

Kinetics of Oxidation of some Phenols by Iron(III)-1,10-Phenanthroline Complex

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Kinetics of oxidation of phenol, *m*-cresol, *p*-cresol, *p*-bromophenol, *p*-chlorophenol have been investigated spectrophotometrically at 35°. The reaction obeys first order kinetics in iron(III); plots of $1/k_1$ versus $1/[1,10\text{-Phenanthroline}]^2$ and $1/k_1$ versus $1/[\text{Substrate}]$ and $1/k_1$ versus $[\text{HSO}_4^-]^2$ are straight lines with positive intercepts on the $1/k_1$ axis in each case. The kinetic evidence is in favour of the formation of a mixed ligand complex of iron(III) with 1,10-Phenanthroline and phenol. The reaction gave a good Hammett plot with a ρ^+ value of -1.6.

THE greater oxidising capacity of iron(III) salts in the presence of 1,10-phenanthroline has been reported earlier by Subba Rao *et al*¹. While extending this kinetic study to oxidation of other classes of organic compounds, the present authors have found that 1,10-phenanthroline catalyses the oxidation of phenol and substituted phenols by iron(III); iron(II) formed is immediately complexed with excess of 1,10-phenanthroline present forming ferriin. In the absence of this ligand the reaction is extremely slow. Some novel kinetic features of this catalysed reaction are reported in this paper. The kinetic pattern of this catalysed reaction is different from that observed in the oxidation of phenols by ferricyanide² and mercury(II)³, detailed kinetic studies of which were already reported.

Experimental

All the materials employed in this kinetic investigation were of analytical reagent grade. The phenols have been redistilled or recrystallised before use. The phenols studied were phenol, *m*-cresol, *p*-cresol, *p*-bromophenol and *p*-chlorophenol. The phenols were standardised bromometrically.

All the kinetic experiments have been carried out keeping the concentration of 1,10-phenanthroline very high in comparison with that of iron(III), so that 1,10-phenanthroline removed through the formation of ferriin (one of the products of the reaction) is negligible, thereby preventing complications due to possible auto-inhibition. To avoid any effects of light, the reaction vessel was coated with the black paint. The course of the reaction has been followed by measuring the optical density of the product ferriin at 510 nm. At this wave length, all the other materials concerned have negligible absorption. The Beer's Law is obeyed under the experimental conditions employed. Control experiments have shown that ferriin is quite stable

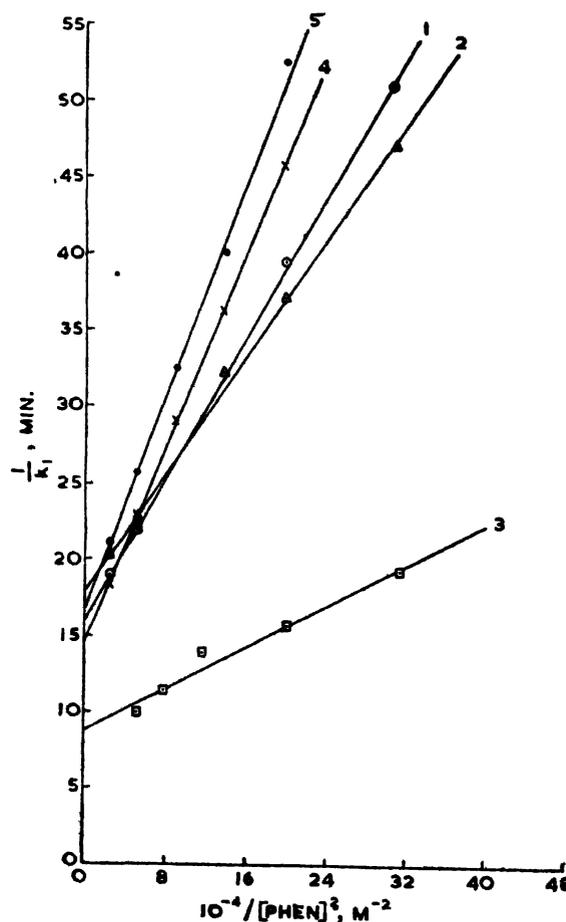


Fig. 1 Plots of $1/k_1$ versus $1/[\text{phen}]^2$
[Fe(III)] = 8.0×10^{-4} M, $[\text{H}^+] = 1.3 \times 10^{-2}$ M.
Temp. = 35°

Substrate = 1. Phenol, 2. *m*-cresol; 3. *p*-cresol
Concentration: 4.97×10^{-2} M, 7.41×10^{-3} M, 5.0×10^{-3} M
Substrate: 4. *p*-Chlorophenol, 5. *p*-Bromophenol
Concentration: 1.91×10^{-2} M, 2.0×10^{-2} M.

under these conditions. Dienone was found to be the product of oxidation as evidenced by the spot test⁴ and I.R. studies.

