OH
OCH3
+ OH⁻
(1)
(GUAIACOL)
O⁻
OCH3
Fe(CN)6 3−
slow
O•
OCH3
(2)
O
OCH3
H
(2a)
O
H
OCH3
(2b)
2a + 2a
OCH3
OCH3
H
H
O
O
(3)
OCH3
OCH3
HO
OH
OCH3
OCH3
O
O
(I)


OH
+ 2 OH⁻
Fe(CN)6 3−
slow
CH3
(1)
(p-CRESOL)
(2a)
(2b)
(2c)
(2d)
(2)
2b+2c
(3)
fast
(I)
(I)+(2)
TRIMER
(III)
(2d) + (1)
(5)
INTRAMOLECULAR
MICHAEL
ADDITION
(II)

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CHAPTER 2

KINETICS OF OXIDATION OF DIHYDRIC PHENOLS*

The oxidation of dihydric phenols(catechol, resorcinol, orcinol and quinol) has been studied by several workers using a variety of oxidizing agents.

EARLIER WORK:

1. Catechol

The oxidation of catechol by ferric chloride and by silver nitrate at pH 5.9(1), as also air/enzyme oxidations (2) had resulted in a variety of coupled products. There have been some reports to show that the oxidation of catechols was accompanied by an aromatic ring cleavage (3-5). The oxidation of catechol by aqueous sodium iodate (6) gave a radical intermediate, I , which then yielded the o-quinone, II . The photooxidation of catechol (7) had yielded

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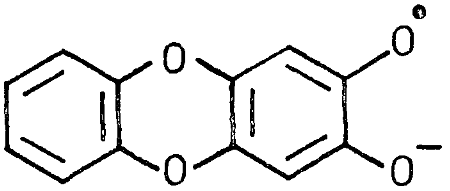
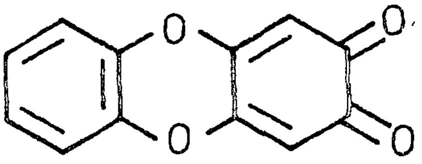
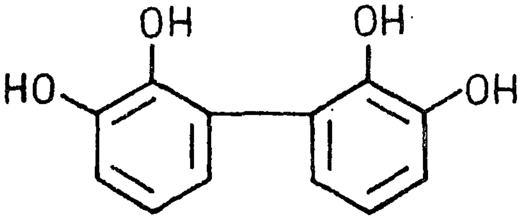


(I)



(II)



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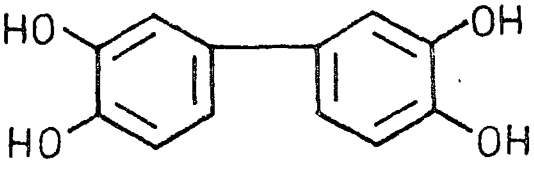


(IV)

two symmetrical carbon-carbon dimers, <u>III</u> and <u>IV</u> . The oxidation of catechol has been carried out by V(v) and Cr(vi) (8), H_2O_2 / Cu^{2+} ions (9), peracetic acid catalysed by Cu^{2+} and Fe^{2+} ions to give cis cis-muconic acid (10), metal acetylacetonates in organic solvents (II). The oxidation of catechol by hexachloroiridate (IV) in aqueous perchloric acid was via an outer sphere process, the product obtained being o-benzoquinone (12). The conversion of catechol to o-benzoquinone has been established in earlier investigations (13-22).

2. <u>Resorcinol and Orcinol</u>

The aerial oxidation or resorcinol in alkaline medium had given diphenoquinone (23-24). The oxidation of resorcinol by hexachloroiridate (IV) in aqueous perchloric acid was initially fast, followed by a much slower reaction (12), and resulted in the formation of coupled products.

In the presence of oxygen or hydrogen peroxide, in alkaline solution, orcinol was converted to the dimeric mono- and diquinones (25). Orcinol has been oxidized to p,p-coupled products, by PbO_2, benzophenone / $h\nu$, and by alkaline hexacyanoferrate (III); however, no kinetic details

details were reported (26). In aqueous ammonia, nitrogen was incorporated to afford a complex mixture of orceine and litmus dyes, having colours from red to violet-blue(27-28).

3. Quinol

The aerial oxidation of quinol had resulted in coupled products(29), whereas the photooxidation of quinol had yielded dimers (7). The oxidation of quinol in perchloric acid medium had been carried out by a variety of oxidants such as Fe^{3+} (30), Cr^{6+} (31), Co^{3+} (32-33), Ce^{4+} (34) and Mn^{3+} (35), to give p-benzoquinone. In the case of oxidations by Co^{3+}, Ce^{4+} and Mn^{3+}, intermediate complexes were observed. These complexes were rapidly decomposed to give the semiquinone radical (or its anion), which was then further oxidized to the quinone. The oxidation of quinol by V(V) was rapid (36), and the variation of the rate with changes in acidity was explained in terms of the decomposition of the various complexes formed as intermediates. Np (VI) has also been used to oxidize quinol (37), but there was no evidence for the formation of a semiquinone intermediate. Thallium (III) trifluoroacetate, taken in either trifluoroacetic acid or in CCl_4 as solvent, has been observed to rapidly oxidize quinol to p-quinone in nearly

70% yield (38-39). The laccase-catalysed oxidation of quinol(40), and the oxidation of quinol by H_2O_2 catalysed by peroxidase (41), gave p-benzoquinone, in both cases. The oxidation of quinol was not catalysed by tyrosinase(42). and this constitutes an important difference between tyrosinase and laccase.

PRESENT WORK

Kinetic studies on the oxidation of dihydric phenols by potassium hexacyanoferrate (III) have not received adequate attention (43-44). The present work is a detailed kinetic investigation of the oxidation of dihydric phenols (Catechol, resorcinol, orcinol and quinol) by potassium hexacyanoferrate (III), in alkaline medium, at constant ionic strength, under a nitrogen atmosphere, using methanol (70%, v/v) as the solvent.

Stoichiometry (vide 'Experimental'):

The stoichiometry of each of the reactions was determined to be:

(a) Catechol

$$\begin{aligned} C_6H_6O_2 + 2OH^- + 2Fe(CN)_6^{3-} \longrightarrow \; & C_6H_4O_2 \\ & + 2\,Fe(CN)_6^{4-} \\ & + 2H_2O \end{aligned}$$

(b) Resorcinol

$$2\ C_6H_6O_2 + 2\ OH^- + 2Fe(CN)_6^{3-} \longrightarrow C_{12}H_{10}O_4 + 2\ Fe(CN)_6^{4-} + 2\ H_2O$$

(c) Orcinol

$$2\ C_7H_8O_2 + 2\ OH^- + 2Fe(CN)_6^{3-} \longrightarrow C_{14}H_{14}O_4 + 2Fe(CN)_6^{4-} + 2\ H_2O$$

(d) Quinol

$$C_6H_6O_2 + 2\ OH^- + 2Fe(CN)_6^{3-} \longrightarrow C_6H_4O_2 + 2Fe(CN)_6^{4-} + 2H_2O$$

Effect of substrate, oxidant and alkali

The rate of the reaction was observed to be dependent on the first powers of the concentrations of substrate, oxidant and alkali (Table I).

Table 1

Rate data for the oxidation of dihydric phenols

[Substrate] (10^2 x M)	[$K_3Fe(CN)_6$] (10^3 x M)	[NaOH] (10^2 x M)	Catechol	Resorcinol	Orcinol	Quinol
			(10^4 x k_{obs}, s^{-1})			
1.0	1.0	5.0	44.7	6.1	64.0	10.8
2.0	1.0	5.0	89.6	12.3	130.0	21.6
5.0	1.0	5.0	225.0	30.7	325.0	54.2
10.0	1.0	5.0	455.0	62.0	652.0	109.0
1.0	0.1	5.0	44.8	6.3	64.5	10.8
1.0	0.5	5.0	44.7	6.0	64.0	10.7
1.0	0.75	5.0	45.0	6.1	64.3	10.8
1.0	1.0	2.5	22.5	3.1	31.8	5.2
1.0	1.0	10.0	89.8	12.5	128.0	21.7

Methanol = 70% (v/v) ; μ = 0.50 M; temp. = 30.0 ± 0.1°C.

When a constant concentration of substrate (large excess) was used, k_{obs} did not show any appreciable variation with changing concentrations of the oxidant, indicating that the rate of the reaction was dependent on the first power of the concentration of the oxidant (Table I).

Rate law:

Under the present experimental conditions, the rate law for resorcinol, orcinol and quinol could be expressed as:

$$\text{Rate} = -\frac{d[\text{Fe(CN)}_6^{3-}]}{dt} = k_{obs}[\text{Substrate}][\text{Fe(CN)}_6^{3-}][\overline{\text{OH}}] \quad \ldots\ldots \quad (1)$$

The pseudo first order rate constant, k_{obs}, was determined by keeping the concentrations of two out of the three reactants (substrate, oxidant and alkali) constant, and was calculated from the equation (45):

$$k_{obs} = \frac{2.303}{t} \log \frac{D_o}{D_t} \quad \ldots\ldots\ldots \quad (2)$$

where D_o was the initial optical absorbance of the reaction mixture, and D_t that at time, t (vide 'Experimental': Calculations).

Effect of solvent:

The rate of the reaction was influenced by a change in solvent composition. The rate of the reaction was found to decrease with increasing amounts of methanol, that is, with a decrease in the dielectric constant of the medium (Tables 2-3).

Table 2

Effect of solvent

$MeOH-H_2O$ (%, v/v)	Catechol	Resorcinol (10^4 x k_{obs}, s^{-1})	Quinol
60-40	72.3	9.8	13.8
65-35	62.2	7.9	12.2
70-30	44.7	6.1	10.8
75-25	30.0	4.8	9.1

[Substrates] = 1×10^{-2}M; [$K_3Fe(CN)_6$] = 1×10^{-3} M;

[NaOH] = 5×10^{-2} M; temp. = 30.0 ± 0.1°C ; μ = 0.50M.

Table 3

Effect of solvent

$MeOH-H_2O$ (%, v/v)	Orcinol (5×10^{-4}M) (10^4 x k_{obs}, s^{-1})
35-65	6.0
40-60	5.3
45-55	4.1
50-50	3.2

[$K_3Fe(CN)_6$] = 1×10^{-3}M; [NaOH] = 5×10^{-2}M; μ= 0.50M;

temp. = 30.0 ± 0.1°C.

The dependence of the rate constant on the dielectric constant of the medium can be expressed by the Scatchard equation (46). The plots of log k_{obs} against the reciprocal of the dielectric constant were linear, with negative slopes (Fig.1). This showed that the reactions under consideration involved ions of the same sign. In the alkaline fading of bromphenol blue in mixturew of ethanol and water, it was shown that the plot of log k versus the reciprocal of the dielectric constant was linear with a negative slope (47), since the reaction was between a univalent negative ion (OH^-) and a divalent negative ion (BPB^{-2}), that is, between ions of the same sign. In the present investigation, the values of r, the distance of approach between the two ions, were calculated from the Scatchard equation (46), and have been shown in Table 4. These values of r were of the correct order of magnitude.

Table 4

Values of 'r'

Substrate	r ($\mathring{A}$)
Catechol	5.2
Resorcinol	4.8
Orcinol	4.4
Quinol	4.1

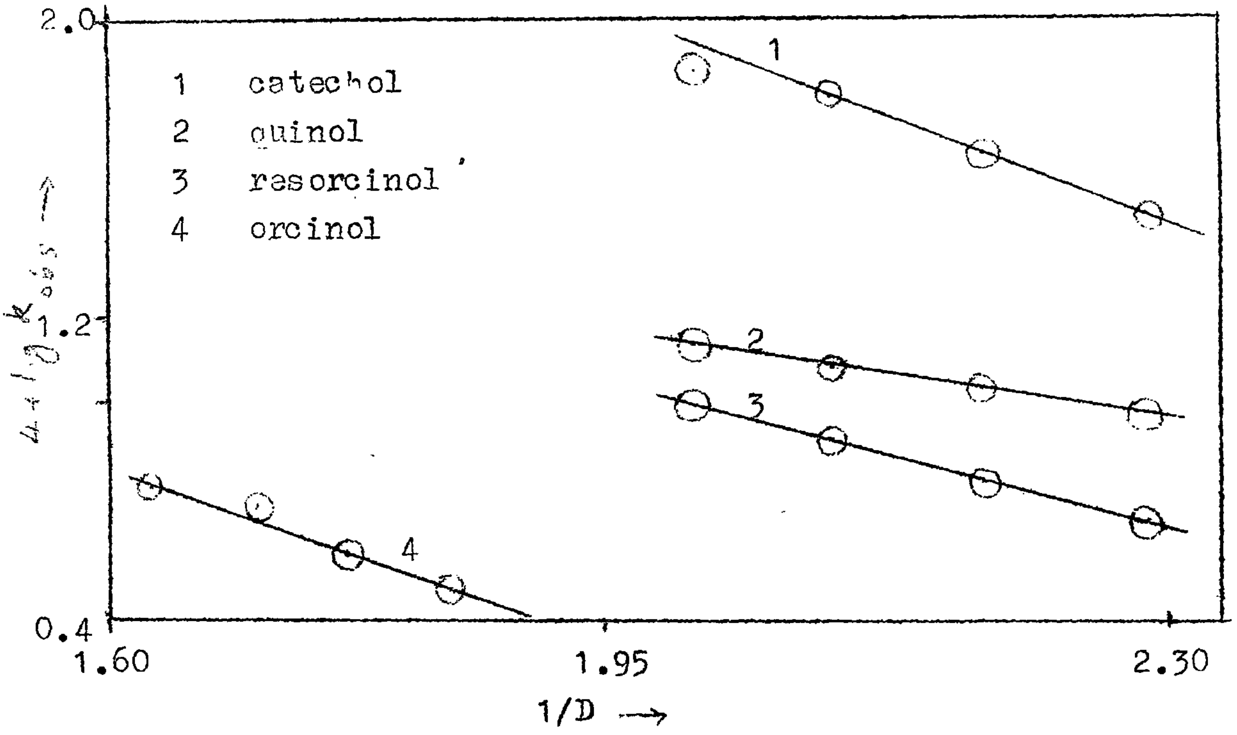


Fig. 1 - Plot of log k_{obs} against 1/D

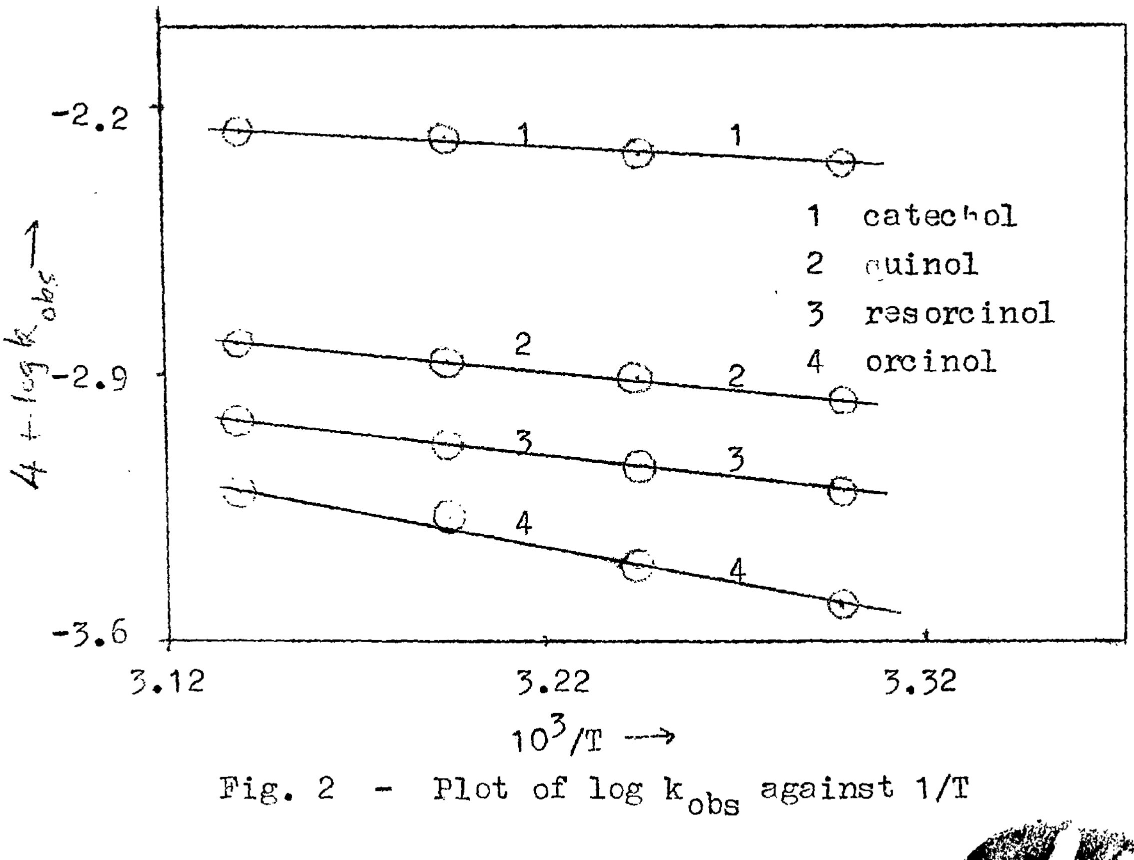


Fig. 2 - Plot of log k_{obs} against 1/T

Effect of temperature:

The rate of the reaction was influenced by changes in temperature, the rate showing an increase with an increase in the temperature (Tables 5-6).

Table 5

Effect of temperature

Temp. (±0.1 °C)	Catechol	Resorcinol (10^4 x k_{obs}, s^{-1})	Quinol
30.0	44.7	6.1	10.8
35.0	47.7	7.2	12.1
40.0	53.8	8.3	13.6
45.0	62.3	9.6	14.8

[Substrates] = 1 x 10^{-2}M; [$K_3Fe(CN)_6$] = 1×10^{-3}M ;
[NaOH] = 5 x 10^{-2}M; Methanol = 70% (v/v); μ = 0.50 M.

Table 6

Effect of temperature

Temp. (± 0.1°C)	Orcinol (5×10^{-4} M) ($10^4 \times k_{obs}$, s^{-1})
30.0	3.2
35.0	4.1
40.0	5.4
45.0	6.2

$[K_3 Fe(CN)_6] = 1 \times 10^{-3}$ M; Methanol = 50% (v/v) ;
$[NaOH] = 5 \times 10^{-2}$ M; $\mu = 0.50$ M.

From the linear plots of log k_{obs} against the reciprocal of temperature (Fig.2), the activation energies were calculated. The other activation parameters have been calculated and are shown in Table 7.

Table 7

Activation parameters

Parameters	Catechol	Resorcinol	Orcinol	Quinol
$E(kJmol^{-1})$	19.1±0.7	24.0±1.2	40.7±1.3	17.6±0.4
$A\ (s^{-1})$	8.6±0.3	8.3±0.5	370± 2.3	1.1
$\Delta H^{\neq}(kJmol^{-1})$	16.6±0.7	21.2±1.0	37.9±1.0	14.9±0.6
$\Delta S^{\neq}(JK^{-1}mol^{-1})$	-235±1.2	-201±2.5	-170±2.0	-115±2.0

The reactions have negative values of $\Delta S^{\neq}$, the entropy of activation. Qualitatively, this would imply that the potential energy of the transition state would be lowered, enabling the facile formation of such a transition state. The negative values of $\Delta S^{\neq}$ may be due to two factors:

(a) since the rate determining step involves a reaction between two negatively charged ions, this should lead to a negative value of $\Delta S^{\neq}$, in going from the reactants to the transition state (48); and

(b) for reactions between ions of the same sign, the transition state will be a more highly charged ion, and hence strongly solvated. More solvent molecules would be required for this transition state than for the separate ions. The net effect would be that in the formation of such a transition state, there would result a negative value of the entropy of activatio (49).

Effect of ionic strength:

Variations in the ionic strength of the medium using $NaClO_4$ (0.10M to 0.50M) did not have any effect on the rates of these reactions.

Effect of added $K_4Fe(CN)_6$:

The addition of $K_4Fe(CN)_6$ in the concentration range (1.0×10^{-4}M to 1.0×10^{-3}M) did not have any effect on the rates of these reactions.

Radical intermediates(vide 'Experimental'):

Earlier investigations had established the formation of semi-quinone radical intermediates (15,20-21) in the oxidation of catechol. The esr spectrum of o-benzosemiquinone, obtained from a solution of catechol in alkaline ethanol, had been reported (15,50). This spectrum was later analysed for its hyperfine splittings (51-52).

The radicals produced by the oxidation of resorcinol, in alkaline medium, have been shown to be the m-benzosemiquinone radical anion (53).

The intermediate p-benzosemiquinone radical anion was detected and identified by esr spectroscopy during the two-step oxidation of quinol catalysed by enzymes such as peroxidase (54-55) and laccase (56). This semiquinone radical anion has also been detected in alkaline solution, and characterized by titration (57), spectroscopically (58-59), and by esr measurements (60-62).

In the present investigation, the esr spectra of the radicals generated from the oxidation of catechol, resorcinol, orcinol and quinol, by alkaline hexacyanoferrate (III), have been studied, and the data is shown in Table 8.

Table 8

ESR data of the radical intermediates

Phenoxy radical from	Number of spectral lines	Characterization
Catechol	6	two triplet splittings from equivalent protons at 3 and 6, and at 4 and 5 positions.
Resorcinol	12	triplet splitting from equivalent protons at 4 and 6; two doublet splittings due to protons at 2 and 5 positions.
Orcinol	24	triplet of doublets; each line split into 4 lines, corresponding to interaction with methyl protons at position 5.
Quinol	5	1:4:6:4:1 quartet. quintet

(a) <u>From the oxidation of catechol</u>:

The esr spectrum of the o-benzosemiquinone radical, obtained from the oxidation of catechol by alkaline hexacyanoferrate (III), gave 6 spectral lines, as a result of two triplet splittings arising from the equivalent protons at the 3 and 6 positions, and at the 4 and 5 positions.

