

Kinetics of Oxidation of Aromatic Amines by Iron(III)-2,2'-Bipyridyl Complex

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Kinetics of oxidation of *p*-toluidine, *m*-toluidine and *p*-chloroaniline by iron(III)-2,2'-bipyridyl complex have been investigated spectrophotometrically. The reaction obeys first order kinetics both in iron(III) and the amine. A plot of $1/k$, versus $1/[2,2'\text{-bipyridyl}]^2$ is a straight line leaving a positive intercept on the $1/k_1$ -axis in each case, showing that 1 : 2 complex of iron(III) and 2,2'-bipyridyl is the active oxidizing species. Hydrogen ion was found to inhibit the reaction. A plot of $1/(k_1[H^+])$ versus $[H^+]$ was found to be a straight line, making a positive intercept on the $1/k_1$ -axis. Bisulphate ion has also been found to inhibit the reaction. The equilibrium constant of the complex formation and the activation parameters were evaluated. A suitable mechanism has been proposed.

WE have noticed that 2, 2'-bipyridyl accelerates the oxidation of many organic substrates by iron (III). With a view to understand the nature of catalysis, we have undertaken the kinetic study of oxidation of some aromatic amines by iron(III) in the presence of 2,2'-bipyridyl. The kinetic results lead to some definite conclusions about the nature of oxidizing species and the mechanism of catalysis, which are now presented.

Materials and Methods :

All the materials employed in the kinetic investigation were of analytical reagent grade. The amines were redistilled or recrystallised before use. About 0.05 M solutions of these amines were prepared in 50% methanol and standardised bromometrically. Iron(III) was taken in the form of iron(III)-perchlorate. The kinetic runs were carried out in perchloric acid medium and the ionic strength was maintained constant by sodium perchlorate.

The course of the reaction was followed spectrophotometrically by measuring the optical density of the product ferrodiin* at 510 nm. At this wavelength, all the other materials concerned have negligible absorption. In all the kinetic runs, 2,2'-bipyridyl was taken in large excess in comparison to iron(III) such that the decrease in the concentration of the ligand through complex formation with iron(II) is negligible, thereby avoiding the complications due to auto-inhibition. To avoid any photochemical effects, the reaction vessel was coated with black paint. Control experiments have shown that ferrodiin is quite stable under the experimental conditions employed (pH 1.5-2.5), and the extent of uncatalysed reaction was found to be negligibly small.

* Ferrodiin is the name given to iron(II)-tris(bipyridyl) complex.

Product Analysis : The aniline solution was mixed with iron(III) in the presence of excess 2,2'-bipyridyl solution. After the reaction was complete, the reaction mixture was neutralised by sodium bicarbonate and the products were extracted into ether and evaporated. The product was found to be azo compound by carrying out the test prescribed by Feigl¹.

Results and Discussion

All the kinetic runs were carried out under the conditions $[Bipy]_0 \gg [Fe(III)]_0$ and $[Substrate]_0 \gg [Fe(III)]_0$. Under these conditions a plot of $\log (D_\infty - D_t)$ (where D_∞ and D_t are the absorbances at infinite time and at time t respectively) versus time is a straight line, 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 2,2'-bipyridyl and at three temperatures, keeping the concentrations of substrate, iron(III) and H^+ constant. The plots of $1/k_1$ versus $1/[Bipy]^2$ were straight lines with positive intercepts on the $1/k_1$ -axes (Fig. 1), showing that 1 : 2 complex of iron(III)-bipyridyl is formed as an intermediate and is a better oxidizing species than the uncomplexed iron(III). The values of k_1 were also determined at different concentrations of the substrate, keeping the concentrations of other materials constant. A plot of k_1 versus [substrate] is a straight line passing through the origin, showing that the reaction is first order with respect to the substrate (Fig. 2).

The values of k_1 were also determined at different concentrations of H^+ , keeping the other materials

* Bipy is the abbreviation used for 2,2'-bipyridyl.