Results and Discussion

All the kinetic runs were carried out under the conditions $[\text{phen}]^* \gg [\text{Fe(III)}]$ and $[\text{Substrate}] \gg [\text{Fe(III)}]$. Under these conditions a plot of $\log(D_\infty - D_t)$ (where D_∞ and D_t are the optical density values at infinite time and at time t , respectively) versus time is a straight line upto at least 50% of the reaction showing that the reaction is first order with respect to iron(III). The pseudo-first order rate constant, k_1 , was calculated from the slope of the straight line.

The values of k_1 were determined at different concentrations of 1,10-phenanthroline, keeping the concentrations of substrate, iron(III) and H^+ constant. The plots of $1/k_1$ versus $1/[\text{Phen}]^2$ were straight lines with positive intercepts on the $1/k_1$ axis (Fig. 1). The values of k_1 were also determined at different concentrations of substrate keeping the concentrations of other materials constant. The plots of $1/k_1$ versus $1/[\text{Substrate}]$ were also straight lines with positive intercepts on the $1/k_1$ axis (Fig. 2).

mixed ligand type, which slowly decomposes to give the products. Earlier studies were made on the iron(III)-phenol complexes by various authors⁵.

The effect of sulphate ions on the reaction was studied by varying $[\text{HSO}_4^-]$, while keeping the concentrations of other materials constant. The ionic strength was maintained constant with sodium nitrate, although it was found that the effect of the ionic strength on the rate is very small. The rate was found to decrease with increase in the sulphate ion concentration and the quantitative relationship between the rate and the sulphate ion concentration is shown by the linear plot of $1/k_1$ versus $[\text{HSO}_4^-]^2$ (since $[\text{SO}_4^{2-}] \propto [\text{HSO}_4^-]$ at constant $[\text{H}^+]$ with positive slope and intercept (Fig. 3). The reaction was found to be inhibited by the increasing concentrations of hydrogen ion.

The studies of Whiteker and Davidson⁶ on the sulphate complexes of iron (III) show that, when $\text{SO}_4^{2-} > 0.01 \text{ M}$, the complex mainly exists as 1:2 form. In the presence of excess of 1,10-phenanthroline, the formation of a 1:2 complex of iron(III) with the ligand has been reported by Gaines (Jr.), Hammett and Walden⁷. In the presence of sulphate ions, the equilibrium may be represented by

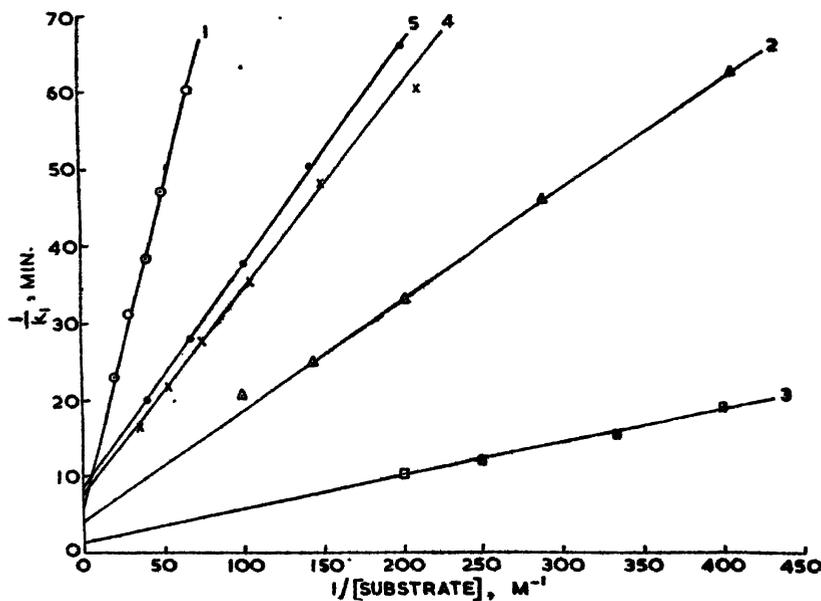
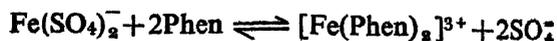