This radical intermediate had an absorption in the visible region at 655 nm, and showed a typical absorption band at 1560 cm^{-1} in the infrared spectrum.

(b) From the oxidation of resorcinol:

The esr spectrum of the radical generated from the oxidation of resorcinol by alkaline hexacyanoferrate (III). exhibited 12 spectral lines. A large triplet splitting was observed, arising from the equivalent protons at positions 4 and 6. The remaining two doublet splittings would correspond to protons at positions 2 and 5. This would indicate that the course of the reaction was via the formation of the m-benzosemiquinone radical. This radical intermediate had an absorption at 650 nm in the visible region, and showed a typical absorption band at 1560 cm^{-1} in the infrared spectrum.

(c) From the oxidation of orcinol:

The esr spectrum of the radical, obtained from the oxidation of orcinol by alkaline hexacyanoferrate(III), gave 24 spectral lines. This spectrum consisted of a triplet of doublets, each line being split further into 4 lines, corresponding to the interaction with the three methyl protons at the 5-position. The rate determining step of the reaction involved the formation of a radical intermediate, which showed an absorption at 660 nm in the visible region, and an absorption band at 1560 cm^{-1} in the infrared spectrum.

(d) From the oxidation of quinol:

The esr spectrum of the p-benzosemiquinone radical ion, obtained from the oxidation of quinol by alkaline hexacyanoferrate (III), exhibited 5 equally spaced lines which were in the intensity ratio of 1:4:6:4:1. This pattern is caused by the coupling of the free electron to four equivalent protons to produce hyperfine splitting. Four such protons in a non-overlapping spectrum would produce a splitting into 5 lines with peak intensity ratios of 1:4:6:4:1. This radical intermediate showed an absorption in the visible region at 650 nm, and a typical absorption band at 1560 cm^{-1} in the infrared spectrum. In general, phenoxy radicals have been characterized by their electronic spectra (63-64). Earlier work had indicated the formation of the p-benzosemiquinone radical ion, which had been characterized by its esr and electronic spectra (65-68).

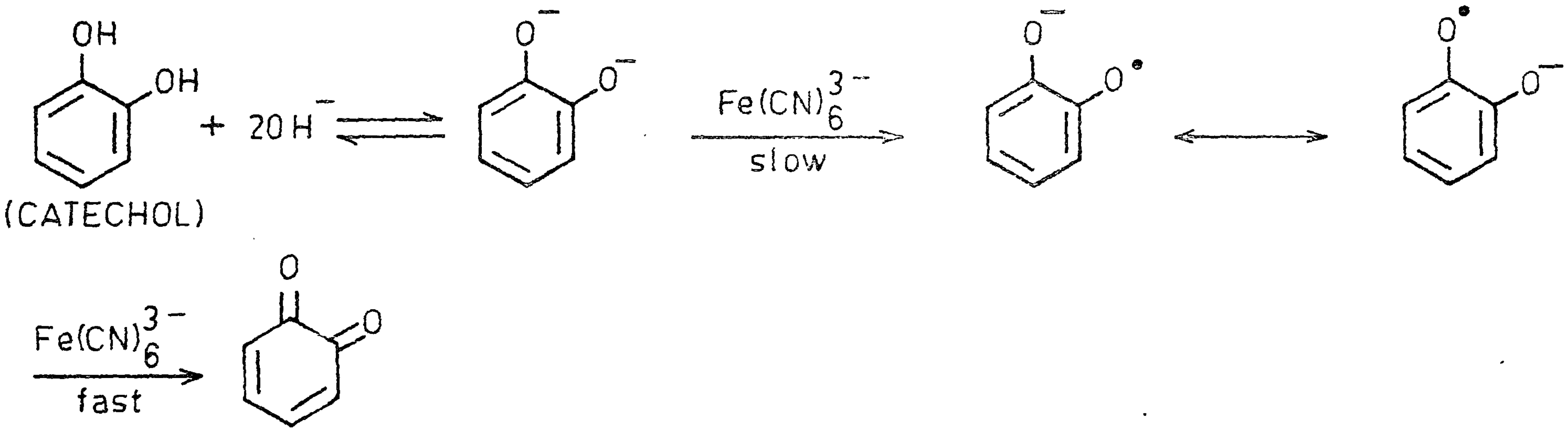
Mechanism

Pummerer et al (69-70) had postulated a free phenoxy radical as the first intermediate in the oxidation of phenols. The oxidation of phenols by hexacyanoferrate(III) in alkaline medium gave the aryloxy anion. This anion transfers an electron to hexacyanoferrate (III), resulting in the formation of an aryloxy radical. This radical is free to react, and further oxidation can yield either the quinone, or result in the formation of coupled products.

1. CATECHOL

Earlier investigations had established the formation of semiquinone radical intermediates(15,20-21) in the oxidation of catechol. The esr spectrum of o-benzosemiquinone, obtained from a solution of catechol in alkaline ethanol had been reported (15,50), and analysed for its hyperfine splittings (51-52).

In the present investigation, the first step in the reaction of catechol with alkaline hexacyanoferrate (III) is the formation of the anion. The removal of one electron from the anion of catechol would lead to the corresponding stable o-benzosemiquinone radical, which was characterized by

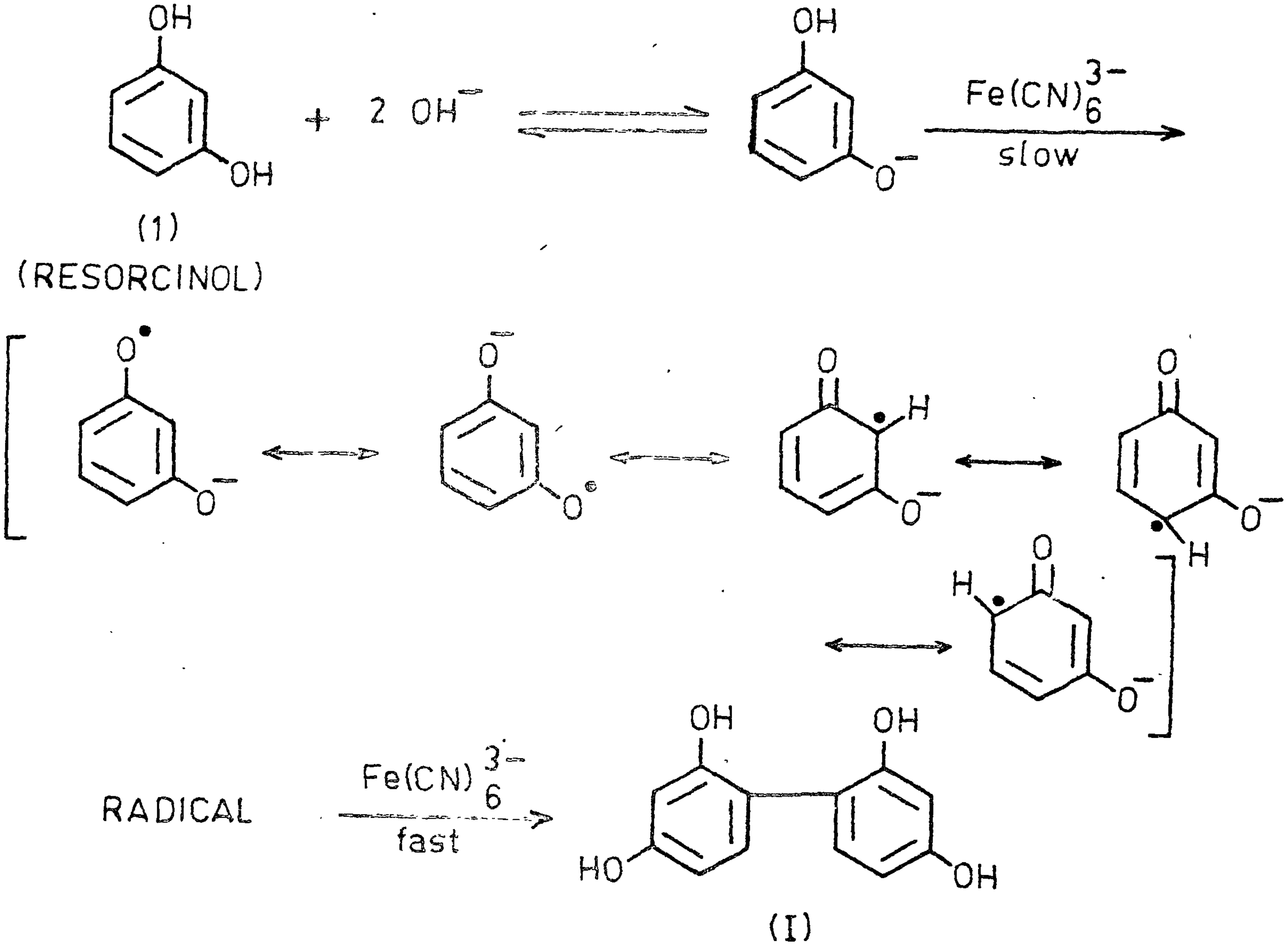

(CATECHOL)
+ 2OH⁻
Fe(CN)$_6^{3-}$
slow
Fe(CN)$_6^{3-}$
fast

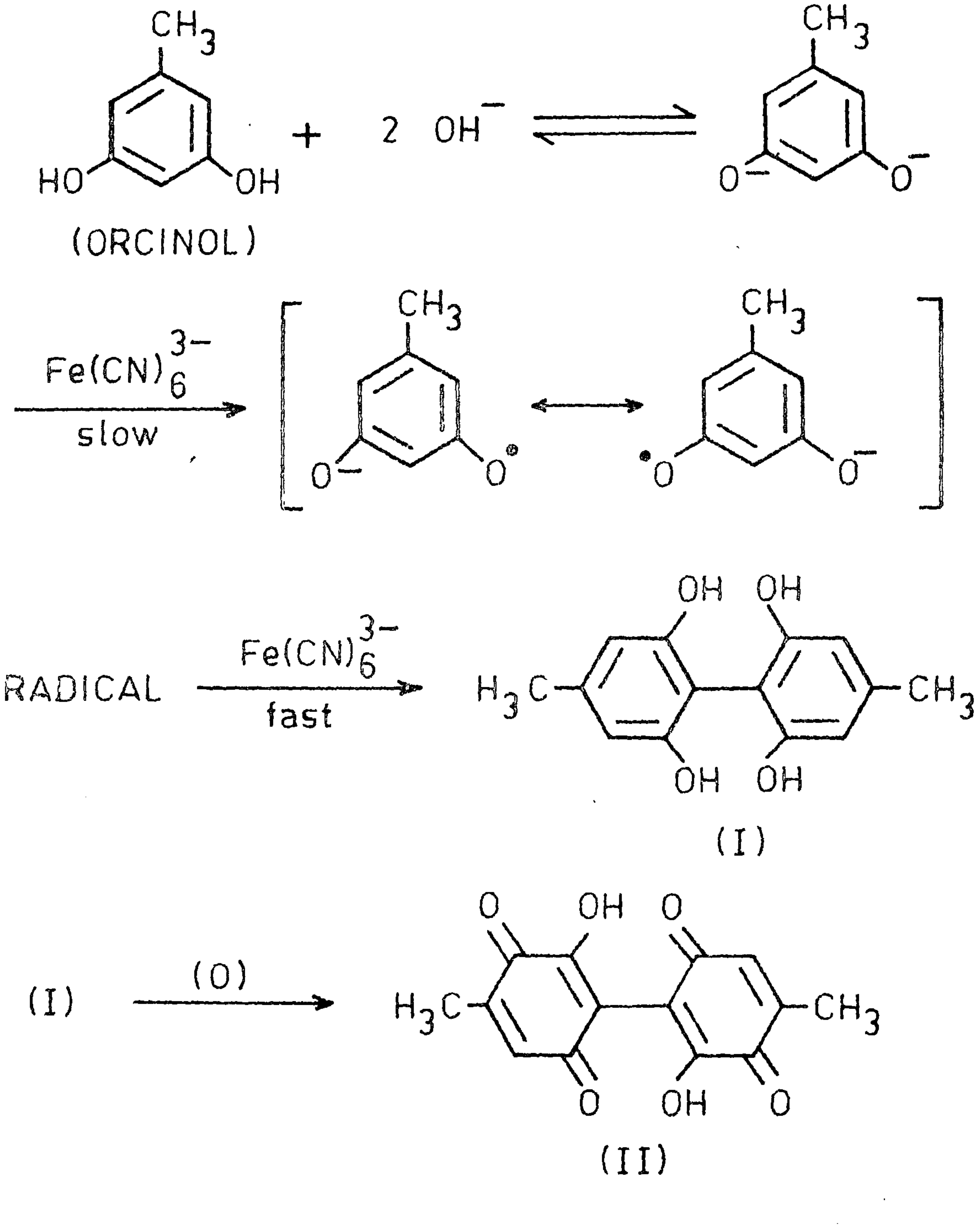
esr spectroscopy as a 6-line spectrum. Further oxidation of the radical intermediate resulted in the removal of the second electron, to afford the product, o-benzoquinone. This product has been isolated and characterized, unequivocally, as o-benzoquinone (vide 'Experimental' : Product analysis). The reaction sequenced is shown in the Scheme.

2. RESORCINOL

For resorcinol, the observed coupling positions (ortho and para) show that a free phenoxy radical is reactive only on the oxygen, and on the ortho and para carbon atoms. Therefore, the unpaired electron has a high probability density at these positions. It is reasonable to postulate that the oxidation of resorcinol would proceed by way of attack at the 4-position, which is activated by being ortho to one of the hydroxy groups, and para to the other.

The first step in the oxidation of resorcinol is the formation of the dianion. The potential for the abstraction of the first electron would be lowered by the presence of the second hydroxyl group. This would afford, upon one-electron oxidation, the m-benzosemiquinone radical. The formation of this radical has been confirmed by esr

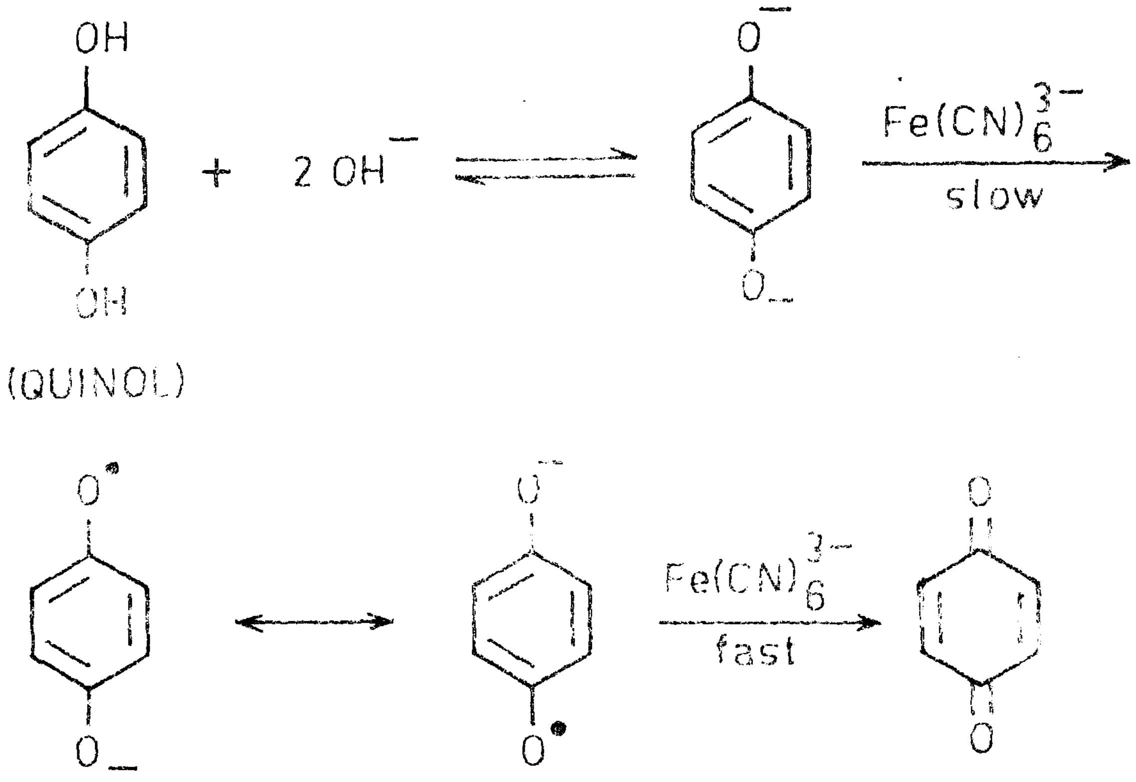

(1)
(RESORCINOL)
+ 2 OH⁻
Fe(CN)₆³⁻
slow
RADICAL
Fe(CN)₆³⁻
fast
(I)


CH3
HO
OH
(ORCINOL)
+ 2 OH−
O−
Fe(CN)6 3−
slow
RADICAL
Fe(CN)6 3−
fast
H3C
OH
(I)
(I)
(O)
O
(II)

spectroscopy as a 12-line spectrum. The next step of the reaction, however, requires a high potential. The diradical cannot be stabilised, since the formation of m-quinones is not possible. Considering the very high spin density at 4 and 6 positions, it is to be expected that further oxidation would occur by the dimerization of the primary radicals at one of these two positions to form a biphenyl compound. Rapid and irreversible coupling of the radicals occurred at the 4-position, to give the product, 3, 3', 5, 5' - tetrahydroxy biphenyl (vide 'Experimental' : Product analysis). The reaction sequence is shown in the Scheme.

3. ORCINOL

In the case of orcinol, the presence of the alkyl substituent decreases the redox potential, making the phenol more easily oxidizable. The position ortho to both the hydroxyl groups would become activated, and the net result would be that the process of oxidative coupling would occur at this position, to give the product, 2, 2', 6, 6' - tetrahydroxybitolyl - 4,4' (vide 'Experimental' : Product analysis). The presence of the methyl group in orcinol enhances the rate of the reaction. The reaction sequence is shown in the Scheme.


OH
OH
(QUINOL)
+
2 OH⁻
O⁻
O⁻
Fe(CN)₆³⁻
slow
O•
O⁻
O⁻
O•
Fe(CN)₆³⁻
fast
O
O

4. QUINOL

The alkali dependence of the oxidation process indicated that the reaction proceeded via an intermediate anion of the reducing substrate formed with hydroxyl ions. For the formation of the dianion of quinol, the pK values for the two steps have been reported (71) as 9.85 and 11.4 . Hexacyanoferrate(III) would react with this dianion to yield the p-benzosemiquinone radical. This radical intermediate, detected by esr spectroscopy, showed a 5-line spectrum with peak intensities of 1:4:6:4:1. Further oxidation of the radical intermediate was rapid, and yielded the product which has been characterized as p-benzoquinone. Redox equilibria data (30) have indicated that the potential for the removal of the second electron is so low, that p-benzoquinone is formed quite rapidly. The product has been characterized as p-benzoquinone (vide 'Experimental': Product analysis). The reaction sequence is shown in the Scheme.

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CHAPTER 3

KINETICS OF OXIDATION OF TRIHYDRIC PHENOLS*

The oxidation of trihydric phenols (pyrogallol and phloroglucinol) has been studied by various workers, using different of oxidizing agents.

Pyrogallol

The aerial oxidation of pyrogallol[1] in the presence of $Ba(OH)_2$ had yielded coupled products(1-2), while the aerial oxidation in alkaline medium had yielded trimeric products(3). Substituted pyrogallols gave trimeric products when oxidized by peroxydisulfate(4), molecular iodine(5), or when aerial oxidations were performed in the presence of ammonia(6-8), $NaHCO_3$(8-9), $Ba(OH)_2$(9-10), or by enzyme(11). Tyrosinase, laccase and peroxidase catalyzed the oxidation of pyrogallol to purpurogallin, and this reaction has been used for the assay of all three enzymes(12-14). The enzymic oxidation of vicinal trihydric phenols to purpurogallin structures plays an important part in the biosynthesis of the tannins in tea(15).

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Phloroglucinol

Coupled products have been obtained when phloroglucinols were oxidized by a variety of oxidizing agents such as hexacyanoferrate(III) in alkaline medium (16-17), and by $FeCl_3$ in ethanol(18). Phloroglucinol trimethyl ether has been converted to 2,6-dimethoxyquinone when the oxidation was performed by LTA in benzene(19).

PRESENT WORK

The kinetics of oxidation of trihydric phenols by hexacyanoferrate(III) in alkaline medium has not received much attention. The present work is a detailed kinetic probe into the oxidation of trihydric phenols (pyrogallol and phloroglucinol) by potassium hexacyanoferrate(III) in alkaline medium, at constant ionic strength, under a nitrogen atmosphere, using aqueous methanol (70%, v/v) as solvent.

Stoichiometry (vide 'Experimental'):

The stoichiometry of the reaction was determined to be 2:4 (substrate : oxidant), according to the equations:

(a) Pyrogallol:

$$2C_6H_6O_3 + 4Fe(CN)_6^{3-} + 2OH^- \longrightarrow C_{12}H_8O_6 + 4Fe(CN)_6^{4-} + 2H_2O + 2H^+$$

(b) Phloroglucinol:

$$2C_6H_6O_3 + 4Fe(CN)_6^{3-} + 2OH^- \longrightarrow C_{12}H_8O_6 + 4Fe(CN)_6^{4-} + 2H_2O + 2H^+$$

Effect of substrate, oxidant and alkali:

The rate of the reaction was observed to be dependent on the first powers of the concentrations of substrate, oxidant and alkali (Tables 1-2).