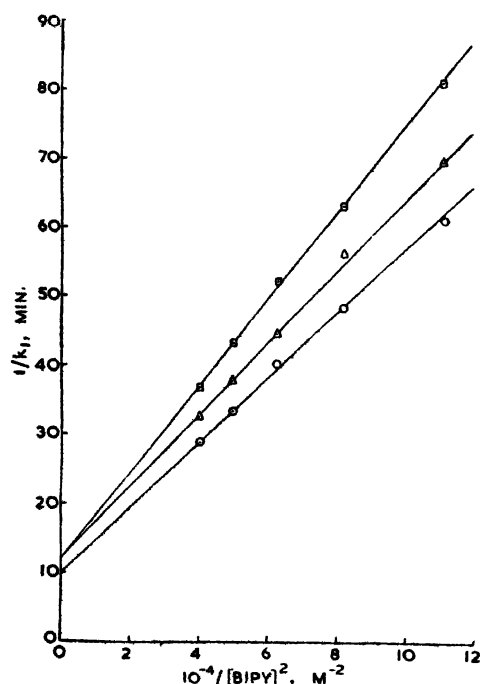


Fig. 1. Plots of $1/k_1$ versus $1/[Bipy]^2$
 $[Fe(III)] = 1.0 \times 10^{-4} M$; $[HClO_4] = 2.0 \times 10^{-2} M$
 $\mu = 0.02$; Temp. $= 30 \pm 0.1^\circ C$
 $\circ - \circ$ $[p\text{-Toluidine}] = 1.0 \times 10^{-3} M$
 $\Delta - \Delta$ $[m\text{-Toluidine}] = 2.0 \times 10^{-3} M$
 $\square - \square$ $[p\text{-Chloroaniline}] = 1.73 \times 10^{-3} M$

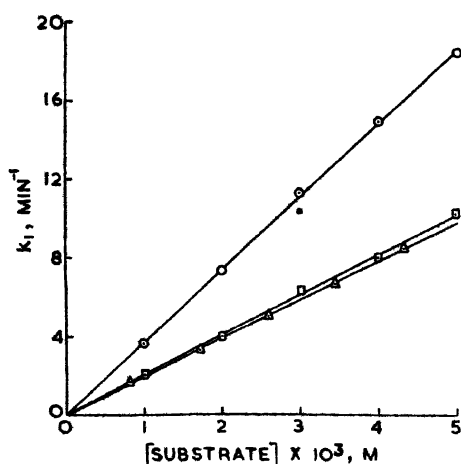


Fig. 2. Plots of k_1 versus [substrate]
 $[Fe(III)] = 1.0 \times 10^{-4} M$; $[HClO_4] = 2.0 \times 10^{-2} M$
 $[Bipy] = 5.0 \times 10^{-3} M$; Temp. $= 30 \pm 0.1^\circ C$
 $\circ - \circ$ $p\text{-Toluidine}$ $\square - \square$ $m\text{-Toluidine}$
 $\Delta - \Delta$ $p\text{-Chloroaniline}$

and the ionic strength constant. Hydrogen ion was found to inhibit the reaction. A plot of $1/(k_1[H^+])$ versus $[H^+]^2$ was a straight line, with a positive intercept on the $1/k_1$ -axis (Fig. 3).

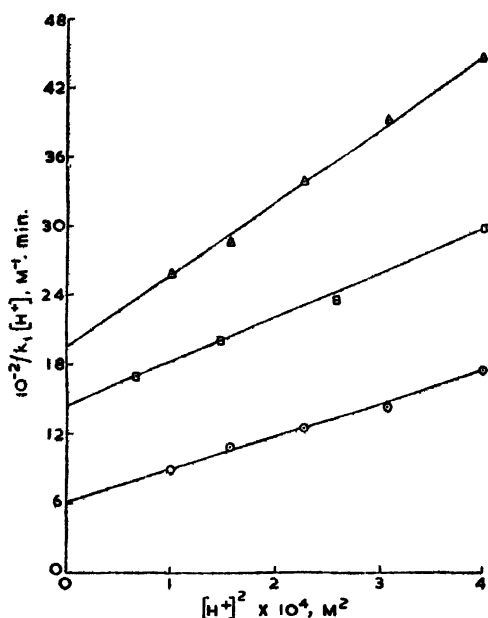


Fig. 3. Plots of $1/k_1[H^+]$ versus $[H^+]^2$
 $[Fe(III)] = 1.0 \times 10^{-4} M$; $[Bipy] = 5.0 \times 10^{-3} M$
 $\mu = 0.02$; Temp. $= 30 \pm 0.1^\circ C$
 $\square - \square$ $[p\text{-Toluidine}] = 1.0 \times 10^{-3} M$
 $\Delta - \Delta$ $[m\text{-Toluidine}] = 1.73 \times 10^{-3} M$
 $\circ - \circ$ $[p\text{-Chloroaniline}] = 1.73 \times 10^{-3} M$

The effect of sulphate ion on the reaction was studied by varying $[HSO_4^-]$ at constant hydrogen ion concentration. The rate was found to decrease with increase in the bisulphate concentration and the quantitative relationship between the rate and the sulphate ion concentration is shown by the linear plot of $1/k_1$ versus $[HSO_4^-]$ (since $[SO_4^{2-}] \propto [HSO_4^-]$ at constant $[H^+]$) with positive slope and intercept (Fig. 4). The hydrogen ions liberated by increasing $[HSO_4^-]$ have been calculated by using ionisation constant of bisulphate ion, reported by Sherrill and Noyes² to be 0.0115, to adjust the hydrogen ion concentration constant.