Fig. 2. Plots of $1/k_1$ versus $1/[\text{Substrate}]$
 $[\text{Fe(III)}] = 8.0 \times 10^{-5} \text{ M}$; $[\text{H}^+] = 1.3 \times 10^{-2} \text{ M}$;
 $[\text{Phen}] = 4.5 \times 10^{-3} \text{ M}$.
 Temp. = 35°
 1. Phenol; 2. *m*-cresol, 3. *p*-cresol;
 4. *p*-chlorophenol; 5 *p*-Bromophenol

Such plots are generally indicative of intermediate complex formation and obtainment of both these plots in the same reaction can be explained by assuming the formation of an intermediate complex of



This complex of iron (III) and phenanthroline was shown to be different from ferriin by Harris and

*Phen is the abbreviation used for 1,10-phenanthroline.

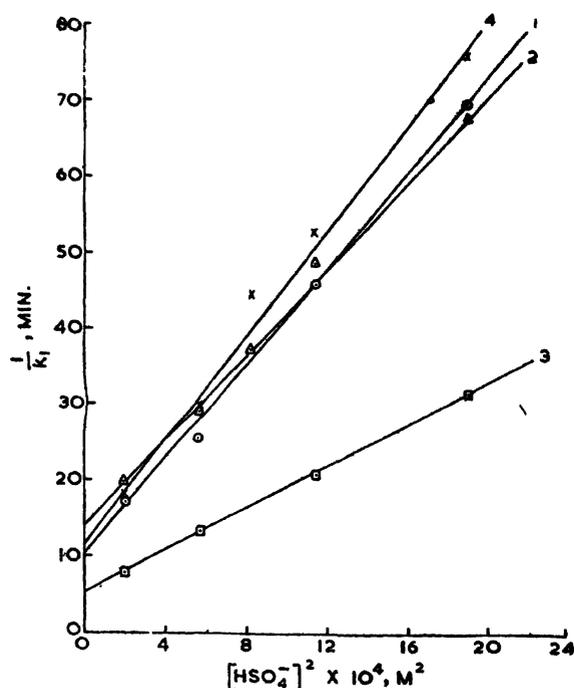
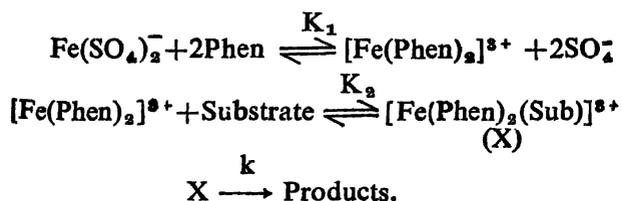


Fig. 3 Plots of $1/k_1$ versus $[\text{HSO}_4^-]^2$
 $[\text{Fe(III)}] = 8.0 \times 10^{-5} \text{ M}$; $[\text{Phen}] = 4.5 \times 10^{-3} \text{ M}$;
 $[\text{H}^+] = 1.3 \times 10^{-2} \text{ M}$; Temp. 35°

Substrate: 1 Phenol, 2. *m*-cresol, 3. *p*-cresol;
 4. *p*-Chlorophenol
 Concentration $4.97 \times 10^{-2} \text{ M}$, $7.35 \times 10^{-3} \text{ M}$,
 $5 \times 10^{-3} \text{ M}$, $1.91 \times 10^{-2} \text{ M}$.

Lockyer⁸ from the magnetic studies. Ferriin cannot be obtained by direct mixing of iron (III) and 1,10-phenanthroline, but only by the oxidation of ferriin. The authors propose the following mechanism to account for their kinetic results.



In the mechanism the authors, on the basis of their kinetic observations, assume the formation of a mixed ligand complex involving iron(III), 1,10-phenanthroline and the substrate, in which the electron transfer occurs; the electron transfer is facilitated by the presence of 1,10-phenanthroline.

The catalysis by 1,10-phenanthroline may be due to a more favourable electron transfer due to its π -electron system. Further this ligand is also known to stabilise the lower valence state more than the higher one. Thus the reaction between $[\text{Co}(\text{en})_2(\text{Phen})]^{3+}$ and Cr^{2+} has been reported to be much faster⁹ than that between $[\text{Co}(\text{en})_3]^{3+}$ and Cr^{2+} .

It is interesting to note that the kinetic pattern

observed in the present reaction is different from that in the case of ferricyanide or mercury (II) oxidation of phenols (*loc. cit*). In the latter cases, the mechanisms involve no intermediate complex formation between the oxidant and the substrate, whereas this has been actually observed in the iron(III) oxidation of phenols in the presence of 1,10-phenanthroline, as supported by the kinetic results.