Table 1

Rate data for the oxidation of pyrogallol at 40.0 ± 0.1°C

[Pyrogallol] (10^2 x M)	[$K_3Fe(CN)_6$] (10^3 x M)	[NaOH] (M)	10^2 x k_{obs} (s^{-1})
1.0	1.0	0.1	40.0
2.0	1.0	0.1	80.7
5.0	1.0	0.1	203.0
10.0	1.0	0.1	410.0
1.0	0.5	0.1	39.6
1.0	0.25	0.1	40.6
1.0	0.10	0.1	40.3
1.0	1.0	0.25	101.0
1.0	1.0	0.50	204.0
1.0	1.0	0.75	308.0

Methanol = 50% (v/v); μ = 0.50M.

Table 2

Rate data for the oxidation of phloroglucinol at $30.0 \pm 0.1^{\circ}C$

[Phloroglucinol] (10^2 x M)	[$K_3Fe(CN)_6$] (10^3 x M)	[NaOH] (10^2xM)	10^2 x k_{obs} (s^{-1})
1.0	1.0	5.0	4.8
2.5	1.0	5.0	12.0
5.0	1.0	5.0	24.2
10.0	1.0	5.0	48.8
1.0	0.2	5.0	4.7
1.0	0.5	5.0	4.9
1.0	0.7	5.0	4.8
1.0	1.0	2.0	2.0
1.0	1.0	7.0	7.2
1.0	1.0	10.0	10.1

Methanol = 70% (v/v); μ = 0.50M

When a constant concentration of substrate (large excess) was used, k_{obs} did not show any appreciable variation with changing concentrations of oxidant, indicating a first order dependence of the reaction on the concentration of the oxidant (Tables 1-2).

Rate law:

Under the present experimental conditions, the rate law could be expressed as:

$$\text{Rate} = - \frac{d[\text{Fe(CN)}_6^{3-}]}{dt} = k_{obs} [\text{substrate}][\text{Fe(CN)}_6^{3-}][\text{OH}^-] \quad \ldots\ldots\ldots (1)$$

The pseudo first order rate constant, k_{obs}, was determined by keeping the concentrations of two out of the three reactants (substrate, oxidant and alkali) constant, and was calculated from the equation(20):

$$k_{obs} = \frac{2.303}{t} \log \frac{D_o}{D_t} \quad \ldots\ldots \quad (2)$$

where D_o was the initial optical density of the reaction mixture, and D_t was the optical density at time, t (vide 'Experimental' : Calculations).

Solvent influences

The rate of the reaction was influenced by a change in the solvent composition of the medium (Tables 3-4).

Table 3

Effect of solvent at 40.0 ± 0.1°C

MeOH - H_2O (%, v/v)	Pyrogallol (10^5 x k_{obs}, s^{-1})
50-50	33.5
45-55	23.2
40-60	14.3
35-65	10.9

[Pyrogallol] = 5 x 10^{-4}M; [$K_3Fe(CN)_6$] = 1 x 10^{-3}M; [NaOH] = 0.1M; μ = 0.50 M.

Table 4

Effect of solvent at 30.0 ± 0.1 °C

MeOH-H_2O (%, v/v)	Phloroglucinol ($10^2 \times k_{obs}$, s^{-1})
70-30	4.8
75-25	4.5
80-20	4.1
85-15	3.7

$[\text{Phloroglucinol}] = 1 \times 10^{-2}$ M; $[K_3Fe(CN)_6] = 1 \times 10^{-3}$ M; $[\text{NaOH}] = 5 \times 10^{-2}$ M; $\mu = 0.50$ M.

The plots of log k_{obs} against the reciprocal of the dielectric constant were linear (Fig.1), suggesting that the reactions under consideration were of the ion-ion type (21). Using the Scatchard equation (22), the values of r, the distance of approach between the ions, were calculated to be 6.2 Å (for pyrogallol), and 5.6 Å (for phloroglucinol). These values of r were of the correct order of magnitude.

Effect of temperature

The rates of the reactions were enhanced, with an increase in the temperature (Table 5). The plots of

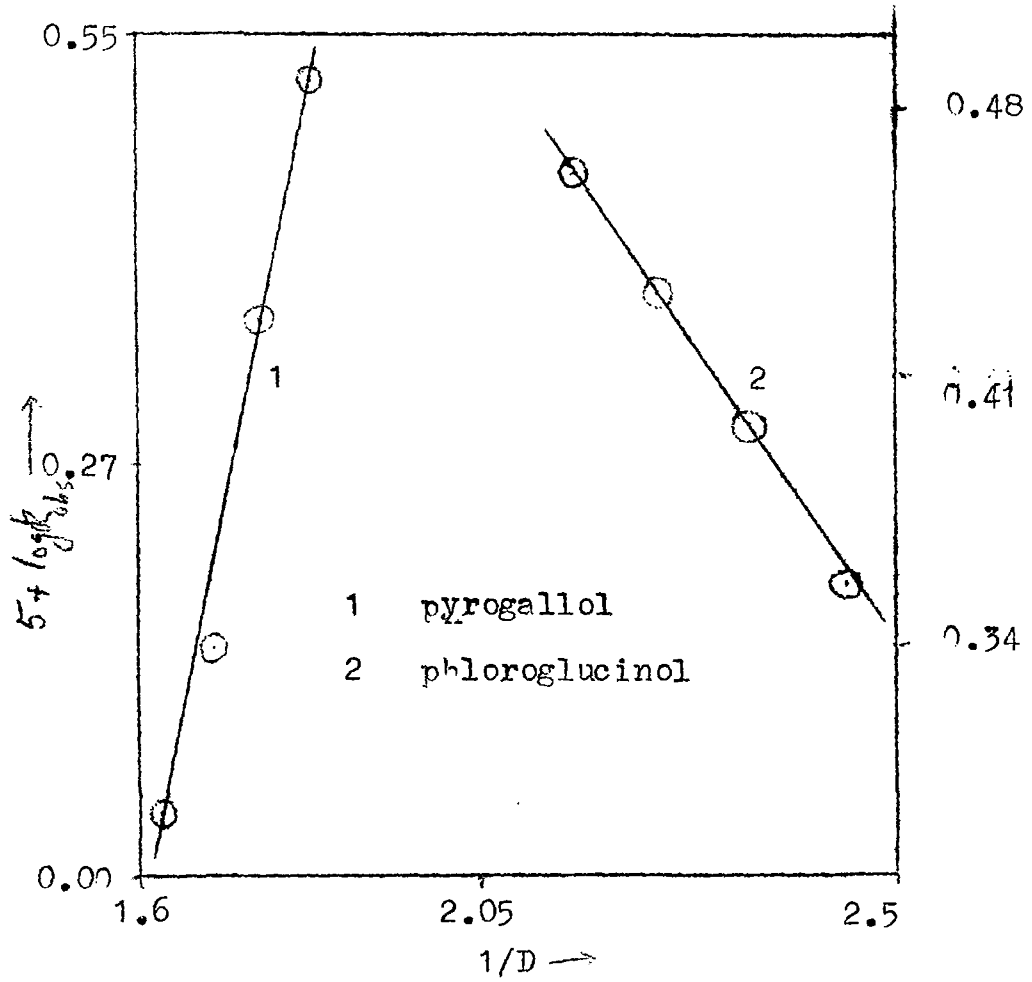


Fig. 1 - Plot of log k_{obs} against 1/D

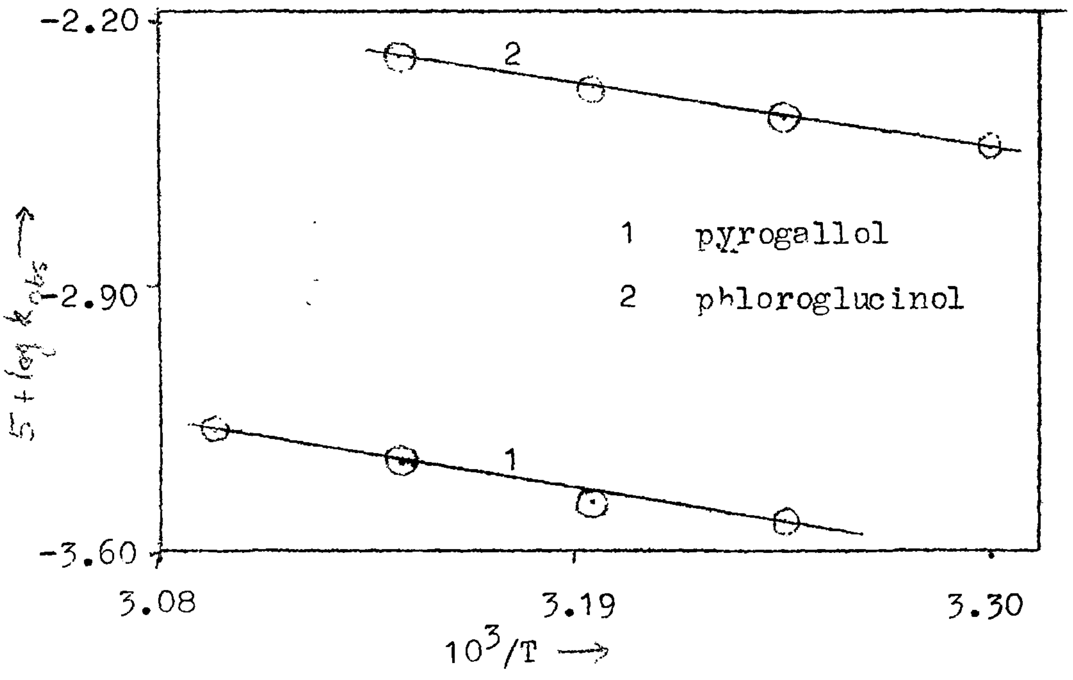


Fig. 2 - Plot of log k_{obs} against 1/T

log k_{obs} against the reciprocal of temperature were linear (Fig.2), and the activation energies were calculated from the slopes of these plots. The other activation parameters were calculated, and have been shown in Table 6.

Table 5

Effect of temperature

Temp (± 0.1°C)	Pyrogallol*	Phloroglucinol#
	$(10^2 \times k_{obs}, s^{-1})$	
30.0	–	4.8
35.0	31.7	5.7
40.0	40.0	6.8
45.0	53.0	8.3
50.0	65.0	–

[Substrates] = 1×10^{-2}M; [$K_3Fe(CN)_6$] = 1×10^{-3} M; μ = 0.50 M.

* [NaOH] = 0.1M; *Methanol = 50% (v/v).

[NaOH] = 5×10^{-2} M; # Methanol = 70% (v/v).

Table 6

Activation parameters

Parameters	Pyrogallol	Phloroglucinol
E(kJ mol^{-1})	38.3 ± 0.8	28.2 ± 0.8
A (s^{-1})	3.2 x 10^{2}	1.3 x 10^{4}
$\Delta H^{\ddagger}$ (kJ mol^{-1})	35.6 ± 0.7	25.6 ± 0.8
$\Delta S^{\ddagger}$ (JK^{-1} mol^{-1})	-163 ± 2.0	-174 ± 1.6

Effect of ionic strength:

The variation of ionic strength by using $NaClO_4$ (0.10M to 0.50M), did not have any effect on the rates of these reactions.

Effect of added $K_4Fe(CN)_6$:

The addition of $K_4Fe(CN)_6$ in the concentration range,
1.0 x 10^{-4}M to 1.0 x 10^{-3}M, did not have any influence on the rates of these reactions.

Radical intermediate (vide 'Experimental'):

(a) From the oxidation of pyrogallol:

The ESR spectrum of the radical, generated from the oxidation of pyrogallol by alkaline hexacyanoferrate(III), gave two groups of three lines each, resulting from the hyperfine interactions of protons on the ring, with the unpaired electron spin. The resonance forms of this semiquinone structure would make protons at positions 4 and 6 equivalent. The observed splitting of the line follows from doubling due to the proton at position 5, followed by tripling of each of these two lines by the remaining equivalent protons at positions 4 and 6. The intensity ratios were (1,2,1) and (1,2,1).

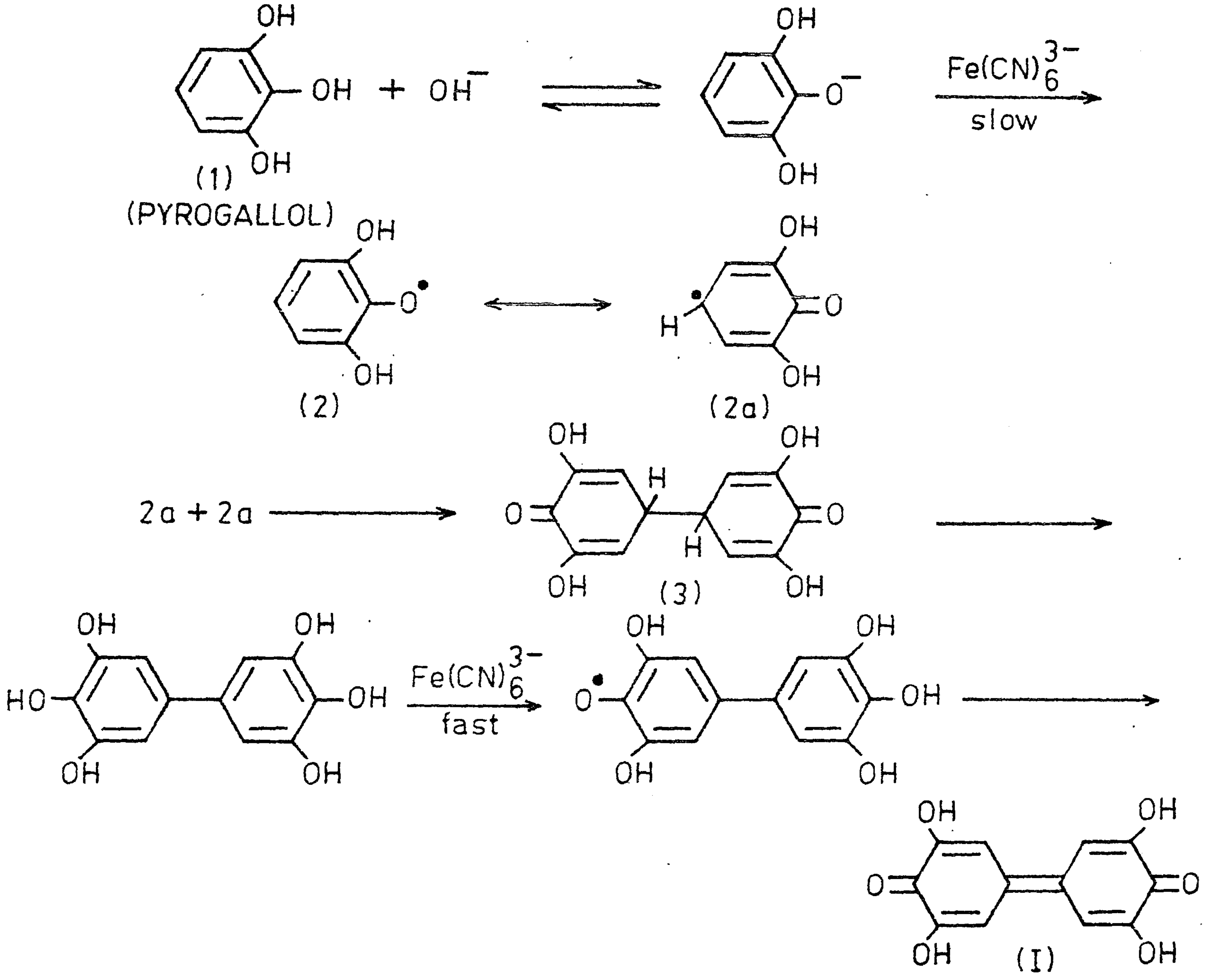
This radical intermediate showed an absorption in the visible region at 655nm, and gave an absorption band at 1560 cm^{-1} in the IR spectrum.

(b) <u>From the oxidation of phloroglucinol:</u>

The ESR spectrum of the radical, generated from the oxidation of phloroglucinol by alkaline hexacyanoferrate (III), showed a 1:3:3:1 quartet spectrum, due to the three equivaldnt protons at positions 2, 4 and 6.

The IR spectrum of the reaction mixture, scanned rapidly at two-minute intervals, exhibited a stable band at 1560 cm^{-1}. These data suggested the formation of a radical intermediate in the rate determining step of the reaction.

In general, phenoxy radicals have been characterized by their electronic spectra(23-24).


(1)
(PYROGALLOL)
OH
+ OH⁻
Fe(CN)$_6^{3-}$
slow
(2)
(2a)
2a + 2a
(3)
Fe(CN)$_6^{3-}$
fast
(I)

Mechanism :

(a) Oxidation of pyrogallol:

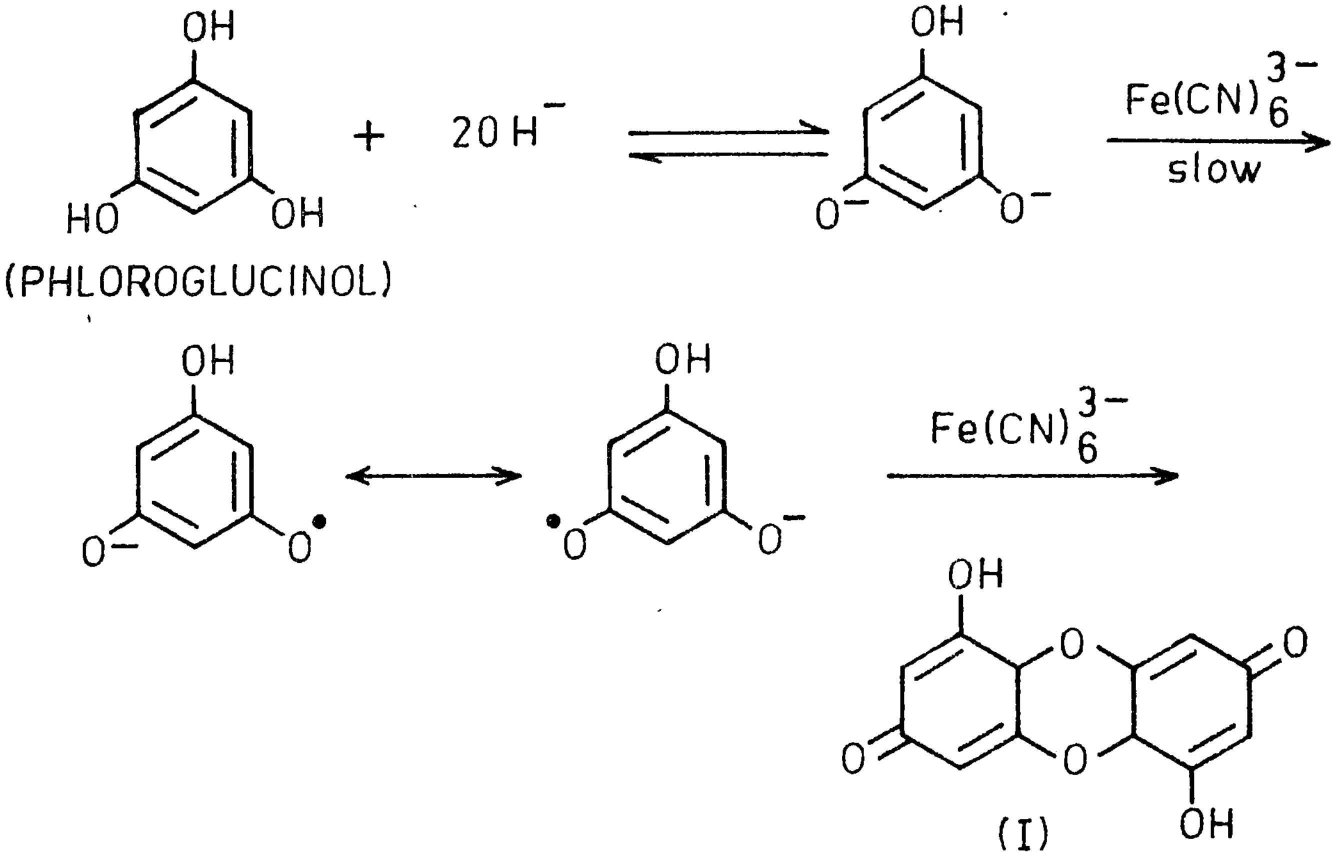
Pummerer et al(25-26) had postulated a free phenoxy radical as the first intermediate in the reactions of phenol coupling. This radical would be reactive on the oxygen, and in the 5 position of pyrogallol. In this investigation, the first step of the reaction was the formation of the anion, which, on reaction with hexacyanoferrate(III), would give the radical, 2 ⟷ 2a. Combination of 2a + 2a gives the dimer, 3. This dimer undergoes tautomerization in methanol rapidly, and is further oxidized, by hexacyanoferrate (III), to yield the extended quinone, I. This product has been characterized by analytical and spectral methods (vide 'Experimental' : Product analysis).

The sequence of reactions is shown in the Scheme.

(b) Oxidation of phloroglucinol :

In the case of phloroglucinol, the observed coupling positions, ortho and para, show that a free phenoxy radical is reactive only on the oxygen and on the ortho and para carbon atoms. Resonance structures would symbolize a high density of the unpaired electron at these positions.

When two radicals combine, dimers are formed. In some cases, dimers thought to be peroxides have been reported (27-30). Later investigations showed these to be of


OH
HO
OH
(PHLOROGLUCINOL)
+
2OH⁻
OH
O⁻
O⁻
Fe(CN)₆³⁻
slow
OH
O⁻
O•
•O
O⁻
Fe(CN)₆³⁻
OH
O
O
O
O
OH
(I)

the phenoxydienone type (31-33). If the potential of the oxidizing agent is high enough, the C-C dimers can be oxidized further to yield extended quinones(34).