The inhibitory effect of bisulphate ion can be explained by assuming that iron(III) forms 1 : 1 complex with sulphate ions. This is also in accordance with the findings by Whiteker and Davidson³ according to whom the important species of iron (III) is $FeSO_4^+$ at $[HSO_4^-] < 0.011 M$ which corresponds to the concentrations of HSO_4^- employed in the present investigation. Thus the effective concentration of the free iron(III) for the formation of complex with bipyridyl decreases as HSO_4^- increases resulting in the inhibition of the reaction. The reaction mixture was found to initiate vinyl polymerisation suggesting the formation of free radical intermediates in the reaction. The ionic strength has negligible effect on the rate of the reaction.

Nature of Species of Iron(III) : The results of Milburn and Vosburgh⁴ show that iron(III) at

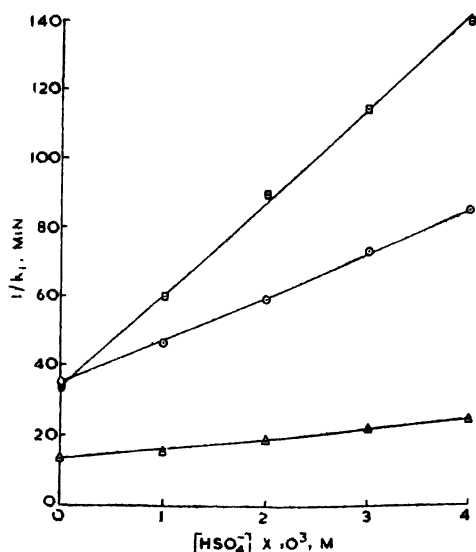


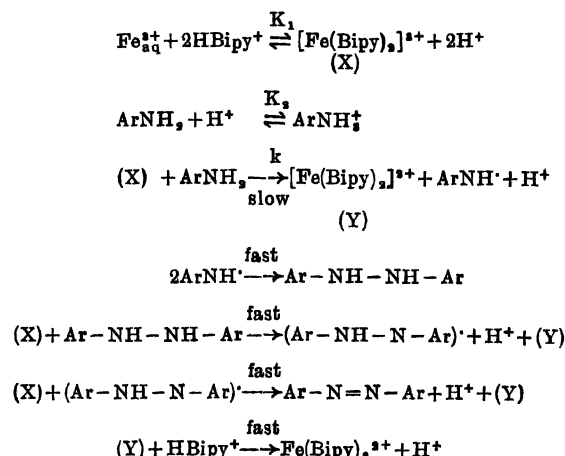
Fig. 4. Plots of $1/k_1$ versus $[\text{HSO}_4^-]$
 $[\text{Fe(III)}] = 1.0 \times 10^{-4} M$; $[\text{Bipy}] = 5.0 \times 10^{-3} M$; $\mu = 0.03$;
 $[\text{HClO}_4] = 2.0 \times 10^{-2} M$; Temp. = $30 \pm 0.1^\circ \text{C}$
 $\Delta - \Delta$ $[\text{p-Toluidine}] = 2.0 \times 10^{-3} M$;
 $\odot - \odot$ $[\text{m-Toluidine}] = 2.0 \times 10^{-3} M$;
 $\square - \square$ $[\text{p-Chloroaniline}] = 1.73 \times 10^{-3} M$

concentrations less than $1.0 \times 10^{-3} M$ (and $[\text{H}^+] = 1.2 \times 10^{-4} M$) does not dimerize. A similar observation has also been made by Siddall and Vosburgh⁶. Ciavatta and Grimaldi⁶ have reported the negative logarithm of the hydrolysis constant of Fe(III) to be 3.1 ± 0.2 . In the present investigation, iron(III) concentration employed was in the order of $10^{-4} M$ and hydrogen ion concentration was in the range 0.005 to 0.02M. Hence it is reasonable to assume that there is no appreciable dimerization under these conditions, and the concentration of hydroxylated iron(III) can be neglected in view of the low hydrolysis constant. The hydrolysis is also suppressed, since the ligand (2,2'-bipyridyl) was present in large excess. Further, it has been reported⁷ that 2,2'-bipyridyl exists in singly protonated form (at $\text{pH} \leq 3.0$). Since the kinetic investigation has been carried out in the range of pH 1.5-2.5, it is reasonable to suppose that 2,2'-bipyridyl is in the form of HBipy^+ .