Rate Law :

The above mechanism proposed by the authors leads to the rate-law,

$$-\frac{d[\text{Fe(III)}]}{dt} = \frac{kK_1K_2[\text{Fe(III)}][\text{Phen}]^2[\text{Substrate}]}{K_1K_2[\text{Phen}]^2[\text{Substrate}] + K_1[\text{Phen}]^2 + [\text{SO}_4^-]^2}$$

The pseudo-first order rate constant k_1 is given by

$$k_1 = \frac{kK_1K_2[\text{Phen}]^2[\text{Substrate}]}{K_1K_2[\text{Phen}]^2[\text{Substrate}] + K_1[\text{Phen}]^2 + [\text{SO}_4^-]^2}$$

Taking the reciprocals, we get

$$\frac{1}{k_1} = \frac{1}{k} + \frac{1}{kK_2[\text{Substrate}]} + \frac{[\text{SO}_4^-]^2}{kK_1K_2[\text{Phen}]^2[\text{Substrate}]}$$

It is evident from the rate-law that plots of $1/k_1$ versus $1/[\text{Substrate}]$, $1/k_1$ versus $1/[\text{Phen}]^2$ and $1/k_1$ versus $[\text{SO}_4^-]^2$ or $[\text{HSO}_4^-]^2$ at constant $[\text{H}^+]$, should be straight lines, which were, however, actually observed. This supports the given mechanism.

The values of k , K_1 and K_2 can be calculated from the values of slopes and intercepts of the plots of $1/k_1$ versus $1/[\text{Substrate}]$ and $1/k_1$ versus $1/[\text{Phen}]^2$. A value of 0.075 was used for the second ionization constant of sulphuric acid as reported by Doyle and Davidson¹⁰. The values of the above constants at 35° were presented in Table 1. It is evident that the values of K_1 calculated from the data of oxidation of various phenols are in the same order and reasonably good agreement.

TABLE 1—VALUES OF k , K_1 , K_2 , AT, 35° FOR THE OXIDATION OF VARIOUS PHENOLS

Substrate	k min^{-1}	K_1^*	K_2 litre. mole^{-1}
Phenol	0.18	12.30	10.06
<i>p</i> -Cresol	0.63	12.10	46.77
<i>m</i> -Cresol	0.25	17.20	38.57
<i>p</i> -Chlorophenol	0.13	6.20	52.25
<i>p</i> -Bromophenol	0.12	7.30	50.00

*The value reported is the mean of the two values that can be calculated from the slope and intercepts of the plots in Figures 1 and 2.

The authors found that a Hammett plot of $\log k$ versus σ^- was a straight line (Fig.4), which yielded

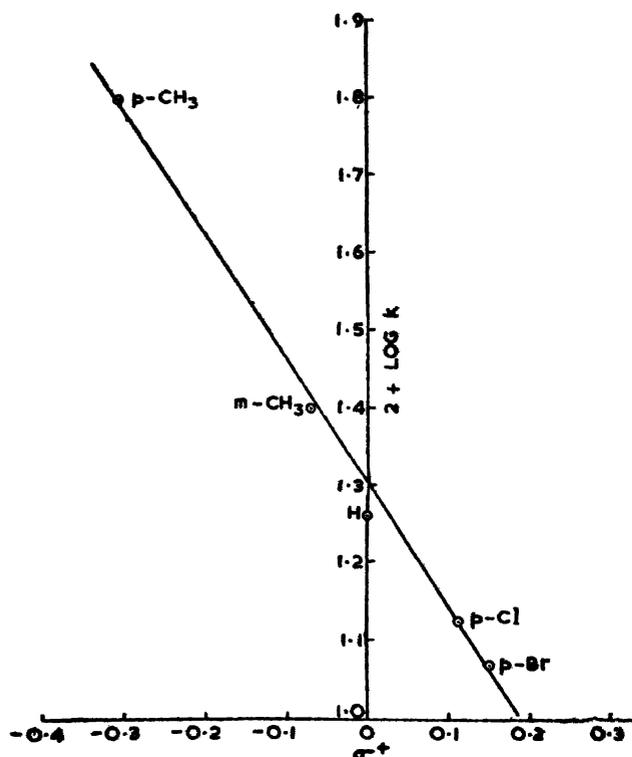


Fig. 4 Plot of $(2 + \log k)$ versus σ^+

a ρ^+ value of -1.6 . The negative value of ρ^+ shows that the reaction proceeds through a cationic centre. The values of σ^+ used were those of Okamoto and Brown¹¹.

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