The results of the present study indicate that in alkaline solution, the potential for the first electron transfer from the anion should be lower than that for the second from the radical. Therefore, the first step should be much faster than the second, assuming that the rate of oxidation increases with the potential difference between the substrate and the oxidant.

In the present investigation, the alkali dependence of the oxidation process indicated that the reaction proceeded via an intermediate anion of the reducing substrate formed with hydroxyl ions. Hexacyanoferrate(III) reacted with this anion to yield the radical. This radical intermediate has been detected and characterized by ESR spectroscopy. Rapid and irreversible coupling of this radical gave the product. It would be reasonable to assume that the coupling occurred fastest at the positions of highest density of the free electron. The product was characterized by analytical and spectral methods (vide 'Experimental':Product analysis).

The reaction sequence is shown in the Scheme.

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CHAPTER 4

KINETICS OF OXIDATION OF NAPHTHOLS*

The oxidation of naphthols has been studied by various workers, using a variety of oxidizing agents.

α-naphthol:

The oxidation of α-naphthol by $FeCl_3$ had yielded all three possible ortho and para carbon-carbon coupled products(1-7). Trimeric products were obtained when α-naphthol was oxidized by air/$ZnCl_2$(8), and by PbO_2(9-11). The oxidationo of α-naphthol by 2,4,6-triphenylphenoxyl gave O-diphenoquinone(12).

β-naphthol:

Coupled products were obtained when β-naphthol was oxidized by $FeCl_3$(1, 13-15), hexacyanoferrate(III) in alkaline medium (16-18), PbO_2(8, 11), Cu(II) acetate in the presence of ammonia(11), and by Cu(II) salt (19). Trimers

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* M. Bhattacharjee and M.K. Mahanti, Int. J. Chem. Kinetics, 15 , 197 (1983).

were obtained when β-naphthol was oxidized by H_2O_2 in the presence of acetic acid and sodium molybdate (20). Coupled products and trimers were obtained when β-naphthol was oxidized by oxygen in the presence of V_2O_5, WO_3 or CaO at temperatures around 300°C(3,21), and by air/NaOH(22). A mixture of ortho-ortho, ortho-para and carbon-oxygen coupled products were obtained when β-naphthol was oxidized by O_2 in the presence of Cu(II) salt and collidine(23).

PRESENT WORK

The kinetics of oxidation of naphthols by hexacyanoferrate(III) in alkaline medium has not received much attention. The present work is a detailed kinetic study of the oxidation of naphthols (α-naphthol and β-naphthol) by potassium hexacyanoferrate(III) in alkaline medium, at constant ionic strength, under a nitrogen atmosphere, using aqueous methanol (70%, v/v) as solvent.

Stoichiometry (vide 'Experimental'):

The stoichiometry of the reactions were determined to be:

(a) α-naphthol:

$$6C_{10}H_8O + 6\,Fe(CN)_6^{3-} + 2OH^- \longrightarrow 3C_{20}H_{14}O_2 + 6Fe(CN)_6^{4-} + 2H_2O + 4H^+$$

(b) β-naphthol:

$$6C_{10}H_8O + 6Fe(CN)_6^{3-} + 2\,OH^- \longrightarrow C_{20}H_{10}O_2 + 6Fe(CN)_6^{4-} + 2H_2O + 4H^+$$

Effect of substrate, oxidant and alkali:

The rate of the reaction was observed to be dependent on the first powers of the concentrations of substrate, oxidant and alkali (Table 1).

Table 1

Rate data for the oxidation of Naphthols at 30.0± 0.1°C

[Substrate]	$[K_3Fe(CN)_6]$	[NaOH]	α-naphthol	β-naphthol
(10^3x M)	(10^3 x M)	(10^2xM)	$(10^4 \text{ x } k_{obs}, s^{-1})$	
8.0	1.0	5.0	110.0	9.6
10.0	1.0	5.0	137.0	12.0
25.0	1.0	5.0	345.0	30.0
10.0	0.5	5.0	139.0	12.2
10.0	0.1	5.0	137.0	12.0
10.0	0.05	5.0	138.0	12.1
10.0	1.0	1.0	27.0	2.6
10.0	1.0	2.5	68.0	6.3
10.0	1.0	10.0	272.0	24.2

Methanol = 70% (v/v); μ = 0.50 M.

When a constant concentration of substrate (large excess) was used, k_{obs} did not show any appreciable variation with changing concentrations of oxidant, indicating a first order dependence of the rate of the reaction on the concentration of the oxidant (Table 1).

Rate law:

Under the present experimental conditions, the rate law can be expressed as follows:

$$\text{Rate} = -\frac{d[\mathrm{Fe(CN)_6^{3-}}]}{dt} = k_{obs}\,[\text{Naphthol}]\,[\mathrm{Fe(CN)_6^{3-}}]\,[\mathrm{OH^-}] \;\ldots\ldots \quad (1)$$

The pseudo first order rate constant, k_{obs}, was determined by keeping the concentrations of two out of the three reactants (substrate, oxidant and alkali) constant, and was calculated from the equation (24):

$$k_{obs} = \frac{2.303}{t}\log\frac{D_o}{D_t} \quad \ldots\ldots \quad (2)$$

where D_o was the initial optical density of the reaction mixture, and D_t was the optical density at time, t (vide 'Experimental' : Calculations).

Solvent influences:

The rate of the reaction was influenced by changes in the solvent composition of the medium. The rate of the reaction was influenced by changes in the solvent composition of the medium. The rate of the reaction was found to increase with increasing amounts of methanol, that is, with a decrease in the dielectric constant of the medium (Table 2).

Table 2

Effect of solvent at 30.0 ± 0.1°C

MeOH-H_2O (%, v/v)	α- naphthol	β-naphthol
	(10^4 x k_{obs} , s^{-1})	
70-30	137.0	12.0
75-25	152.0	15.5
80-20	173.0	19.9
85-15	201.0	26.5

[Substrates] = 1×10^{-2}M; [$K_3Fe(CN)_6$] = 1×10^{-3} M;
[NaOH] = 5×10^{-2} M; μ = 0.50 M

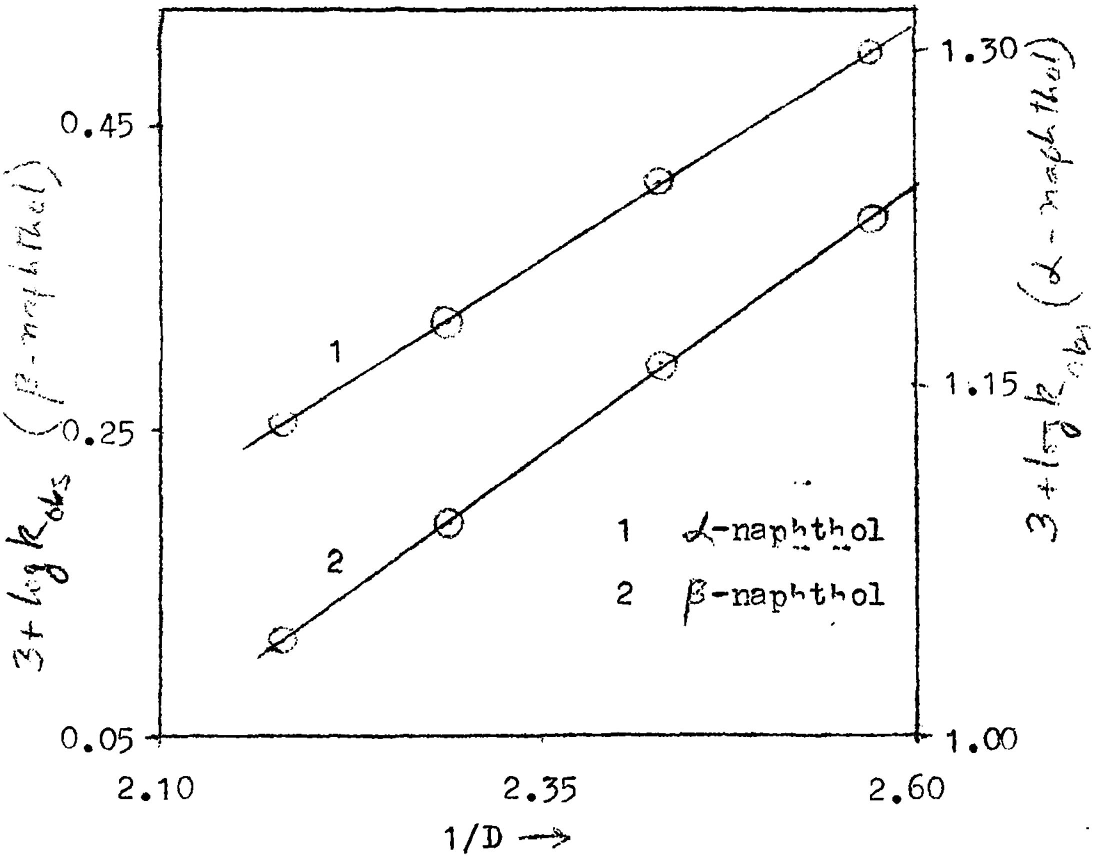


Fig. 1 - Plot of log k_{obs} against 1/D

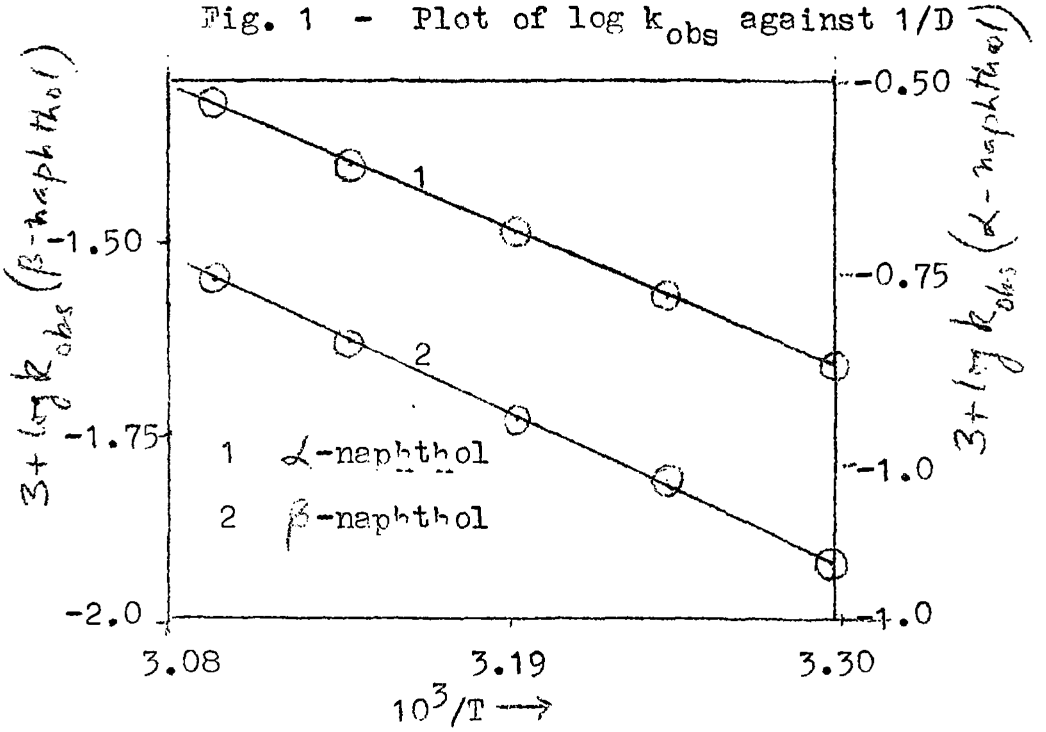


Fig. 2 - Plot of log k_{obs} against 1/T

The dependence of the rate constant on the dielectric constant of the medium can be expressed by the Scatchard equation(25). From the linear plots of log k_{obs} against the reciprocal of the dielectric constant (Fig. 1), the values of r, the distance of approach between the ions, were calculated to be 11.4 Å (for α-naphthol) and 8.5 Å (for β-naphthol). These values of r were of the correct order of magnitude. Solvent effects on the rates of reactions may also be due to factors such as the solvating power of the solvent (26), solute-solvent interactions (27-28), and solvent structure.

Effect of temperature:

The rate of the reaction was increased with an increase in the temperature (Table 3). The plots of log k_{obs} against the reciprocal of temperature were linear (Fig.2), and the activation energies were calculated from the slopes of these linear plots. The other activation parameters were evaluated, and have been shown in Table 4.

Table 3

Effect of temperature

Temp. (± 0.1°C)	α-naphthol	β-naphthol
	($10^4 \times k_{obs}$, s^{-1})	
30.0	137.0	12.0
35.0	170.0	15.5
40.0	202.0	18.3
45.0	250.0	23.1
50.0	303.0	28.5

$[\text{Substrates}] = 1\times10^{-2}$ M; $[K_3Fe(CN)_6] = 1\times10^{-3}$ M;

$[NaOH] = 5 \times 10^{-2}$ M; $\mu = 0.50$ M

Table 4

Activation parameters

Parameters	α-naphthol	β-naphthol
E ($kJmol^{-1}$)	31.8 ± 0.5	34.5 ± 0.5
A (s^{-1})	2.7×10^4	1.2×10^5
$\Delta H^{\ddagger}$ ($kJmol^{-1}$)	29.2 ± 0.5	31.9 ± 0.5
$\Delta S^{\ddagger}$ ($JK^{-1}mol^{-1}$)	− 32 ± 1.3	− 30 ± 1.3

Effect of ionic strength:

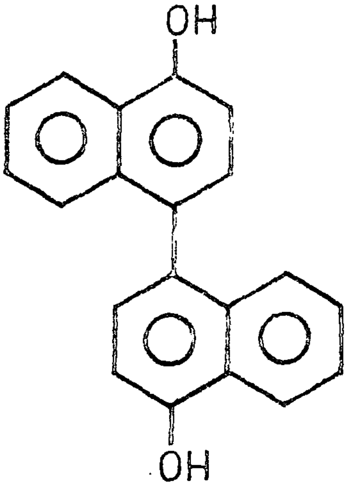
The variation of ionic strength of the medium by using $NaClO_4$ (0.10M to 0.50M), did not have any effect on the rate of the reaction.

Effect of added $K_4Fe(CN)_6$:

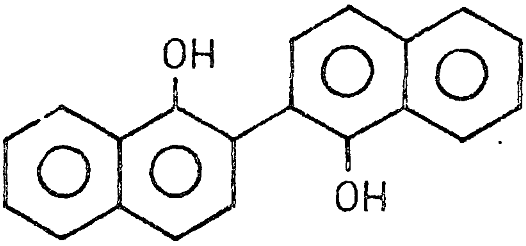
The addition of $K_4Fe(CN)_6$ in the concentration range (1.0×10^{-4}M to 1.0×10^{-3}M), did not have any influence on the rate of the reaction.

Radical intermediate (vide 'Experimental'):

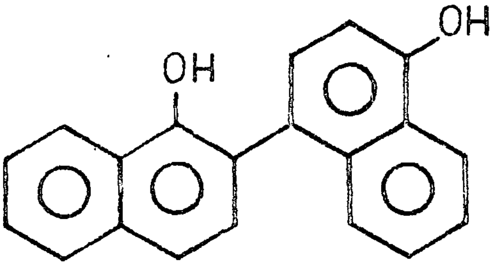
Naphthols are known to give rise to stable radicals, which have been detected and characterized(29-31). In this investigation, the ESR spectrum of the radical obtained from the oxidation of α-naphthol by alkaline hexacyanoferrate(III) gave 9 spectral lines. The radical obtained from the oxidation of β-naphthol by alkaline hexacyanoferrate(III), gave 17 spectral lines. Similar spectra have been observed earlier, and have been analyzed (29-31). For the present, it can be concluded that the rate determining step of the reaction involved the formation of a radical intermediate. It was further observed that this radical intermediate showed a typical absorption band at



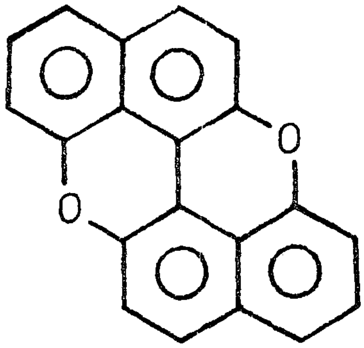
(I)



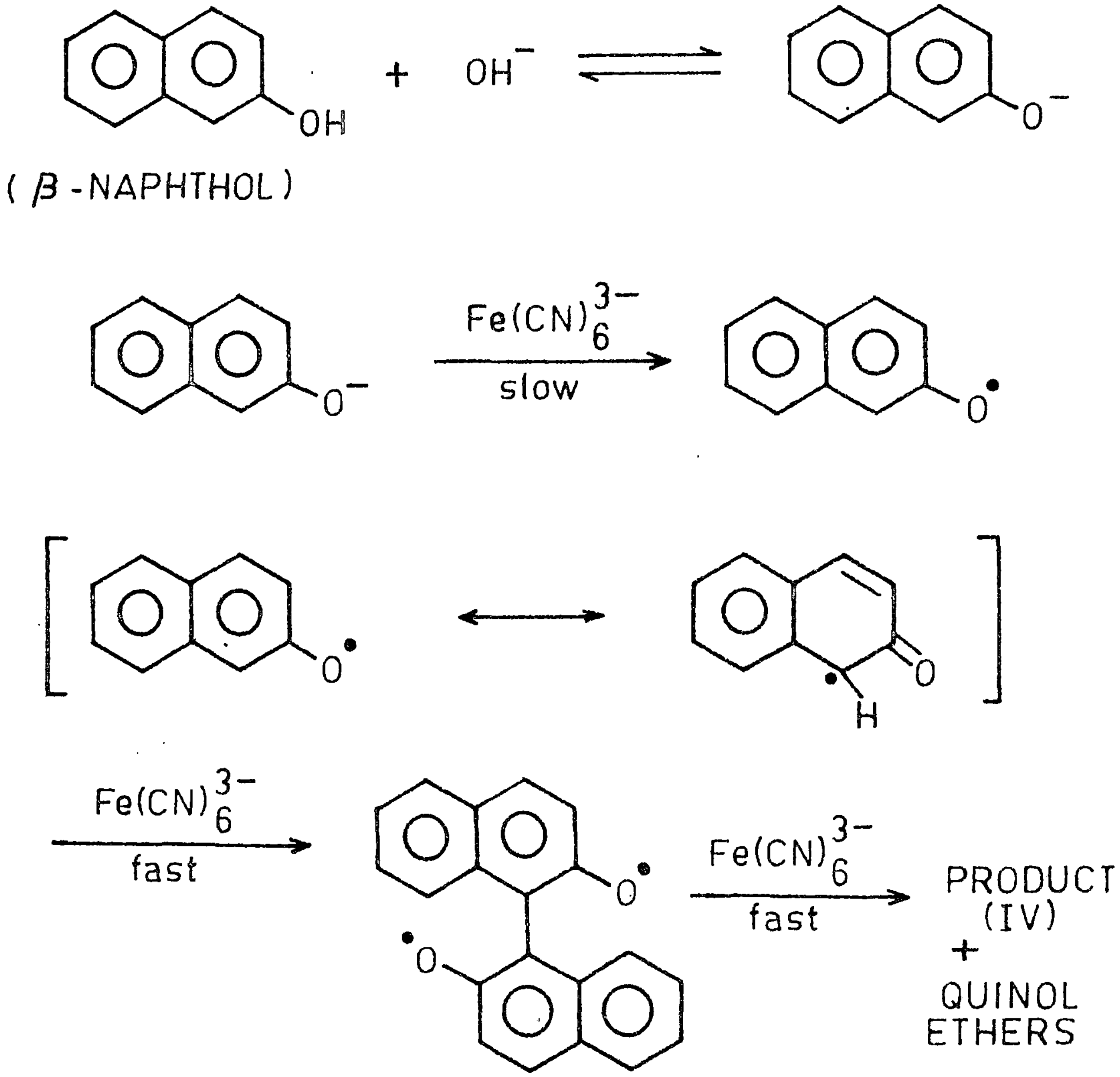
(II)

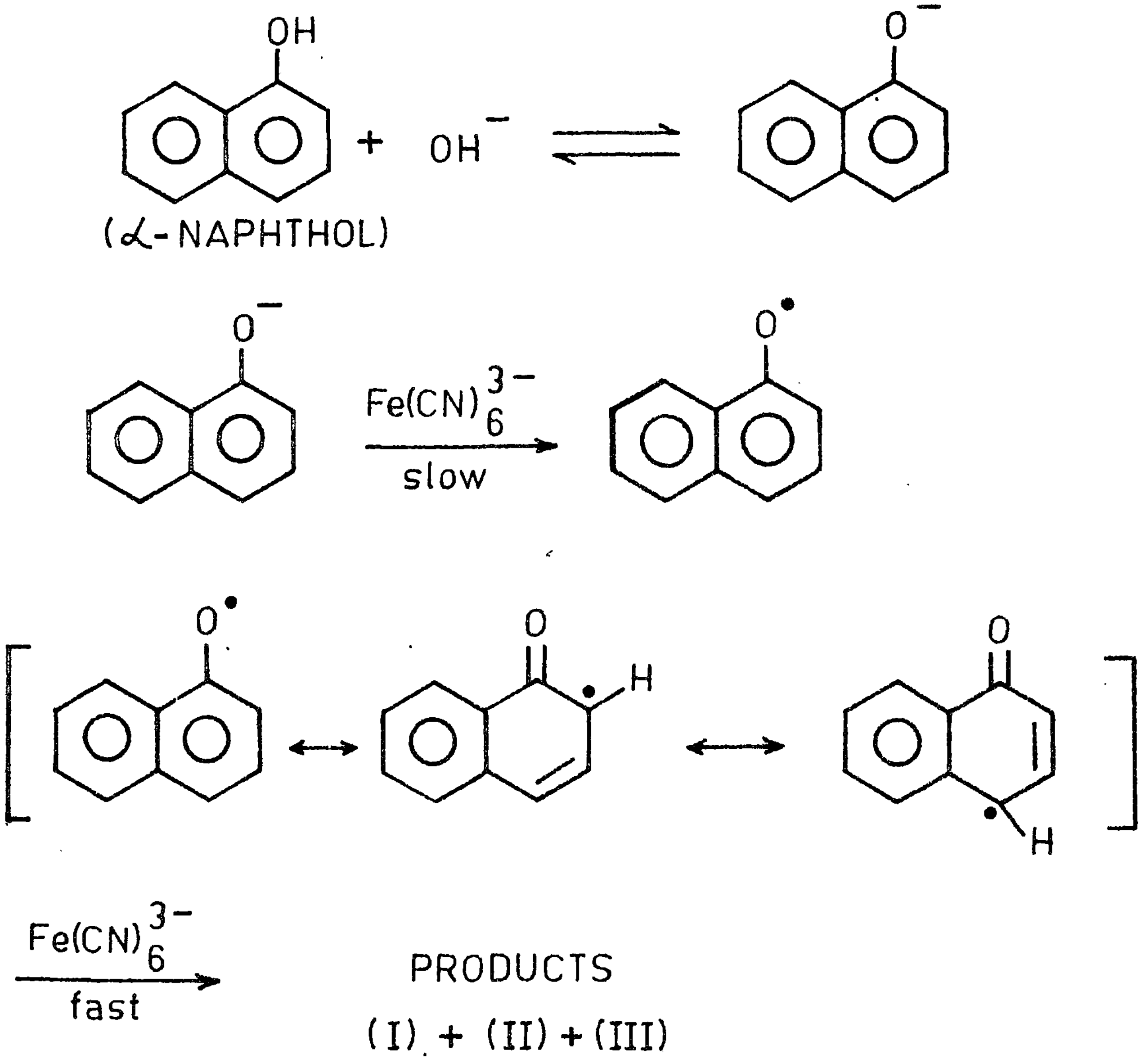


(III)



(IV)


OH
(β -NAPHTHOL)
+
OH⁻
O⁻
Fe(CN)6 3−
slow
O•
O
H
Fe(CN)6 3−
fast
•O
Fe(CN)6 3−
fast
PRODUCT
(IV)
+
QUINOL
ETHERS


OH
(α-NAPHTHOL)
OH⁻
O⁻
Fe(CN)₆³⁻
slow
O•
O
H
Fe(CN)₆³⁻
fast
PRODUCTS
(I) + (II) + (III)

1560cm^{-1} in the infrared spectrum. In general, phenoxy radicals have been characterized by their electronic spectra(32-33).