The authors propose that iron(III) when mixed with bipyridyl forms a 1 : 2 complex with bipyridyl ligand and the complex is a better oxidising species than uncomplexed iron(III). The formation of 1 : 2 complex of iron(III) with bipyridyl ligand has also been reported in the literature⁸. The complex of iron(III) and bipyridyl was shown to be different from ferridin*, which cannot be obtained by direct mixing of iron(III) and bipyridyl but only by the oxidation of ferrodiin⁹.

* Ferridin is the name given to iron(III)-tris (bipyridyl) complex.

The authors propose the following mechanism to account for their kinetic results.



The catalysis by 2,2'-bipyridyl may be due to the possibility that electron-transfer is facilitated by π -electron system present in the ligand. Further, this ligand is also known to stabilize the lower valence state more than the higher one.

It is interesting to note that the kinetic pattern observed in the present reaction is different from that of oxidation of phenols by iron(III)-2,2'-bipyridyl complex¹⁰. In the latter case, the mechanism involves an intermediate complex of mixed ligand type involving Fe(III) and bipyridyl with phenol, whereas this has not been observed in the case of iron(III) oxidation of amines in the presence of 2,2'-bipyridyl.

Rate-law : The above mechanism leads to the rate-law,

$$-\frac{d[\text{Fe(III)}]}{dt} = \frac{kK_1[\text{Fe(III)}]_t[\text{ArNH}_2]_t[\text{Bipy}]^2}{K_1K_2[\text{H}^+][\text{Bipy}]^2 + K_2[\text{H}^+]^2}$$

The pseudo-first order rate constant k_1 is given by

$$k_1 = \frac{kK_1[\text{ArNH}_2]_t[\text{Bipy}]^2}{K_1K_2[\text{H}^+][\text{Bipy}]^2 + K_2[\text{H}^+]^2}$$

Taking the reciprocals, one gets,

$$\frac{1}{k_1} = \frac{K_2[\text{H}^+]}{k[\text{ArNH}_2]_t} + \frac{K_2[\text{H}^+]^2}{kK_1[\text{ArNH}_2]_t[\text{Bipy}]^2}$$

It is evident from the rate-law that plots of $1/k_1$ versus $1/[\text{Bipy}]^2$ and $1/(k_1[\text{H}^+])$ versus $[\text{H}^+]^2$ should be straight lines with positive intercepts on the $1/k_1$ -axes, which were actually observed supporting the mechanism.

The values of K_1 have been calculated from the values of slopes and intercepts of the plots of $1/k_1$

versus $1/[\text{Bipy}]^2$. The values of these stability constants were presented in Table 1. The rate constants

TABLE 1—VALUES OF STABILITY CONSTANTS (K_1)

| Substrate | Stability Constant, K_1 | | |
|-------------------------|----------------------------|----------------------------|----------------------------|
| | $30 \pm 0.1^\circ\text{C}$ | $35 \pm 0.1^\circ\text{C}$ | $40 \pm 0.1^\circ\text{C}$ |
| <i>p</i> -Toluidine | 8.5 | 6.0 | 4.2 |
| <i>m</i> -Toluidine | 9.2 | 7.2 | 5.0 |
| <i>p</i> -Chloroaniline | 7.6 | 6.1 | 3.7 |

were determined at different temperatures for each amine and the activation energies were calculated from the slopes of the plots of \log (rate constant) versus $1/T$ which were linear. The activation parameters were presented in Table 2. The results show that the stability constant, K_1 , of the Fe(III)-bipyridyl complex calculated from the data obtained

TABLE 2—ACTIVATION PARAMETERS

| Substrate | Rate Constant (k_1) $\times 10^3, \text{min}^{-1}$ | | | $E \pm 1$ Kcals. mole^{-1} | $\Delta S^\ddagger \pm 1$ e.u. |
|-------------------------|--|----------------------------|----------------------------|---|-----------------------------------|
| | $30 \pm 0.1^\circ\text{C}$ | $35 \pm 0.1^\circ\text{C}$ | $40 \pm 0.1^\circ\text{C}$ | | |
| <i>p</i> -Toluidine | 3.5 | 5.8 | 9.8 | 21.8 | +4.7 |
| <i>m</i> -Toluidine | 3.1 | 5.0 | 7.9 | 19.2 | -3.8 |
| <i>p</i> -Chloroaniline | 2.7 | 4.6 | 7.9 | 21.9 | +7.1 |

with different aromatic amines as substrates are in reasonable agreement with one another.

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