Mechanism:

Pummerer et al (17-18) had postulated a free phenoxy radical as the first intermediate in the reactions of phenol coupling. The oxidation of β-naphthol with alkaline hexacyanoferrate(III) had given mostly polymeric products(16-18,35), from which a small amount of hydroxynaphthyl naphthyl ether could be isolated (17-18).

In the present investigation, the mechanism of phenol coupling can be best explained by visualizing that the anion is formed in the first step of the reaction. This anion is then oxidized by hexacyanoferrate(III), in a slow step, to give a radical intermediate, which was detected by ESR spectroscopy. The radical intermediate undergoes rapid and irreversible coupling to give the products. These products have beenisolated and characterized by analytical and spectral methods (vide 'Experimental' : Product analysis).

The reaction sequences for the oxidations of the naphthols (α-naphthol and β-naphthol) are shown in the Schemes.

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RECORD OF EXPERIMENTAL
VALUES

Phenol

(a) [Phenol] = 1.0 x 10^{-2}M; [NaOH] = 0.5M; Temp = (50.0±0.1)°C

solvent = [MeOH: H_2O = 50:50% v/v]

O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0.0005M	0.00075M	0.001M
0	0.210	0.295	0.395
5	0.175	0.250	0.335
10	0.160	0.235	0.315
20	0.135	0.220	0.285
30	0.120	0.190	0.262
35	0.115	0.180	0.255

(b) [$K_3Fe(CN)_6$] = 1.0 x 10^{-3}M; [NaOH] = 0.5M; Temp =(50.0±0.1)°C

Solvent = [MeOH: H_2O = 50: 50% v/v]

O.D. (420 nm) for [Phenol] at

t_m	0.001M	0.0025M	0.005M	0.0075M	0.01M
0	0.390	0.390	0.390	0.390	0.395
5	0.375	0.350	0.355	0.345	0.335
10	0.365	0.335	0.345	0.330	0.315
20	0.352	0.325	0.320	0.305	0.285
30	0.345	0.320	0.305	0.285	0.262
45	0.340	0.315	0.285	0.265	0.240

(c) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}M$; [Phenol] = $1.0 \times 10^{-2}M$;
[NaOH] = 0.5M; Solvent = [MeOH:H_2O = 50:50% v/v]
O.D. (420 nm) for temperature in °C at

t_m	35°C	40°C	45°C	50°C
0	0.385	0.395	0.395	0.395
5	0.360	0.350	0.360	0.335
10	0.345	0.340	0.330	0.315
20	0.335	0.315	0.295	0.285
30	0.325	0.305	0.275	0.262
40	0.305	0.295	0.255	0.248
45	-	0.290	0.250	0.240

(d) $[K_3 Fe(CN)_6] = 1.0 \times 10^{-3}M$; [Phenol] = $1.0 \times 10^{-2}M$;
[NaOH] = 0.5M ; Temp = (50.0 ± 0.1)°C
O.D. (420 nm) for [Solvent = MeOH: H_2O % v/v] at

t_m	50:50%	55:45%	60:40%	70:30%
0	0.395	0.360	0.365	0.355
5	0.335	0.335	0.340	0.350
10	0.315	0.315	0.330	0.335
20	0.285	0.300	0.300	0.325
30	0.262	0.278	0.295	0.305
45	0.240	0.260	0.280	0.295

(e) $[K_3 Fe(CN)_6] = 1.0 \times 10^{-3}M$; $[Phenol] = 1.0 \times 10^{-2}M$;

Temp = (50.0 + 0.1)°C ; $[Solvent = MeOH:H_2O = 50:50\%\ v/v]$

O.D. (420 nm) for $[NaOH]$ at

t_m	0.10M	0.20M	0.03M	0.40M	0.5M.
0	0.415	0.405	0.385	0.395	0.395
5	0.405	0.385	0.362	-	0.335
10	0.400	0.380	0.345	0.350	0.315
20	0.396	0.365	0.335	0.300	0.285
30	0.392	0.360	0.325	0.270	0.262
35	0.390	0.350	0.320	0.255	0.255

O-Cresol

(a) $[o\text{-}cresol] = 1.0 \times 10^{-2}M$; $[NaOH] = 0.5M$; Temp =(50±0.1)°C

Solvent : $MeOH : H_2O = 50:50\%\ v/v$

O.D. (420 nm) for $K_3Fe(CN)_6$ at

t_m	0.0005M	0.00075M	0.001M
0	0.262	0.390	0.504
10	0.239	0.359	0.472
20	0.225	0.333	0.436
30	0.226	0.324	0.426
40	0.219	0.319	0.416

(b) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}M$; $[NaOH] = 0.5$ M.

Temp = $(50.0 \pm 0.1)^{o}C$. Solvent $MeOH:H_2O$ = 50:50% v/v

O.D. (420 nm) for [o-cresol] at

t_m	0.0025M	0.005M	0.0075M	0.01M.
0	0.365	0.423	0.449	0.504
5	0.358	0.415	0.440	0.486
10	0.356	0.405	0.426	0.472
20	0.350	0.390	0.404	0.436
30	0.343	0.377	0.391	0.426
40	0.337	0.374	0.383	0.416

(c) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}M$ $[\text{o-cresol}] = 1.0 \times 10^{-2}M$;

$[NaOH]$ = 0.5M; solvent = $MeOH:H_2O$ = 50:50% v/v

O.D.(420 nm) for temperature in ^{o}C at

t_m	35^{o}	40^{o}	45^{o}	50^{o}
0	0.434	0.463	0.458	0.504
5	0.419	0.449	0.446	0.486
10	0.421	0.443	0.431	0.472
20	0.408	0.419	0.412	0.436
30	0.395	0.404	0.403	0.426
40	0.379	0.394	0.394	0.416

(d) $[\mathrm{K_3Fe(CN)_6}] = 1.0 \times 10^{-3}\mathrm{M}$; $[\text{o-cresol}] = 1.0 \times 10^{-2}\mathrm{M}$;

$[\mathrm{NaOH}] = 0.5\mathrm{M}$; Temp = $(50.0 \pm 0.1)^{\circ}\mathrm{C}$

O.D. (420 nm) for MeOH: v/v at

t_m	50%	55%	60%	65%
0	0.504	0.450	0.452	0.558
5	0.486	0.439	0.441	0.516
10	0.472	0.427	0.432	0.537
20	0.436	0.418	0.412	0.527
30	0.426	0.380	0.404	0.500
40	0.416	-	0.396	0.485

(e) $[\mathrm{K_3Fe(CN)_6}] = 1.0 \times 10^{-3}\mathrm{M}$; $[\text{o-cresol}] = 1.0 \times 10^{-2}\mathrm{M}$;

Temp = $(50 \pm 0.1)^{\circ}\mathrm{C}$; solvent = $\mathrm{MeOH:H_2O}$ = 50:50% v/v

O.D. (420 nm) for $[\mathrm{NaOH}]$ at

t_m	0.1M	0.2M	0.3M	0.4M	0.5M
0	0.558	0.533	0.543	0.572	0.504
5	0.555	0.521	0.529	0.557	0.486
10	0.550	0.526	0.520	0.533	0.472
20	0.544	0.499	0.495	0.499	0.436
30	0.537	0.491	0.472	0.490	0.426
40	0.530	0.478	0.469	0.484	0.416

m-cresol

(a) [m-cresol] = 1.0 x 10^{-2}M; [NaOH] = 0.5M;

Temp = (50.0 ± 0.1)°C ; Solvent: MeOH: H_2O = 50:50% v/v

O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0.0005M	0.00075	0.001
0	0.190	0.295	0.395
2	0.145	0.195	0.280
5	0.130	0.150	0.220
10	0.080	0.110	0.170
15	0.065	0.090	0.135
25	-	0.070	0.100

(b) $K_3Fe(CN)_6$ = 1.0 x 10^{-3}M; [NaOH] = 0.5M;

Temp = (50.0 ± 0.1)°C Solvent [MeOH:H_2O = 50:50% v/v]

O.D. (420 nm) for [m-cresol] at

t_m	0.001M	0.0025M	0.005M	0.0075M	0.01M
0	0.365	0.365	0.395	0.395	0.395
2	0.345	0.325	0.330	0.305	0.280
5	0.335	0.305	0.295	0.265	0.220
10	0.325	0.280	0.255	0.215	0.170
20	0.305	0.250	0.210	0.152	0.120
30	0.285	0.230	0.170	0.130	0.095
40	0.275	0.210	0.150	0.105	0.080

(c) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$ M; [m-cresol] $= 1.0 \times 10^{-2}$ M;
[NaOH] = 0.5M; Solvent [MeOH: H_2O = 50:50% v/v]
O.D. (420 nm) for temperature in °C at

t_m	35°	40°	45°	50°
0	0.400	0.385	0.385	0.395
5	0.295	0.250	0.230	0.220
10	0.268	0.210	0.190	0.170
15	0.210	0.185	0.160	0.135
20	0.190	0.160	0.140	0.120
30	0.150	0.135	0.115	0.095
40	0.140	0.115	0.100	0.080

(d) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$ M; [m-cresol] $= 1.0 \times 10^{-2}$ M;
[NaOH] = 0.5M; Temp = (50.0 ± 0.1)°C.
O.D. (420 nm) for [Solvent = MeOH, % , v/v] at

t_m	50%	55%	60%	~~70~~%
0	0.395	0.325	0.300	
2	0.280	0.250	0.260	
5	0.220	0.200	0.220	
10	0.170	0.150	0.160	
20	0.120	0.100	0.090	
30	0.095	0.080	0.065	
35	0.085	0.075	0.060	

(e) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}M$; [m-cresol] = $1.0 \times 10^{-2}M$;

Temp = (50.0 ± 0.1)°C; Solvent = [MeOH:H_2O = 50:50% v/v]

O.D. (420 nm) for [NaOH] at

t_m	0.1M	0.2M	0.3 M	0.4M	0.5M
0	0.425	0.405	0.375	0.395	0.395
5	0.360	0.315	0.260	0.245	0.220
10	0.335	0.280	0.205	0.205	0.170
20	0.315	0.250	0.155	0.150	0.120
30	0.295	0.220	0.135	0.130	0.095
40	0.285	0.205	0.115	0.110	0.080

P-Cresol

(a) [p-cresol] = $1.0 \times 10^{-2}M$; [NaOH] = 0.05M ;

Temp = (50.0 ± 0.1) °C ; solvent = [MeOH:H_2O = 50:50% v/v]

O.D. (420 nm) for $[K_3Fe(CN)_6]$ at

t_m	0.0005M	0.00075M	0.001M
0	0.160	0.232	0.340
5	0.103	0.150	0.184
8	0.080	0.120	0.162
10	0.070	0.100	0.148
15	0.045	0.085	0.126
20	-	0.062	0.107
30	-	-	0.088

(b) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}M$; $[NaOH] = 0.05M$;

Temp = (50.0 ± 0.1)°C; Solvent = [MeOH: H_2O = 50:50% v/v]

O.D. (420 nm) for [p-cresol] at

t_m	0.0025M	0.005M	0.0075M	0.01M
0	0.334	0.340	0.314	0.340
5	0.272	0.234	0.202	0.184
8	0.260	0.208	0.174	0.162
10	0.254	0.204	0.162	0.148
15	0.235	0.173	0.139	0.126
20	0.224	0.157	0.120	0.107
30	0.202	0.132	0.100	0.088

(e) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}M$; $[p\text{-cresol}] = 1.0 \times 10^{-2}M$;

Temp = (50.0 ± 0.1)°C; Solvent = MeOH:H_2O = 50:50% v/v/v.

O.D. (420 nm) for [NaOH] at

t_m	0.01M	0.05M	0.075M	0.1M
0	0.332	0.340	0.336	0.324
5	0.294	0.184	0.139	0.106
8	0.270	0.162	0.113	0.085
10	0.261	0.148	0.101	0.074
15	0.248	0.126	0.075	0.055
20	0.239	0.107	0.067	0.040
30	0.221	0.088	0.052	-

(d) $[K_3Fe(CN)_6] = 1.0\times10^{-3}$M; [p-cresol] = 1.0×10^{-2}M ; [NaOH] = 0.05M; solvent [MeOH : H_2O = 50:50% v/v]

O.D. (420 nm) for temperature (°C) at

t_m	35°	40°	45°	50°
0	0.365	0.366	0.366	0.340
2	0.271	0.256	0.261	0.226
5	0.238	0.230	0.210	0.184
8	0.217	0.212	0.189	0.162
10	0.209	0.198	0.178	0.148
15	0.202	0.177	0.161	0.126
20	0.175	0.164	0.147	0.107
30	0.154	0.137	0.120	0.088

(e) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$M; [p-cresol] = 1.0×10^{-2}M; [NaOH] = 0.05M; temp = (50.0 ± 0.1)°C

O.D. (420 nm) for solvent [MeOH, %, v/v] at

t_m	50%	60%	70%	80%
0	0.340	0.340	0.330	0.325
2	0.226	0.263	0.293	0.300
5	0.184	0.230	0.263	0.285
8	0.162	0.212	0.249	0.275
10	0.148	0.205	0.236	0.265
15	0.126	0.187	0.223	0.258
20	0.107	0.170	0.209	0.254
30	0.088	0.154	0.192	0.254

O-chlorophenol

(a) [o-cl phenol] = 1.0 x 10^{-2}M; [NaOH] = 0.5M;

Temp = (40.0 ± 0.1)°C

Solvent = [MeOH: H_2O = 50:50% v/v]

O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0.0005M	0.00075	0.001M
0	0.100	0.130	0.290
5	0.097	0.124	0.278
10	0.094	0.122	0.264
20	0.087	0.116	0.256
30	0.080	0.110	0.247
40	0.074	-	0.239

(b) [$K_3Fe(CN)_6$] = 1.0 x 10^{-3}; [NaOH] = 0.5M;

Temp = (40.0± 0.1)°C Solvent [MeOH:H_2O = 50:50% v/v]

O.D. (420 nm) for [o-cl phenol] at

t_m	0.0025M	0.005M	0.0075M	0.01M.
0	0.323	0.327	0.310	0.290
5	0.310	-	0.297	0.278
10	0.306	0.312	0.290	0.264
20	0.304	0.303	0.286	0.256
30	0.305	0.299	0.274	0.247
40	-	0.292	0.276	0.239

(c) $[K_3Fe(CN)_6]$ = 1.0 x 10^{-3}M; [O-cl Phenol] = 1.0x10^{-2}M;
[NaOH] = 0.5M; Solvent = [MeOH:H_2O 50:50% v/v].
O.D. (420 nm) for Temperature(°C) at

t_m	35°	40°	45°	50°
0	0.291	0.290	0.284	0.265
5	0.287	0.278	0.265	0.240
10	0.284	0.264	0.256	0.229
20	0.272	0.256	0.242	0.225
30	0.268	0.247	0.236	0.217
40	0.263	0.239	0.228	0.207

(d) $[K_3Fe(CN)_6]$ = 1.0x10^{-3}M [O-cl Phenol] = 1.0x10^{-2}M;
[NaOH] = 0.5M; Temp = (40.0 ± 0.1)°C.
O.D. (420nm) for [MeOH, % , v/v] at

t_m	50%	55%	60%	65%
0	0.290	0.286	0.266	0.295
5	0.278	0.267	0.255	0.270
10	0.264	0.263	0.250	0.265
20	0.256	0.259	0.241	0.263
30	0.247	0.254	0.240	0.260
40	0.239	0.248	0.235	0.257

(e) [$K_3Fe(CN)_6$] = 1.0 x 10^{-3}M; [O-cl phenol] = 1.0 x10^{-2}M;
Temp = (40.0 ± 0.1)°C; Solvent = [MeOH:H_2O = 50:50% v/v]
O.D. (420 nm) for [NaOH] at

t_m	0.1M	0.2M	0.3M	0.4M	0.5M
0	0.269	0.300	0.304	0.309	0.290
5	0.267	0.289	-	0.292	0.278
10	0.266	0.284	0.289	0.286	0.264
15	0.263	0.285	0.281	0.283	0.263
20	0.264	0.286	0.281	0.276	0.256
25	0.262	0.284	0.278	0.273	0.249
30	0.260	0.283	0.277	0.274	0.247

P-Chlorophenol

(a) [P-Chlorophenol] = 1.0 x 10^{-2}M; [NaOH] = 0.5M;
Temp = (40.0 ± 0.1)°C; Solvent = [MeOH: H_2O = 50:50% v/v]
O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0.0005M	0.00075M	0.001M
0	0.155	0.231	0.268
5	0.135	-	0.235
10	0.125	0.180	0.220
20	0.112	0.163	0.199
30	0.103	0.139	0.193
40	0.096	0.134	0.179

(b) $[K_3Fe(CN)_6]$ = 1.0×10^{-3}M; [NaOH] = 0.5M;

Temp = (40.0±0.1)°C; solvent = [MeOH:H_2O= 50:50% v/v]

O.D. (420 nm) for [p-chloro phenol] at

t_m	0.001M	0.0025M	0.005M	0.0075M	0.01M
0	0.288	0.288	0.288	0.286	0.268
5	0.275	0.271	0.270	0.249	0.235
10	0.266	0.260	0.260	0.236	0.220
20	0.259	0.253	0.237	0.225	0.199
30	0.257	0.242	0.225	0.210	0.187
40	0.255	0.237	0.221	0.203	0.179

(c) $[K_3Fe(CN)_6]$ = 1.0×10^{-3}M; [NaOH] =0.5M;

[P-Chloro phenol] = 1.0×10^{-2}M; solvent [MeOH:H_2O=50:50% v/v]

O.D.(420 nm) for temperature at

t_m	35°C	40°C	45°C	50°C
0	0.266	0.268	0.266	0.289
5	0.246	0.235	0.239	0.240
10	0.233	0.220	0.216	0.219
20	0.214	0.199	0.188	0.187
30	0.203	0.187	0.170	0.180
40	0.198	0.179	0.152	0.152

(d) $[K_3Fe(CN)_6]$ = 1.0x10^{-3}M; [P-Chlorophenol] = 1.0 x10^{-2}M; [NaOH] = 0.5M; Temp = (40.0±0.1)°C.

O.D. (420 nm) for [Solvent = MeOH, %, at]

t_m	50%	55%	60%	65%
0	0.268	0.258	0.294	0.246
5	0.235	0.227	0.265	0.218
10	0.220	0.214	0.253	0.213
20	0.199	0.195	0.235	0.204
30	0.187	0.186	0.226	0.204
40	0.179	0.179	0.216	0.190

(e) $[K_3Fe(CN)_6]$ = 1.0x10^{-3}M; [P-chloro phenol]=1.0x10^{-2}M; Temp = (40.0±0.1)°C; Solvent = [MeOH:H_2O = 50:50% v/v]

O.D. (420 nm) for [NaOH] at

t_m	0.1M	0.2M	0.3M	0.4M	0.5M
0	0.289	0.305	0.296	0.313	0.268
5	0.283	0.271	0.271	0.264	0.235
10	0.278	0.263	0.261	0.256	0.220
20	0.275	0.258	0.252	0.241	0.199
30	0.274	0.252	0.245	0.233	0.187
40	0.272	0.247	0.240	0.223	0.179

Salicylic acid

(a) [Salicylic acid] = 1.0×10^{-2}M; [NaOH] = 0.5M;

Temp = (40.0 ± 0.1)°C; Solvent [MeOH: H_2O=50:50% v/v]

O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0.0005M	0.00075M	0.001 M
0	0.169	0.244	0.301
5	0.162	-	0.286
10	0.155	-	0.276
20	0.145	0.207	0.264
30	0.130	0.197	0.258
45	0.121	0.179	0.242

(b) [$K_3Fe(CN)_6$] = 1.0×10^{-3}M ; [NaOH] = 0.5 M;

Temp = (40.0 ± 0.1)°C Solvent = MeOH:H_2O=50:50% v/v

O.D. (420 nm) for [Salicylic acid] at

t_m	0.005M	0.0075M	0.01M
0	0.301	0.301	0.301
5	0.295	0.291	0.286
10	0.289	0.281	0.276
20	0.278	0.272	0.264
30	0.268	0.263	0.258
45	0.262	0.250	0.242

(c) $[K_3Fe(CN)_6]$ = 1.0×10^{-3}M; [Salicylic acid] = 1.0×10^{-2}M;

[NaOH] = 0.5M; solvent = [MeOH: H_2O = 50:50% v/v]

O.D. (420 nm) for temperature (°C) at

t_m	35°	40°	45°	50°
0	0.305	0.301	0.301	0.297
5	0.295	0.286	0.283	0.274
10	0.290	0.276	0.272	0.270
20	—	0.264	0.257	0.251
25	0.264	0.265	0.247	0.240
35	0.253	0.254	0.233	—
50	0.253	0.240	0.223	—

(d) $[K_3Fe(CN)_6]$ = 1.0×10^{-3}M; [Salicylic acid] = 1.0×10^{-2}M;

[NaOH] = 0.5M ; Temp = (40.0 ± 0.1)°C

O.D. (420 nm) for solvent MeOH, % , v/v at

t_m	50%	55%	60%	65%
0	0.301	0.370	0.287	0.306
5	0.286	0.358	0.280	0.293
10	0.276	0.350	0.275	0.288
20	0.264	0.335	0.265	0.288
35	0.254	0.310	0.249	0.285
45	0.242	0.293	0.247	0.280

(e) [$K_3Fe(CN)_6$] = 1.0×10^{-3}M; [Salicylic acid] = 1.0×10^{-2}M

Temp = (40.0 ± 0.1)°C Solvent = MeOH:H_2O = 50:50% v/v

O.D. (420 nm) for [NaOH] at

t_m	0.1M	0.2M	0.3M	0.4M	0.5M
0	0.324	0.325	0.317	0.315	0.301
5	0.322	0.320	0.306	0.306	0.286
10	0.320	0.316	0.302	0.300	0.276
20	0.316	0.312	0.296	0.291	0.264
30	0.313	0.309	0.296	0.288	0.258
40	0.310	-	0.294	0.279	0.250

m-Carboxy phenol

(a) [m-carboxy phenol] = 1.0×10^{-2}M; [NaOH] = 0.5M;

Temp = (40.0 ± 0.1)°C; Solvent: MeOH:H_2O = 50:50% v/v

O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0.0005M	0.00075M	0.001M
0	0.129	0.193	0.226
5	-	0.177	0.201
10	0.114	0.165	0.197
20	0.102	0.152	0.185
30	0.092	0.140	0.178
45	0.083	0.120	0.163

(c) /‾K$_3$Fe(CN)$_6$_7 = 1.0 x 10^{-3}M; /‾m-carboxy phenol_7 = 1.0x10^{-2}M.

/‾NaOH_7 = 0.5M NaOH Solvent = /‾MeOH:H$_2$O = 50:50% v/v_7

O.D. (420 nm) for Temperature (^{o}C) at

t_m	35^{o}	40^{o}	45^{o}	50^{o}
0	0.231	0.226	0.232	0.243
5	0.211	0.201	0.209	0.223
10	0.203	0.197	0.198	0.204
20	0.200	0.185	0.183	0.179
30	0.191	0.178	0.168	0.165
40	0.183	0.169	0.157	0.152

(d) /‾K$_3$Fe(CN)$_6$_7 = 1.0x10^{-3}M; /‾m-carboxyphenol_7 = 1.0x10^{-2}M

/‾NaOH_7 = 0.5M NaOH ; Temp. = (40.0 ± 0.1)^{o}C

O.D. (420 nm) for /‾MeOH, % , v/v_7 at

t_m	50%	55%	60%	65%
0	0.226	0.225	0.220	0.200
5	0.201	0.207	0.210	0.199
10	0.197	0.200	0.204	0.196
20	0.185	0.191	0.193	0.181
30	0.178	0.184	0.187	0.174
45	0.163	0.170	0.179	0.165

(e) [$K_3Fe(CN)_6$] = 1.0x10^{-3}M; [m-carboxy phenol] =1.0x10^{-2}M;

Temp = (40.0+0.1)°C; Solvent =[MeOH:H_2O=50:50% v/v]

O.D.(420 nm) for [NaOH] at

t_m	0.1M	0.3M	0.4M	0.5M
0	0.248	0.228	0.225	0.226
5	0.245	0.214	0.215	0.201
10	0.241	0.210	0.208	0.197
20	0.237	0.203	0.195	0.185
30	0.233	0.194	0.188	0.178
35	0.231	0.192	0.181	0.174

P-Carboxy Phenol

(a) [P-Carboxy phenol] = 1.0 x 10^{-2}M; [NaOH] = 0.5 M;

Temp = (50.0+0.1)°C ; Solvent= [MeOH:H_2O=50:50% v/v]

O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0.0005M	0.00075M	0.001M
0	0.182	0.250	0.360
5	0.169	0.233	0.335
10	0.167	0.226	0.327
20	0.158	0.222	0.319
30	0.145	0.210	0.314
40	0.139	0.206	0.309

(b) $[K_3Fe(CN)_6]$ = 1.0×10^{-3}M; $[NaOH]$ = 0.5M; Temp=$(50.0 \pm 0.1)^{o}$C

Solvent = $[MeOH:H_2O$ = 50:50% v/v$]$

O.D.(420 nm) for $[$P-Carboxy phenol$]$ at

t_m	0.001M	0.0025M	0.005M	0.0075M	0.01M
0	0.338	0.342	0.360	0.342	0.360
5	0.336	0.336	0.355	0.327	0.335
10	0.334	0.335	0.350	0.324	0.327
20	0.328	0.331	0.343	0.315	0.319
30	0.320	0.326	0.340	0.303	0.314
40	-	0.325	0.334	0.301	0.309

(c) $[K_3Fe(CN)_6]$ = 1.0×10^{-3}M; $[$P-carboxy phenol$]$ =1.0×10^{-2}M;

$[NaOH]$ = 0.5M; Solvent $[MeOH:H_2O$ = 50:50% v/v$]$

O.D. (420 nm) for temperature (^{o}C) at

t_m	35^{o}	40^{o}	45^{o}	50^{o}
0	0.347	0.347	0.340	0.360
5	0.334	0.330	0.330	0.335
10	0.327	0.321	0.322	0.327
20	0.322	0.320	0.310	0.319
30	0.314	0.319	0.303	0.314
40	0.311	0.316	0.301	0.309

(d) $[K_3Fe(CN)_6] = 1.0\times10^{-3}$M; [P-Carboxy phenol] $=1.0\times10^{-2}$M;
[NaOH] = 0.5 ; Temp = (50.0 ± 0.1)°C
O.D. (420 nm) for [MeOH, % , v/v]

t_m	50%	55%	60%	65%
0	0.360	0.328	0.307	0.280
5	0.335	0.307	0.294	0.266
10	0.327	0.304	0.295	0.263
20	0.319	0.292	0.282	0.260
30	0.314	0.289	0.282	0.257
40	0.309	0.287	0.273	0.257

(e) $[K_3Fe(CN)_6] = 1.0\times10^{-3}$M; [P-Carboxy phenol]$=1.0\times10^{-2}$M;
Temp = (50.0 ± 0.1)°C; Solvent = [MeOH:H_2O = 50:50% v/v]
O.D. (420 nm) for [NaOH] at

t_m	0.1M	0.2M	0.3M	0.4M	0.5M
0	0.363	0.364	0.367	0.322	0.360
5	0.360	-	0.360	0.308	0.335
10	0.358	0.344	0.342	0.305	0.327
20	0.356	0.338	0.333	0.305	0.319
30	0.354	0.340	0.332	0.299	0.314
40	0.351	0.337	0.330	0.293	0.309

P-Methoxy Phenol

(a) [P-Methoxy Phenol] = 1.0×10^{-4}M; [NaOH] = 0.05M;

Temp = (30.0 ± 0.1)°C; Solvent = [MeOH:H_2O=50:50% v/v]

O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0.0001M	0.0005M	0.00075M	0.001M
0	0.060	0.138	0.200	0.258
5	-	-	-	0.215
10	-	0.120	-	0.210
15	0.045	0.105	0.145	0.208
20	0.044	0.100	0.146	0.206
25	0.042	0.100	0.144	0.200
30	0.040	0.098	0.142	0.200

(b) [$K_3Fe(CN)_6$]=1.0×10^{-3}M; [NaOH] = 0.05 M;

Temp = (30.0 ± 0.1)°C; Solvent = [MeOH:H_2O = 70:30% v/v]

O.D. (420 nm) for [P-Methoxy Phenol] at

t_m	0.0001M	0.0005M	0.001M
0	0.258	0.255	0.251
5	0.215	0.152	0.108
10	0.210	0.138	0.070
15	0.208	0.131	0.056
20	0.206	0.123	0.048
25	0.200	0.120	-
30	0.200	0.118	-

(c) $[K_3Fe(CN)_6] = 1.0\times10^{-3}M$; [P-Methoxyphenol]$=1.0\times10^{-4}M$;
[NaOH] = 0.05M; Solvent = [$MeOH:H_2O$ = 70:30% v/v]
O.D. (420 nm) for Temperature in °C at

t_m	30°	35°	40°	45°
0	0.258	0.229	0.236	0.240
5	0.215	0.186	0.195	0.194
10	0.210	0.182	0.190	0.190
15	0.208	0.180	0.185	0.183
20	0.206	0.177	0.183	0.182
25	0.200	0.177	0.180	0.179
30	0.200	0.175	0.179	0.176

(d) $[K_3Fe(CN)_6] = 1.0\times10^{-3}M$; [P-Methoxy Phenol] $=1.0\times10^{-4}M$;
Temp = (30.0±0.1)°C; [NaOH] = 0.05M
O.D. (420 nm) for [Solvent = MeOH % v/v] at

t_m	50%	60%	70%	80%
0	0.182	0.260	0.258	0.240
5	0.164	0.204	0.215	0.219
10	0.160	0.206	0.210	0.216
15	0.159	0.195	0.208	0.211
20	0.158	0.194	0.206	0.210
25	-	0.194	0.200	0.209
30	-	0.190	0.200	0.206

(e)

$[K_3Fe(CN)_6] = 1.0\times10^{-3}$ M; [p-Methoxy Phenol] = 1.0×10^{-4} M;

Temp = (30.0±0.1)°C; Solvent = [MeOH : H_2O = 70:30% v/v]

O.D. (420 nm) for [NaOH] at

t_m	0.01M	0.05M	0.075M
0	0.219	0.258	0.255
5	-	0.215	0.204
10	0.197	0.210	0.201
15	0.195	0.208	0.200
20	0.194	0.206	0.195
25	0.193	0.200	0.194
30	0.194	0.200	0.192

2-4 DICHLOROPHENOL

(a) [2,4 dichlorophenol] = 1.0×10^{-2} M; [NaOH] = 0.5 M;
Temp = (40.0 ± 0.1)°C ; Solvent = [MeOH: H_2O 50:50% v/v]
O.D. (420 nm) for $K_3Fe(CN)_6$ at

t_m	0.0005M	0.00075M	0.001M
0	0.095	0.139	0.275
5	0.091	0.132	0.255
10	0.088	0.130	0.247
15	0.085	0.128	0.246
20	0.081	0.126	0.249
30	0.076	0.122	0.233
40	0.070	0.120	0.230

(b) [$K_3Fe(CN)_6$] = 1.0×10^{-3} M; [NaOH] = 0.5 M;
Temp = (40.0 ± 0.1)°C ; Solvent = [MeOH:H_2O = 50:50% v/v]
O.D. (420 nm) for [2,4 dichlorophenol] at

t_m	0.001M	0.0025M	0.005M	0.0075M	0.01M
0	0.278	0.290	0.269	0.269	0.275
5	0.276	0.287	0.265	0.256	0.255
10	0.274	0.285	0.260	0.248	0.247
15	0.272	0.281	0.256	0.250	0.246
20	0.270	0.280	0.250	0.249	0.249
30	0.266	0.277	0.242	0.238	0.233
40	0.260	0.273	0.236	0.234	0.230

(c) $[K_3Fe(CN)_6]$ = 1.0x10^{-3}M; [2,4 dichlorophenol] = 1.0x10^{-2}M;
[NaOH] = 0.5M; Solvent = [MeOH:H$_2$O = 50:50% v/v]
O.D. (420 nm) for temperature (°C) at

t_m	35°C	40°C	45°C	50°C.
0	0.267	0.275	0.267	0.267
5	0.254	0.255	0.256	0.254
10	0.249	0.247	0.249	0.242
20	0.234	0.249	0.231	0.225
30	0.230	0.233	0.219	0.210
40	0.225	0.230	0.217	0.195
50	0.221	0.217	0.204	0.191

(d) $[K_3Fe(CN)_6]$ = 1.0 x 10^{-3}M; [2,4 dichlorophenol] = 1.0x10^{-2}M;
[NaOH] = 0.5M; Temp. = (40.0 ± 0.1)°C.
O.D. (420 nm) for [MeOH; %, v/v] at

t_m	50%	55%	60%	65%
0	0.275	0.280	0.260	0.283
5	0.255	0.260	0.236	0.272
10	0.247	0.258	0.245	0.269
20	0.249	0.250	——	0.265
30	0.233	0.245	0.232	0.260
40	0.230	0.243	0.228	0.260
50	0.217	0.236	0.226	0.258

(e) $[K_3Fe(CN)_6] = 1.0x10^{-3}M$; [2,4 dichlorophenol]$=1.0x10^{-2}M$
Temp = (40.0 ± 0.1)°C; Solvent = [MeOH:H_2O=50:50% v/v]
O.D. (420 nm) for [NaOH] at

t_m	0.1M	0.2M	0.3M	0.4M	0.5M
0	0.277	0.302	0.276	0.273	0.275
5	0.275	0.299	0.270	0.260	0.255
10	0.273	0.291	0.267	0.254	0.247
20	0.271	0.287	0.260	0.243	0.249
30	0.269	0.286	0.244	0.235	0.233
40	0.265	0.283	0.236	0.230	0.230

2,4,5 Trichlorophenol

(a) [2,4,5 trichlorophenol] $= 1.0x10^{-2}M$; [NaOH] = 0.5 M;
Temp = (40.0 ± 0.1)°C; Solvent = [MeOH:H_2O = 50:50% v/v]
O.D. (420 nm) for $[K_3Fe\ (CN)_6]$ at

t_m	0.005 M	0.00075M	0.001M
0	0.128	0.185	0.244
5	0.125	0.180	0.239
10	0.123	0.176	0.235
15	0.121	0.175	0.231
20	0.119	0.173	0.227
25	0.116	0.175	0.225
30	0.115	0.171	0.226

(b) $[K_3Fe(CN)_6] = 1.0\times10^{-3}M$; $[NaOH] = 0.5M$;

Temp = (40.0 ± 0.1)°C; Solvent = $[MeOH:H_2O = 50:50\%\ v/v]$

O.D. (420 nm) for [2,4,5 trichlorophenol] at

t_m	0.005M	0.0075	0.01M
0	0.243	0.255	0.244
5	0.239	0.250	0.239
10	0.237	0.248	0.235
20	0.233	0.243	0.227
30	0.232	0.238	0.226
45	0.228	0.236	0.223

(c) $[K_3Fe(CN)_6] = 1.0\times10^{-3}M$; $[2,4,5\ \text{trichlorophenol}] = 1.0\times10^{-2}M$

Temp = (40.0 ± 0.1)°C ; solvent = $[MeOH:H_2O = 50:50\%\ v/v]$

O.D. (420 nm) for [NaOH] at

t_m	0.1M	0.2M	0.3M	0.4M	0.5M
0	0.229	0.249	0.242	0.254	0.244
5	0.228	0.245	0.239	0.247	0.239
10	0.227	0.240	0.236	0.244	0.235
20	0.225	0.240	0.233	0.240	0.227
30	0.223	0.237	0.230	0.238	0.226
40	-	0.236	0.226	0.233	0.222

(d) $[K_3Fe(CN)_6]$ = 1.0 x 10^{-3}M; [2,4,5 trichlorophenol]=1.0x10^{-2}M;

[NaOH] = 0.5M; solvent $[MeOH:H_2O$ = 50:50% v/v]

O.D. (420 nm) for temperature (°C) at

t_m	30°	35°	40°	45°
0	0.234	0.247	0.244	0.244
5	0.233	0,245	0.239	0.236
10	0.230	0.242	0,235	0.227
20	0.228	0,240	0.227	0,226
30	0.225	0.237	0.226	0.223
40	0.225	0.233	0.222	0.220

(e) $[K_3Fe(CN)_6]$ = 1.0 x 10^{-3}M; [2,4,5 trichlorophenol] =1.0x10^{-2}M;

[NaOH] = 0.5M; Temp. = (40.0 ± 0.1)°C

O.D. (420 nm) for [MeOH, % , v/v] at

t_m	50%	50%	60%	65%
0	0.244	0.231	0.230	0.260
5	0.239	0.228	0.227	—
10	0.235	0.227	0.228	0.259
20	0.227	0.220	0.223	0.255
30	0.226	0.220	0.220	0.254
45	0.223	0.213	0.218	—

O-aminophenol

(a) [o-aminophenol] = 1.0 x 10^{-4}M; [NaOH] = 0.1M.

Temp = (40.0 ± 0.1)°C, solvent = [MeOH: H_2O = 50:50% v/v]

O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0.0001	0.0005	0.00075	0.001M
0	0.095	0.338	0.396	0.430
10	0.086	0.305	0.362	0.386
15	0.082	0.291	0.355	0.370
20	0.081	0.275	0.345	0.359
25	0.078	0.268	0.338	0.343
30	0.071	0.259	0.332	0.335
40	0.068	0.245	0.322	0.314

(b) [$K_3Fe(CN)_6$] = 1.0 x 10^{-3} M; [NaOH] = 0.1M ;

Temp = (40.0 ± 0.1)°C ; solvent = [MeOH: H_2O = 50:50% v/v]

O.D. (420 nm) for [O-amino phenol] at

t_m	0.001M	0.0005M	0.001M
0	0.430	0.385	0.385
10	0.386	0.265	0.208
15	0.370	0.205	0.156
20	0.359	0.175	0.130
25	0.343	0.140	0.100
30	0.335	0.120	-

(c) $[K_3Fe(CN)_6] = 1.0\times10^{-3}M$; [o-aminophenol] $= 1.0\times10^{-4}M$;
$[NaOH] = 0.1M$ NaOH; Solvent = [$MeOH:H_2O$ = 50:50% v/v]
O.D. (420 nm) for temperature (°C) at

t_m	30°	35°	40°	45°
0	0.410	0.400	0.430	0.410
5	0.407	0.385	0.405	0.382
10	0.387	0.363	0.386	0.360
20	0.366	0.344	0.359	0.315
30	0.352	0.323	0.335	0.289
40	0.340	0.310	0.314	0.259

(d) $[K_3Fe(CN)_6] = 1.0\times10^{-3}M$; [o-amenophenol] $= 1.0\times10^{-4}M$;
$[NaOH] = 0.1M$; Temp = (40.0 ± 0.1)°C
O.D. (420 nm) for [MeOH, % , v/v] at

t_m	50%	55%	60: 40%	65: 35%
0	0.430	0.391	0.390	0.363
5	0.405	0.383	0.380	—
10	0.386	0.362	0.370	0.353
20	0.359	0.335	0.350	0.330
30	0.335	0.314	0.325	0.322
45	0.307	0.295	0.315	0.311

(e) $[K_3Fe(CN)_6]$ = 1.0 x 10^{-3}M; [O-aminophenol] = 1.0x10^{-4}M

Temp = (40.0 ± 0.1)°C ; solvent = [MeOH : H_2O = 50:50% v/v]

O.D. (420 nm) for [NaOH] at.

t_m	0.01M	0.05M	0.1M.	0.2M	0.3M
0	0.330	0.368	0.430	0.407	0.419
10	0.326	0.348	0.386	0.347	0.350
15	0.324	0.344	0.370	0.329	0.334
20	0.322	0.341	0.359	0.316	0.315
25	0.319	0.330	0.343	0.305	0.301
30	0.319	0.328	0.335	0.291	0.286

m-amino phenol

(a) [m-NH_2 phenol] = 1.0 x 10^{-3}M ; [NaOH]=0.1M;

Temp = (40.0 ± 0.1)°C ; Solvent = [MeOH:H_2O = 50:50% v/v]

O.D. (420 nm) for $[K_3Fe(CN)_6]$ at

t_m	0.0001	0.0005M	0.00075M	0.001M .
0	0.090	0.237	0.350	0.439
10	0.083	0.205	0.326	0.402
15	0.079	0.202	0.303	0.385
20	0.076	0.190	0.296	0.368
25	0.074	0.183	0.297	0.363
30	0.071	0.179	0.283	0.357

(b) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$ M; $[NaOH] = 0.1$ M;

Temp = (40.0 ± 0.1)°C; solvent = [MeOH:H_2O = 50:50% v/v]

O.D. (420 nm) for [m-amino phenol] at

t_m	0.0001M	0.0005M	0.00075M	0.001M
0	0.356	0.397	0.417	0.439
10	0.353	0.378	0.391	0.402
15	0.351	0.370	0.366	0.385
20	0.349	0.365	0.349	0.368
25	0.345	0.358	0.343	0.363
30	0.342	0.350	0.333	0.357

(c) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$ M; [m-aminophenol] = 1.0×10^{-3} M;

Temp = (40.0 ± 0.1)°C. Solvent = [MeOH:H_2O = 50:50% v/v]

O.D. (420 nm) for [NaOH] at

t_m	0.01M	0.05M	0.075M	0.1M
0	0.395	0.395	0.426	0.439
10	0.389	0.376	0.390	0.402
15	0.385	0.363	0.378	0.385
20	0.383	0.360	0.366	0.368
25	0.380	0.349	0.359	0.363
30	0.374	0.341	0.359	0.357

(d) $[K_3Fe(CN)_6]$ = 1.0×10^{-3}M; [m-aminophenol] = 1.0×10^{-3}M;
[NaOH] = 0.1M NaOH;Solvent [MeOH:H_2O = 50:50% v/v]
O.D. (420 nm) for temperature (^oC) at

t_m	35^0	40^0	45^0	50^0
0	0.426	0.439	0.460	[illegible]
5	0.427	0.419	0.443	0.425
10	0.405	0.402	0.423	0.402
20	0.375	0.368	0.397	0.370
30	0.342	0.357	0.377	0.347
40	0.333	0.335	0.356	

(e) $[K_3Fe(CN)_6]$ = 1.0×10^{-3}M; [m-amino phenol] = 1.0×10^{-3}M;
[NaOH] = 0.1M NaOH; Temp. = (40.0 ± 0.1)^oC
O.D. (420 nm) for [MeOH, %, v/v] at

t_m	50%	55%	60%	65%
0	0.439	0.397	0.330	0.385
5	0.419	0.389	0.313	—
10	0.402	0.373	0.300	—
20	0.368	0.360	0.285	0.362
30	0.357	0.336	0.274	0.343
45	0.333	0.312	0.260	0.333

2-3 dimethyl phenol

(a) [2-3 dimethyl phenol] = 1.0x10^{-3}M; [NaOH] = 0.1M;
Temp = (40.0 ± 0.1)°C; solvent = [MeOH:H_2O = 50:50% v/v]
O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0.0001M	0.0005M	0.00075M	0.001M
0	0.102	0.154	0.215	0.242
10	0.060	0.087	0.140	0.153
15	0.045	0.080	0.131	0.149
20	0.035	0.077	0.128	0.140
25	0.028	0.070	0.129	0.140
40	—	—	0.116	0.136

(b) [$K_3Fe(CN)_6$] = 1.0x10^{-3}M; [NaOH] = 0.1M;
Temp = (40.0 ± 0.1)°C ; solvent = [MeOH:H_2O = 50:50% v/v]
O.D. (420 nm) for [2,3 dimethyl phenol] at

t_m	0.0001M	0.00025M	0.0005M	0.00075M	0.001M
0	0.289	0.280	0.246	0.241	0.242
10	0.263	0.230	0.190	0.169	0.153
15	0.259	0.232	0.180	0.163	0.149
20	0.260	0.224	0.177	0.154	0.140
25	0.253	0.221	0.172	0.152	0.140
40	0.253	0.217	0.165	0.143	0.136

(c) [$K_3Fe(CN)_6$] = 1.0 x 10^{-3}M; [2,3 dimethyl phenol]
= 1.0 x 10^{-3}M;
[NaOH] = 0.1M; Solvent = [MeOH:H_2O = 50:50%]
O.D. (420 nm) for temperature (°C) at

t_m	35°	40°	45°	50°
0	0.241	0.242	0.253	0.310
5	0.194	0.165	0.186	0.222
10	0.177	0.153	0.171	0.200
20	0.169	0.140	0.160	0.190
30	0.162	0.141	0.155	—
40	0.156	0.136	—	—

(d) [$K_3Fe(CN)_6$] = 1.0 x 10^{-3}M; [2,3 dimethyl phenol]
= 1.0 x 10^{-3}M;
[NaOH] = 0.1M; Temp = (40.0 ± 0.1)°C
O.D. (420 nm) for solvent = [MeOH; %, v/v] at

t_m	50%	55%	60%	65%
0	0.242	0.265	0.253	0.252
5	0.165	0.225	0.205	0.183
10	0.153	0.207	0.186	0.171
20	0.140	0.194	0.173	0.160
30	0.141	0.193	0.169	0.155
40	0.136	0.189	0.170	0.152

(e) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}M$; $[2,3 \text{ dimethyl phenol}] = 1.0\times10^{-3}M$;
Temp = $(40.0 \pm 0.1)^{\circ}C$; solvent = $[MeOH:H_2O = 50:50\% \ v/v]$
O.D. (420 nm) for [NaOH] at

t_m	0.01M	0.025M	0.05M	0.075M	0.1M
0	0.268	0.254	0.292	0.300	0.242
10	0.250	0.187	0.209	0.203	0.153
15	0.248	0.180	0.203	0.195	0.149
20	0.244	0.174	0.192	0.181	0.140
25	-	0.167	0.186	0.179	0.140
40	0.232	0.157	0.174	0.176	0.136

2,5 Dimethyl phenol

(a) $[2,5 \text{ dimethyl phenol}] = 1.0\times10^{-3}M$; [NaOH] = 0.1M;
Temp = $(40.0 \pm 0.1)^{\circ}C$, solvent = $[MeOH:H_2O = 50:50\% \ v/v]$
O.D. (420 nm) for $[K_3Fe\ (CN)_6]$ at

t_m	0.0001M	0.0005	0.001M
0	0.100	0.137	0.267
5	0.095	0.073	0.168
10	0.093	0.059	0.146
15	0.089	0.057	0.137
20	0.085	0.048	0.127
30	0.069	-	0.114

(c) $[K_3Fe(CN)_6]$ = 1.0 x 10^{-3}M; [2,5 dimethyl phenol] = 1.0 x 10^{-3}M;

[NaOH] = 0.1M ; Solvent = [MeOH:H_2O = 50:50 %, v/v]

O.D. (420 nm) for Temperature °C at

t_m	35°C	40°C	45°C	50°C
0	0.263	0.267	0.269	0.269
5	0.166	0.168	0.154	0.157
10	0.150	0.146	0.136	0.127
20	0.130	0.127	0.120	0.115
30	0.118	0.114	0.107	0.104
40	0.114	0.108	0.101	—

(d) $[K_3Fe(CN)_6]$ = 1.0 x 10^{-3}M; [2,5 dimethyl phenol] = 1.0 x 10^{-3}M;

[NaOH] = 0.1M; Temp. = (40.0 ± 0.1) °C.

O.D. (420 nm) for [MeOH, %, v/v] at

t_m	50%	60%	65%	70%
0	0.267	0.240	0.244	0.27[illegible]
5	0.163	0.177	0.171	[illegible]
10	0.146	0.163	0.157	0.1[illegible]4
20	0.127	0.146	0.140	0.18[illegible]
30	0.114	0.140	0.133	0.17[illegible]
40	0.108	0.129	0.128	0.164

(b) $[K_3Fe(CN)_6]$ = 1.0 x 10^{-3}M; [NaOH] = 0.1 M;

Temp = (40.0 ± 0.1)°C; solvent = [MeOH:H_2O = 50:50% v/v]

O.D. (420 nm) for [2,5 dimethyl phenol] at

t_m	0.0001M	0.00025M	0.0005M	0.00075M	0.001M
0	0.267	0.267	0.267	0.267	0.267
10	0.246	0.220	0.180	0.167	0.146
15	0.238	0.213	0.168	0.165	0.137
20	0.234	0.211	0.163	0.147	0.127
30	0.229	0.206	0.158	0.134	0.114
40	-	0.202	0.156	0.127	0.108

(e) $[K_3Fe(CN)_6]$ = 1.0 x 10^{-3}M; [2,5 dimethyl phenol] =1.0x10^{-3}M;

Temp = (40.0± 0.1)°C; solvent = [MeOH:H_2O = 50:50% v/v]

O.D. (420nm) for [NaOH] at

t_m	0.01M	0.025M	0.05M	0.075M	0.1M.
0	0.274	0.253	0.267	0.264	0.267
10	0.250	0.174	0.164	0.149	0.146
15	0.245	0.170	0.153	0.136	0.137
20	0.238	0.165	0.145	0.131	0.127
30	0.232	0.154	0.131	0.116	0.114
40	0.228	0.151	0.122	0.109	0.108

3, 4 dimethyl phenol

(a) [3,4 dimethyl phenol] = 1.0×10^{-3}M; [NaOH] = 0.1M;

Temp = (40.0 ± 0.1)°C; solvent = [MeOH:H_2O=50:50% v/v]

O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0.0001M	0.0005M	0.001M
0	0.105	0.204	0.247
5	0.074	0.123	0.170
10	0.050	0.103	0.143
15	0.040	0.089	0.130
20	0.028	0.083	0.120

(b) [$K_3Fe(CN)_6$] = 1.0×10^{-3}M; [NaOH] = 0.1 M;

Temp = (40.0 ± 0.1)°C ; solvent = [MeOH:H_2O = 50:50% v/v]

O.D. (420 nm) for [3,4 dimethyl phenol] at

t_m	0.0001M	0.00025M	0.0005M	0.00075M	0.001M
0	0.265	0.246	0.250	0.247	0.247
10	0.246	0.210	0.194	0.167	0.143
15	0.243	0.206	0.186	0.154	0.130
20	0.238	0.198	0.176	0.148	0.120
30	0.233	0.190	0.163	0.134	0.110
40	0.229	0.186	0.158	0.126	0.099

(c) $[K_3Fe(CN)_6]$ = 1.0 x 10^{-3}M; [3,4 dimethyl phenol]=1.0x10^{-3}M;
[NaOH] = 0.1M; Solvent = [MeOH: H_2O = 50:50% v/v]
O.D. (420 nm) for temperature in (°C) at

t_m	35	40	45	50
0	0.264	0.247	0.254	0.263
5	0.167	0.170	0.149	0.155
8	0.163	0.152	0.133	0.140
10	0.159	0.143	0.124	0.125
15	0.143	0.130	0.112	0.105
20	0.135	0.120	0.100	0.089
30	0.118	0.110	0.081	0.075

(d) $[K_3Fe(CN)_6]$ = 1.0x10^{-3}M; [NaOH] = 0.1 M;
Temp = (40.0 ± 0.1)°C; [3,4 dimethyl phenol]= 1.0x10^{-3}M
O.D. (420 nm) for [Solvent = MeOH,%, v/v] at

t_m	50%	60%	65%	70%
0	0.247	0.245	0.270	0.270
5	0.170	0.171	0.213	0.190
8	0.152	0.160	0.204	0.183
10	0.143	0.153	0.204	0.180
15	0.130	0.139	0.189	0.169
20	0.120	0.130	0.186	0.162
30	0.110	0.113	0.173	0.146

(e) [$K_3Fe(CN)_6$] = 1.0 x 10^{-3}M; [3,4 dimethyl phenol]=1.0x10^{-3}M;
Temp = (40.0 + 0.1)°C ; solvent = [MeOH:H_2O = 50:50% v/v]
O.D. (420 nm) for [NaOH] at

t_m	0.01M	0.025M	0.05M	0.075M	0.1M
0	0.255	0.272	0.243	0.260	0.247
10	0.236	0.216	0.178	0.162	0.143
15	0.224	0.206	0.165	0.152	0.130
20	0.219	0.195	0.157	0.142	0.120
30	0.206	0.187	0.141	0.126	0.110
40	0.197	0.178	0.135	0.118	0.099

2,6 dimethyl Phenol

(a) [2,6 dimethyl phenol] = 1.0 x 10^{-4}M; [NaOH] = 0.1M;
Temp = (30.0 ± 0.1)°C; Solvent = [MeOH:H_2O=50:50% v/v]
O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0.0001M	0.0005M	0.00075M	0.001M
0	0.080	0.132	0.185	0.259
5	0.077	0.127	0.180	0.250
10	0.075	0.124	0.174	0.240
15	0.072	0.120	0.168	0.238
20	0.072	0.118	0.164	0.227
30	0.069	0.106	0.158	0.219
35	-	0.104	0.155	0.216

(b) $[K_3Fe(CN)_6]$ = 1.0 x 10^{-3}M; [NaOH] = 0.1M;

Temp = (30.0 ± 0.1)°C; Solvent = [MeOH:H_2O = 50:50% v/v]

O.D. (420 nm) for [2,6 dimethyl phenol] at

t_m	0.0001M	0.0005M
0	0.259	0.237
5	0.250	0.200
10	0.240	0.180
15	0.238	0.170
20	0.227	0.165
30	0.219	0.152
35	0.216	-

(c) $[K_3Fe(CN)_6]$ = 1.0 x 10^{-3}M; [2,6 dimethyl Phenol]=1.0x10^{-4}M;

Temp = (30.0 ± 0.1)°C; Solvent =[MeOH:H_2O=50:50% v/v]

O.D. (420 nm) for [NaOH] at

t_m	0.01M.	0.05M	0.075M	0.1M
0	0.335	0.295	0.258	0.259
5	-	0.291	0.249	0.250
10	0.332	0.286	0.237	0.240
15	0.332	0.277	0.233	0.238
20	0.320	0.274	0.228	0.227
30	0.328	0.269	0.220	0.219
35	0.327	0.263	0.218	0.216

(d) $[K_3Fe(CN)_6]$ = 1.0x10^{-3}M; [2,6 dimethyl phenol] = 1.0x10^{-4}M

[NaOH] = 0.1M; solvent MeOH : H_2O = 50:50% v/v

O.D. (420 nm) for temperature (°C) at

t_m	25°	30°	35°	40°
0	0.259	0.259	0.246	0.243
5	0.251	0.250	0.232	0.232
10	0.243	0.240	0.224	0.222
20	0.229	0.227	0.215	0.216
25	0.227	0.226	0.212	—
30	0.220	0.219	0.208	—

(e) $[K_3Fe(CN)_6]$ = 1.0x10^{-3}M; [2,6 dimethyl phenol] = 1.0x10^{-4}M;

[NaOH] = 0.1M ; Temp = (30.0 ± 0.1)°C

O.D. (420 nm) for [MeOH, % , v/v] at

t_m	50%	55%	60%	65%
0	0.259	0.248	0.233	0.248
5	0.250	0.238	0.229	0.233
10	0.240	0.230	0.220	0.229
20	0.227	0.220	0.213	0.225
30	0.219	0.213	0.208	0.223
40	-	0.212	-	0.217

2,4,6 Trichloro phenol

(a) [2,4,6 Trichlorophenol] = 1.0×10^{-2}M; [NaOH] = 0.5M;
Temp= (40.0 ± 0.1)°C ; Solvent = [MeOH:H_2O=50:50% v/v]
O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0.0005M	0.00075	0.001M
0	0.124	0.197	0.253
5	0.115	-	0.236
10	0.114	-	0.234
15	0.111	0.175	0.229
20	0.110	0.172	0.231
25	0.108	0.171	0.227
30	0.106	0.170	0.226
40	0.103	0.165	0.222

(b) [$K_3Fe(CN)_6$] = 1.0×10^{-3}M; [NaOH] =0.5M; Temp=(40.0±0.1)°C
Solvent = [MeOH:H_2O = 50:50% v/v]
O.D. (420 nm) for [2,4,6 Trichlorophenol] at

t_m	0.0025M	0.0050M	0.0075M	0.01M
0	0.250	0.250	0.253	0.253
5	0.239	0.245	0.240	0.236
10	0.243	0.240	0.239	0.234
15	0.242	0.238	0.236	0.229
20	0.239	0.233	0.232	0.231
25	0.238	0.232	0.232	0.227
30	0.235	0.231	0.231	0.226
40	-	0.229	0.228	0.222

(c) $[K_3Fe(CN)_6]$ = 1.0 x 10^{-3}M; [2,4,6 trichlorophenol] = 1.0x10^{-2}M;
[NaOH] = 0.5M; solvent = [MeOH : H_2O = 50:50% v/v]
O.D. (420 nm) for temperature (°C) at

t_m	30°	35°	40°	45°
0	0.247	0.247	0.253	0.257
5	0.234	0.237	0.236	0.249
10	0.232	0,236	0.234	0.242
20	0.227	0.230	0.231	0.232
30	0.229	0.228	0.226	0.222
45	0.221	0.224	0.220	0.216

(d) $[K_3Fe(CN)_6]$ = 1.0 x 10^{-3}M; [2,4,6 trichlorophenol] = 1.0x10^{-2}M;
[NaOH] = 0.5M; Temp = (40.0 ± 0.1)°C.
O.D. (420nm) for [MeOH, %, v/v] at

t_m	50%	55%	60%	65%
0	0.253	0.265	0.239	0.273
5	0.236	0.252	0.231	0.262
10	0.234	0.250	0.227	0.261
20	0.231	0.247	0.227	0.260
30	0.226	0.244	0.219	0.259
45	0.220	0.240	0.217	0.255

(e) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$M; [2,4,6 trichlorophenol]$=1.0\times10^{-2}$M;
Temp = (40.0 ± 0.1) °C; Solvent = $MeOH:H_2O$ = 50:50% v/v.
O.D. (420 nm) for [NaOH] at

t_m	0.1M	0.3M	0.4M	0.5M
0	0.250	0.263	0.262	0.253
5	-	0.250	0.249	0.236
10	0.246	0.250	0.247	0.234
15	-	0.248	0.246	0.229
20	0.244	0.249	0.241	0.231
25	-	0.252	0.240	0.227
30	0.242	0.247	0.243	0.226
40	0.240	0.245	0.238	0.222

VANILLIN

(a) [Vanillin] $= 1.0\times10^{-2}$M; [NaOH]=0.5M; Temp=(40.0±0.1) °C
Solvent = [$MeOH:H_2O$ = 50:50% v/v]
O.D.(420 nm) for $[K_3Fe(CN)_6]$ at

t_m	0.0005M	0.00075M	0.001M
0	0.113	0.167	0.239
5	0.105	0.145	0.213
10	0.098	0.130	0.194
20	0.085	0.115	0.186
30	0.077	0.103	0.170
40	-	0.100	0.167

(b) $[K_3Fe(CN)_6]$ = 1.0 x 10^{-3}M; $[NaOH]$ = 0.5M;
Temp = (40.0 ± 0.1)°C; Solvent = $[MeOH:H_2O$ = 50:50% v/v$]$
O.D. (420 nm) for $[\text{Vanillin}]$ at

t_m	0.001M	0.0025M	0.005M	0.0075M	0.01M
0	0.237	0.239	0.211	0.211	0.239
5	0.232	0.230	0.200	0.193	0.213
10	0.229	0.222	0.195	0.186	0.194
20	0.220	0.216	0.185	0.176	0.186
30	0.214	0.207	0.180	0.170	0.170
40	0.219	0.203	0.169	0.159	0.167

(e) $[K_3Fe(CN)_6]$ = 1.0x10^{-3}M; $[\text{Vanillin}]$ = 1.0x10^{-2}M;
Temp = (40.0±0.1)°C; Solvent = $[MeOH:H_2O$=50:50% v/v$]$
O.D. (420 nm) for $[NaOH]$ at

t_m	0.1M	0.2M	0.3M	0.4M	0.5M
0	0.217	0.213	0.203	0.189	0.239
5	0.214	0.206	0.190	0.169	0.213
10	0.212	0.200	0.182	0.166	0.194
20	0.206	0.185	0.186	0.146	0.186
30	0.199	0.177	0.174	0.146	0.170
40	0.196	0.175	0.167	0.142	0.167

EUGENOL

(a) $[\text{EUGENOL}] = 1.0 \times 10^{-3}$M; $[\text{NaOH}] = 0.05$ M;

Temp = (30.0 ± 0.1)°C; $[\text{Solvent} = \text{MeOH:H}_2\text{O} = 50:50\%\ \text{v/v}]$

O.D. (420 nm) for $[\text{K}_3\text{Fe(CN)}_6]$ at

t_m	0.0001M	0.0005M	0.001M
0	0.085	0.140	0.200
5	0.074	0.120	0.169
10	0.070	0.116	0.163
15	0.066	0.110	0.160
20	0.066	0.110	0.160
30	0.063	0.108	0.158

(b) $[\text{K}_3\text{Fe(CN)}_6] = 1.0 \times 10^{-3}$M; $[\text{NaOH}] = 0.05$M ;

Temp = (30.0±0.1)°C Solvent = $[\text{MeOH:H}_2\text{O} = 50:50\%\ \text{v/v}]$

O.D. (420 nm) for $[\text{EUGENOL}]$ at

t_m	0.0001M	0.00025M	0.0005M
0	0.200	0.213	0.213
2	-	0.137	0.103
5	0.169	0.123	0.086
10	0.163	0.113	0.075
15	0.160	0.110	0.069
20	0.160	0.103	0.065
30	0.158	0.102	-

(c) $[K_3Fe(CN)_6]$=1.0x10^{-3}M; [Eugenol] = 1.0 x 10^{-4}M; [NaOH] = 0.05M; Solvent = [MeOH: H_2O=50:50% v/v]

O.D. (420 nm) for Temperature in (°C) at

t_m	30	35	40	45
0	0.200	0.220	0.226	0.220
5	0.169	0.180	0.177	0.160
10	0.163	0.176	0.174	0.157
15	0.160	0.174	0.170	0.156
20	0.160	0.172	0.170	0.153
30	0.158	0.171	0.169	0.149
35	0.156	0.170	0.170	0.147

(d) $[K_3Fe(CN)_6]$ = 1.0x10^{-3}M; [Eugenol] = 1.0x10^{-4}M;

Temp = (30.0±0.1)°C; [NaOH] = 0.05M.

O.D. (420 nm) for [Solvent = MeOH % v/v] at

t_m	50%	60%	65%	70%
0	0.200	0.190	0.203	0.180
5	0.169	0.164	–	0.171
10	0.163	0.160	0.164	0.167
15	0.160	0.154	0.160	0.165
20	0.160	0.151	0.156	0.165
30	0.158	0.151	0.155	0.157
35	0.156	–	–	–

(e) $[K_3Fe(CN)_6] = 1.0\times10^{-3}M$; $[\text{Eugenol}] = 1.0\times10^{-4}M$;
Temp = $(30.0\pm0.1)^{o}C$; Solvent = $[MeOH:H_2O = 50:50\% \ v/v]$
O.D. (420 nm) for $[NaOH]$ at

t_m	0.01M	0.025M	0.05M	0.015M	0.1M
0	0.200	0.198	0.200	0.199	0.207
5	0.180	-	0.169	0.162	0.159
10	0.178	0.165	0.163	0.160	0.154
15	0.170	0.160	0.160	0.158	0.153
20	0.170	0.160	0.160	0.157	0.152
30	0.169	0.157	0.158	0.153	0.150
35	0.168	0.156	-	0.153	0.147

METHYL EUGENOL

(a) $[\text{Methyl Eugenol}] = 7.5\times10^{-3}M$; $[NaOH] = 0.5M$,
Temp = $(40.0 \pm 0.1)^{o}C$; Solvent = $[MeOH:H_2O=50:50\% \ v/v]$
O.D. (420 nm) for $K_3Fe(CN)_6$ at

t_m	0.0001M	0.0005M	0.0010M
0	0.056	0.122	0.176
5	0.053	0.111	0.159
10	0.050	0.107	0.160
15	0.049	0.106	0.155
20	0.047	0.102	0.154
30	0.043	0.100	0.155

(b) [$K_3Fe(CN)_6$] = 5.0 x 10^{-4}M; [NaOH] = 0.5 M;
Temp = (40.0 ± 0.1)°C ; Solvent = [MeOH:H_2O = 50:50% v/v]
O.D. (420 nm) for [Methyl Eugenol] at

t_m	0.0025M	0.005M	0.0075M	0.01M
0	0.120	0.122	0.122	0.120
5	0.111	0.112	0.111	0.101
10	0.110	0.110	0.107	0.102
15	0.109	0.107	0.106	0.100
20	0.107	0.104	0.102	0.097
30	-	0.103	0.100	0.096
35	-	-	0.100	0.097

(c) [$K_3Fe(CN)_6$] = 5.0x10^{-4}M; [Methyl Eugenol]=7.5x10^{-3}M ;
[NaOH] = 0.5 ; solvent = [MeOH:H_2O=50:50% v/v]
O.D. (420 nm) for Temperature in °C at

t_m	30	35	40	45
0	0.094	0.100	0.122	0.120
5	0.091	0.094	0.111	0.104
10	0.087	0.090	0.107	0.103
15	0.085	0.088	0.106	0.102
20	0.084	0.087	0.102	0.100
30	0.086	0.082	0.100	0.100
35	0.083	0.084	0.100	0.099

(d) $[K_3Fe(CN)_6] = 5.0\times10^{-4}M$; [Methyl Eugenol] $= 7.5\times10^{-3}M$;
Temp = $(40.0 \pm 0.1)^{\circ}C$; [NaOH] = 0.5 M
O.D. (420 nm) for [Solvent = MeOH % v/v]

t_m	50%	55%	60%	65%
0	0.122	0.100	0.084	0.204
5	0.111	0.095	0.080	0.203
10	0.107	0.092	0.079	0.202
15	0.106	0.090	0.076	0.200
20	0.102	0.090	0.075	0.200
30	0.100	0.088	0.076	0.199
35	0.100	0.087	-	-

(e) $[K_3Fe(CN)_6] = 5.0\times10^{-4}M$; [Methyl Eugenol] $= 7.5\times10^{-3}M$;
Temp = $(40.0\pm0.1)^{\circ}C$; Solvent = [MeOH:H_2O = 50:50% v/v]
O.D. (420 nm) for [NaOH] at

t_m	0.1M	0.3M	0.5 M
0	0.110	0.125	0.122
5	0.108	0.119	0.111
10	0.107	0.117	0.107
15	0.106	0.115	0.106
20	0.104	0.113	0.102
30	0.104	0.112	0.100
35	-	-	0.100

Catechol

$[K_3Fe(CN)_6] = 1.0 \times 10^{-3}M$; $[\text{Catechol}] = 1.0 \times 10^{-2}M$;
$[NaOH] = 0.05M$; Solvent = $[MeOH:H_2O = 70:30\% \ v/v]$
O.D. (420 nm) for t perature in (°C) at

t_m	30°	35°	40°	45°
0	0.393	0.451	0.398	0.398
2	0.218	0.255	0.205	0.154
5	0.137	0.180	0.112	0.100
8	0.120	0.140	0.090	0.067
10	0.110	0.120	0.050	0.030

$[K_3Fe(CN)_6] = 1.0 \times 10^{-3}M$; $[\text{Catechol}] = 1.0 \times 10^{-2}M$;
$[NaOH] = 0.05M$; Temp = (30.0 ± 0.1)°C
O.D. (420 nm) for $[\text{Solvent} = MeOH \ \% \ v/v]$ at

t_m	60%	65%	70%	75%
0	0.388	0.393	0.393	0.405
2	0.115	0.135	0.218	0.230
5	0.101	0.110	0.137	0.225
8	0.067	0.085	0.120	0.205
10	0.040	0.053	0.110	0.203

Resorcinol

$[K_3Fe(CN)_6] = 1.0 \times 10^{-3}M$; [Resorcinol] = $1.0 \times 10^{-2}M$;
[NaOH] = 0.05M; Solvent = [MeOH: H_2O = 70:30% v/v]
O.D. (420 nm) for temperature in (°C) at

t_m	30°	40°	45°	50°
0	0.586	0.595	0.595	0.595
5	0.428	0.370	0.360	0.347
10	0.368	0.330	0.328	0.322
15	0.338	0.320	0.320	0.308
20	0.321	0.312	0.312	0.305
30	0.300	0.300	0.302	0.290

$[K_3Fe(CN)_6] = 1.0 \times 10^{-3}M$; [Resorcinol] = $1.0 \times 10^{-2}M$;
[NaOH] = 0.05M; Temperature = (30 ± 0.1)°C
O.D. (420 nm) for solvent [MeOH % v/v] at

t_m	60%	65%	70%	75%
0	0.407	0.580	0.586	0.580
5	0.254	0.365	0.428	–
10	0.220	0.341	0.368	–
15	0.204	0.326	0.338	0.332
20	0.194	0.320	0.321	0.290
30	–	0.328	0.300	0.276
40	–	–	–	0.265

Orcinol

(c) $[K_3Fe(CN)_6] = 1.0x10^{-3}M$; $[\text{Orcinol}] = 5.0 \times 10^{-4}M$;
$[NaOH] = 0.05M$; Solvent = $[MeOH:H_2O = 50:50\%\ v/v]$
O.D. (420 nm) for Temperature in (°C) at

t_m	30°	35°	40°	45°
0	1.027	1.042	1.006	0.956
6	0.915	0.895	0.835	0.790
9	0.890	0.860	0.792	0.745
12	0.858	0.825	0.758	0.710
15	0.830	0.798	0.730	0.688
21	0.790	0.745	0.686	0.672
30	0.722	0.683	0.662	0.661

(d) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}M$; $[\text{Orcinol}] = 5.0 \times 10^{-4}M$;
$[NaOH] = 0.05M$; Temp = $(30.0 \pm 0.1)°C$;
O.D. (420 nm) for $[\text{Solvent} = MeOH\ \%\ v/v]$ at

t_m	35%	40%	45%	50%
0	0.915	0.966	1.00	1.027
6	0.750	0.790	0.860	0.915
9	0.738	0.760	0.830	0.890
12	0.730	0.738	0.805	0.858
15	0.718	0.718	0.780	0.830
21	0.710	0.680	0.740	0.790
30	-	0.648	0.680	0.722

Quinol

$[K_3Fe(CN)_6] = 1.0 \times 10^{-3}M$; $[\text{quinol}] = 1.0 \times 10^{-2}M$;

$[NaOH] = 0.5M$; solvent = $[MeOH: H_2O = 70:30\%$ v/v$]$

O.D. (420 nm) for temperature in(°C) at

t_m	30^0	35^0	40^0	45^0
0	0.421	0.544	0.544	0.544
5	0.233	0.303	0.288	0.297
8	0.224	0.288	0.270	0.285
10	0.220	0.283	0.264	0.282
15	0.210	0.276	0.260	0.280
30	0.208	0.272	0.260	0.278

$[K_3Fe(CN)_6] = 1.0 \times 10^{-3}M$; $[\text{quinol}] = 1.0 \times 10^{-2}M$;

$[NaOH] = 0.05M$; Temp = $(30.0 \pm 0.1)^oC$

O.D. (420 nm) for [Solvent = MeOH % v/v] at

t_m	65%	70%	75%
0	0.503	0.421	0.520
5	0.293	0.233	0.273
8	0.274	0.224	0.267
10	0.268	0.220	0.260
15	-	0.210	0.261
30	-	0.208	0.259

Pyrogallol

(a) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$M; [Pyrogallol] $= 5.0 \times 10^{-4}$M;
[NaOH] = 0.1M; Solvent = [MeOH:H_2O = 50:50% v/v]
O.D. (420 nm) for Temperature in (^{o}C) at

t_m	35°	40°	45°	50°
0	1.40	1.20	1.20	1.50
10	1.20		0.925	1.00
15	1.10	0.900	0.890	0.980
20	1.00	0.880	0.870	0.900
25	0.970	0.860	0.850	0.890
30	0.958	0.858	0.850	0.900
40	0.925	0.830	0.820	0.880

(b) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$M; [Pyrogallol] $= 5.0 \times 10^{-4}$M;
[NaOH] = 0.1M; Temp = $(40.0 \pm 0.1)^{o}$C;
O.D. (420 nm) for [Solvent = MeOH % v/v] at

t_m	35%	40%	45%	50%
0	0.640	0.880	1.10	1.20
10	0.600	0.840	0.900	-
15	0.590	0.800	0.870	0.900
20	0.580	0.760	-	0.880
25	0.573	0.740	0.840	0.860
30	0.540	0.735	0.820	0.858
40	-	0.710	0.810	0.830

Phloroglucinol

$[K_3Fe(CN)_6] = 1.0 \times 10^{-3}M$; $[\text{Phloroglucinol}] = 5.0 \times 10^{-4}M$;

$[NaOH] = 0.05M$; Solvent = $[MeOH:H_2O = 70:30\%\ v/v]$

O.D. (420 nm) for temperature in (°C) at

t_m	30°	35°	40°	45°
0	0.500	0.500	0.430	0.420
2	0.383	0.382	0.319	0.290
5	0.344	0.336	0.275	0.258
8	0.317	0.301	0.244	0.225
10	0.304	0.286	0.225	0.215

$[K_3Fe(CN)_6] = 1.0 \times 10^{-3}M$; Phloroglucinol = $5.0 \times 10^{-4}M$;

$[NaOH] = 0.05M$; Temp = $(30.0 \pm 0.1)°C$

O.D. (420 nm) for [Solvent = MeOH % v/v] at

t_m	70%	75%	80%
0	0.500	0.480	0.500
2	0.383	0.396	0.391
5	0.344	0.319	0.361
8	0.317	0.282	0.338
10	0.304	0.247	0.323

α-Naphthol

(a) [α-naphthol] = 1.0 x 10^{-3}M; [NaOH] = 0.05M;

Temp = (30.0 ± 0.1)°C; Solvent = [MeOH:H_2O=70:30% v/v]

O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0.0001M	0.0005M	0.001M
0	0.200	0.526	1.036
2	0.168	-	-
5	0.140	0.333	0.659
8	0.100	0.276	0.572
10	0.080	0.231	0.524
20	-	0.I90	0.450
30	-	0.160	0.396

(b) [$K_3Fe(CN)_6$] = 1.0 x 10^{-3}M; [NaOH] = 0.05M;

Temp = (30.0 ± 0.1)°C; Solvent = [MeOH:H_2O =70:30% v/v]

O.D. (420 nm) for [α-naphthol] at

t_m	0.001M	0.005M	0.008M	0.0IM
0	I.036	1.133	I.133	1.136
2	0.795	0.223	0.215	0.200
3		0.I99	0.180	0.120
4		0.188	0.130	0.080
5	0.659	0.I80	0.108	0.040
8	0.572	0.170	0.079	-
10	0.524	0.167	0.060	-

α- Naphthol.

(c) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}M$; $[\alpha\text{-naphthol}] = 1.0 \times 10^{-3}M$;
$[NaOH] = 0.05M$; Solvent = $[MeOH:H_2O = 70:30\%\ v/v]$
O.D. (420 nm) for temperature in (°C) at

t_m	30°	35°	40°	45°
0	1.036	1.146	1.146	1.146
2	-	0.940	0.903	0.892
5	0.659	0.658	0.665	0.634
8	0.572	-	0.546	0.529
10	0.524	0.630	0.508	0.482
20	0.450	0.466	0.425	0.365
30	0.396	0.420	0.389	-

(d) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}M$; $[\alpha\text{-naphthol}] = 1.0 \times 10^{-3}M$;
$[NaOH] = 0.05M$; Temp = $(30.0 \pm 0.1)^{\circ}C$.
O.D. (420 nm) for [Solvent = MeOH % v/v] at

t_m	70%	75%	80%	85%
0	1.036	1.046	1.146	1.146
2	-	0.838	0.895	0.835
5	0.659	0.680	0.754	0.710
8	0.572	0.590	0.658	0.613
10	0.524	0.563	0.609	0.568
20	0.450	0.485	0.462	0.412
30	0.396	0.385	-	0.345

(e) $[K_3Fe(CN)_6]$ = 1.0 x 10^{-3}M; [α-naphthol] = 1.0x1 0^{-3}M;

Temp = (30.0±0.1)°C; Solvent = [MeOH:H_2O=70:30% v/v]

O.D. (420 nm) for [NaOH] at

t_m	0.01M	0.025M	0.05M	0.01M
0	0.750	0.930	1.036	1.229
5	0.690	0.776	0.659	0.600
8	0.668	0.634	0.572	0.488
10	0.612	0.602	0.524	0.435
20	0.555	0.515	0.450	0.298
30	0.497	0.455	0.396	0.270

β - Naphthol

(a) [β- naphthol] = 1.0×10^{-2}M; [NaOH] = 0.05M;

Temp = (30.0 ± 0.1)°C; Solvent = [MeOH:H_2O = 70:30% v/v]

O.D. (420 nm) for [$K_3Fe(CN)_6$] at

t_m	0.0001M	0.0005M	0.00075M	0.001M
0	0.220	0.402	0.550	0.737
5	0.130	0.210	0.295	0.400
8	0.129	0.203	0.273	0.386
10	0.120	0.191	0.262	0.365
15	0.115	0.189	0.249	0.349
20	-	0.178	0.236	0.318
30	-	0.175	0.225	0.310

(b) [$K_3Fe(CN)_6$] = 1.0 x 10^{-3}M; [NaOH] = 0.05M;

Temp = (30.0 ± 0.1)°C; Solvent = [MeOH: H_2O = 70:30% v/v]

O.D. (420 nm) for [β- naphthol] at

t_m	0.005M	0.008M	0.01
0	0.642	0.609	0.737
5	0.352	0.348	0.400
8	0.343	0.347	0.386
10	0.339	0.345	0.365
15	0.333	0.330	0.349
20	0.334	0.335	0.318
30	0.320	0.329	0.310

(c) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$M; [β- naphthol] = 1.0×10^{-2}M;
[NaOH] = 0.05M; Solvent = [MeOH: H_2O = 70:30% v/v]
O.D. (420 nm) for temperature in (°C) at

t_m	30°	35°	45°	50°
0	0.737	1.073	1.206	1.207
5	0.400	0.480	0.436	0.412
8	0.386	0.420	0.398	0.362
10	0.365	0.403	0.387	0.340
15	0.349	0.378	0.349	0.316
20	0.318	-	0.330	0.312
30	0.310	0.349	0.309	-

(d) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$M; [β -naphthol] = 1.0×10^{-2}M
[NaOH] = 0.05M; Temp = (30.0 ± 0.1)°C ;
O.D. (420 nm) for [Solvent = MeOH % v/v] at

t_m	70%	75%	80%	85%
0	0.737	0.606	1.057	1.057
5	0.400	0.310	0.474	0.459
8	0.386	0.285	0.426	0.400
10	0.365	0.275	0.412	0.375
15	0.349	0.272	0.383	0.353
20	0.318	0.269	0.357	-
30	0.318	-	0.329	-

(e) $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}M$; $[\beta$-naphthol$] = 1.0 \times 10^{-2}M$;

Temp = (30.0 ± 0.1)°C; solvent = [MeOH:H_2O=70:30% v/v]

O.D. (420 nm) for [NaOH] at

t_m	0.01M	0.025M	0.05M	0.1M
0	0.936	0.945	0.737	1.120
5	-	-	0.400	0.590
8	0.750	0.623	0.386	0.450
10	0.745	0.605	0.365	0.335
15	0.734	0.584	0.349	0.285
20	0.733	0.560	0.318	-
30	0.713	0.550	0.310	-

1. OXIDATION OF MONOHYDRIC PHENOLS BY ALKALINE HEXACYANOFERRATE (III).

The kinetics of oxidation of monohydric phenols (phenol and substituted phenols, vanillin and eugenol) by alkaline hexacyanoferrate (III) has been studied in methanol - water mixtures. The reactions showed a first order dependance on the concentrations of each - substrate, oxidant and alkali.

The rates of these reactions showed a decrease, with increasing proportions of methanol, that is, with a decrease in the dielectric constant of the medium. The role of the solvent has been rationalised on the basis of the dielectric constant, indicating that the reactions under consideration involved ions of the same sign.

The effect of changes in temperature on the rates of the reactions has been studied, and the activation parameters have been evaluated.

The presence of radical intermediates in the rate determining step of the reaction has been detected by esr spectroscopy.

The reaction pathway has been mechanistically visualized as proceeding via the formation of a radical intermediate in the rate determining step. The radical then undergoes further reaction to yield coupled products. The products were characterized by analytical and spectral methods.

2. OXIDATION OF DIHYDRIC PHENOLS BY ALKALINE HEXACYANOFERRATE (III).

The kinetics of oxidation of dihydric phenols (catechol, resorcinol, orcinol and quinol) by alkaline hexacyanoferrate (III), has been investigated in methanol - water mixtures. The reactions showed a first order dependence on the concentrations of each - substrate, oxidant and alkali.

Increasing proportions of methanol resulted in a decrease in the rate of the reaction. Plots of log k_{obs} against the reciprocal of the dielectric constant were linear, with negative slopes. This showed that the reactions under consideration involved ions of the same sign.

The rate of the reaction was enhanced, with an increase in the temperature of the medium. The activation parameters have been evaluated.

The presence of radical intermediates was detected by esr spectroscopy.

The mechanism of the reaction involved the formation of a radical intermediate in the rate determining step. Further oxidation of the radical yielded either the quinone, or resulted in the formation of coupled products. These products were obtained in good yields, and were characterised by analytical and spectral methods.

3. OXIDATION OF TRIHYDRIC PHENOLS BY ALKALINE HEXACYANOFERRATE (III).

The kinetics of oxidation of pyrogallol and phloroglucinol by alkaline hexacyanoferrate (III) has been studied in methanol - water mixtures. The reactions showed a first order dependence on the concentrations of each - substrate, oxidant and alkali.

The rate of the reaction was influenced by a change in the solvent composition of the medium. Plots of log k_{obs} against the reciprocal of dielectric constant were linear, suggesting that the reactions under consideration were of the ion-ion type.

The rate of the reaction was increased, with an increase in the temperature of the reaction medium, and the activation parameters have been evaluated.

The presence of radical intermediates was detected by esr spectroscopy.

The mechanism of the reaction involved the formation of a radical intermediate in the rate determining step. Further oxidation of the radical yielded either the extended quinone, or resulted in the formation of coupled products. These products were characterized by analytical and spectral methods.

4. OXIDATION OF NAPHTHOLS BY ALKALINE HEXACYANOFERRATE (III).

The kinetics of oxidation of α-naphthol and β-naphthol by alkaline hexacyanoferrate (III), has been investigated in methanol - water mixtures. The reactions showed a first order dependence on the concentrations of each - substrate, oxidant and alkali.

The rate of the reaction was found to increase with increasing amounts of methanol, that is, with a decrease in the dielectric constant of the medium.

The rate of the reaction was enhanced, with an increase in the temperature of the medium. The activation parameters have been evaluated.

The presence of radical intermediates has been detected by esr spectroscopy.

The mechanism of phenol coupling involves the formation of a radical intermediate in the rate determining step of the reaction. The radical intermediate undergoes rapid and irrversible coupling to give the products. These products have been isolated and characterized by analytical and spectral methods.

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