# Kinetics of Hexacyanoferrate(III) Oxidation of 4-*tert*-Butylthiophenol & 2-Methyl-4-*tert*-butylthiophenol

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The oxidation of 4-*tert*-butylthiophenol and its 2-methyl derivative by hexacyanoferrate (III) in 1$M$ HCl is possibly an inner sphere reaction having a first order dependence in the oxidant, thiols (RSH) and hydrogen ion. The oxidant and substrate react in 1:1 molar ratio whereby thiols are oxidized to the corresponding disulphides (RSSR). The addition of the disulphide and Cl⁻ and CN⁻ does not affect the reaction rate but a slight retardation is observed on the addition of ferrocyanide ion. An increase in dielectric constant of the medium decreases the rate. The inverse dependence of the rate on [water] suggests diffusion of the free radical and ferrocyanide ion, formed in the rate limiting disproportionation of the complex, out of the water cage.

D EPENDENCE of the reaction rate on $[H^+]$ in the oxidation of thiols by hexacyanoferrate(III) in acid medium is reported to be complex[1]. It has been found to be so in the oxidation of thioglycollic acid[2], 2-mercaptoethylamine hydrochloride[3] and thiosalicylic acid[4]. The rate, over a limited range of acidity, has a linear dependence on $[H^+]^{-1}$. A similar dependence of the rate on $H^+$ has also been reported recently in the oxidation of cystein and related thiols[5] in acetate buffer at $pH$ 3·7 to 4·7. It is interesting to note that the thiols studied had an additional ionisable group beside the sulphydryl group.

Considering that the complexity in hydrogen ion dependence of the rate might be due to the presence of two ionisable groups in the molecule, it was decided to examine the oxidation kinetics of such compounds that have only sulphydryl group. The present paper, accordingly, records the results on the oxidation of 4-*tert*-bulylthiophenol and 2-methyl-4-*tert*-butylthiophenol in the presence of 1$M$ HCl in aq. ethanol (70%, v/v). The reactions in fact have shown a linear correlation between the oxidation rate and $[H^+]$ over the range investigated.

## Materials and Methods

4-*tert*-Butylthiophenol and 2-methyl-4-*tert*-butylthiophenol used were products of Pitt-Consol Chemical Co. with a 98% purity rating. Their solutions were always prepared freshly in distilled ethanol and standardized against standard iodine using starch as the indicator. The stock solution of potassium hexacyanoferrate (III) (E. Merck, GR grade) was prepared by dissolving the weighed amount in aq. ethanol (70%). The corresponding disulphides were prepared by the iodine oxidation of the respective thiols. The percentage (v/v) composition of ethanol-water binary

solvent was suitably varied to study the effect of dielectric on the reaction rate. The kinetics were generally studied using the equimolar mixtures of the reactants. However, in certain cases the concentrations of the reactants were varied over a limited range permitted by the solubility considerations in order to ascertain the reaction order with respect to a particular reactant.

*Stoichiometry* — The stoichiometry of the reaction between hexacyanoferrate and the thiol was found to be 1:1. It was determined by two different methods. In one method, the concentration of the unreacted $[Fe(CN)_6]^{3-}$ was determined after the completion of reaction.

In the other method, the stoichiometry and characterization of the oxidation product of thiol was investigated by polarography. 2-Methyl-4-*tert*-butylthiophenol ($5 \times 10^{-4}M$) gave an anodic wave in equimolar ($0·05M$) carbonate-bicarbonate buffer with $E_{1/2}$ at $-0·56$V against SCE. Thereafter polarogram of the unreacted thiol in the reaction mixture $\{[Fe(CN)_6^{3-}] = 5·0 \times 10^{-4}M$ and $[thiol] = 1 \times 10^{-3}M\}$ was recorded. The two waves were found to overlap each other (Fig. 1) confirming 1:1 stoichiometry of the reaction.

The disulphide ($2·5 \times 10^{-4}M$), prepared by the iodine oxidation of thiol, in $0·1M$ HClO₄ produced a cathodic wave with $E_{1/2}$ at $-0·2$ V (Fig. 1) which coincided with that obtained from the oxidised reaction mixture $\{[Fe(CN)_6^{3-}] = '[thiol] = 5 \times 10^{-4}M\}$ thereby confirming disulphide to be the oxidation product.

*Kinetic measurements* — The reaction was followed colorimetrically using a blue filter (No. 42) in a Klett-Summerson photoelectric colorimeter. No interference in the absorbance was observed either by thiol or its oxidation product. 4-*tert*-Butylthiophenol and its disulphide showed $\lambda_{max}$ at 239 and 344nm respectively whereas 2-methyl-4-*tert*-butylthiophenol and its disulphide showed $\lambda_{max}$ at 240 nm.

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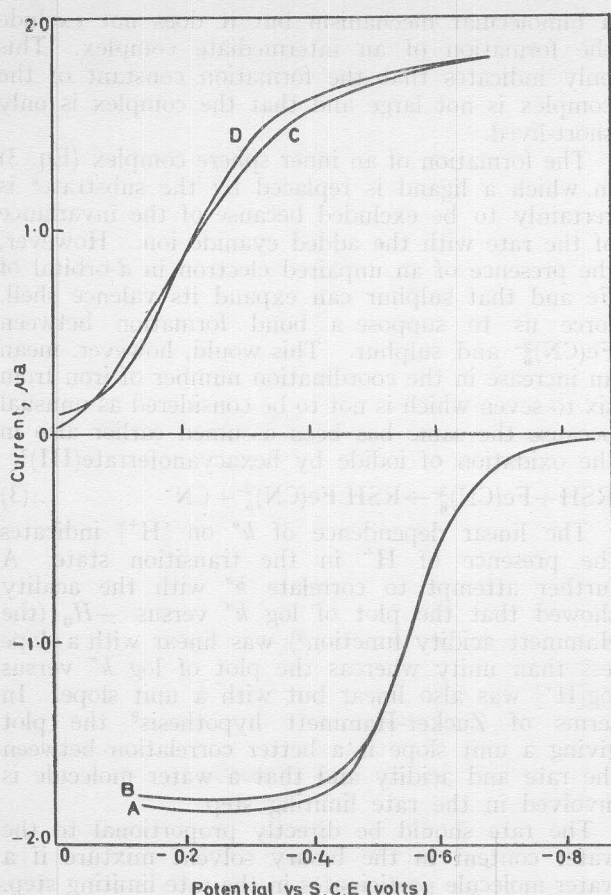\* To whom all correspondence should be addressed.

Fig. 1 — The polarogram of the pure thiol, disulphide and the remaining thiol and disulphide produced in the reaction mixture [(A) pure sample of 2-methyl-4-*tert*-butylthiophenol in carbonate-bicarbonate buffer, (B) 2-methyl-4-*tert*-butylthiophenol present in the reaction mixture, (C) the disulphide of 2-methyl-4-*tert*-butylthiophenol, and (D) the disulphide produced in the reaction mixture as a result of oxidation of the thiol by ferricyanide ion]

The absorbance spectra were measured on a Beckman DU-2 spectrophotometer fitted with a hydrogen lamp. The hexacyanoferrate(III) solution absorbed strongly at 420 nm and the Beer's law was applicable for its entire range of concentration.

The reactant solutions were flushed with nitrogen, equilibrated at the desired temperature, and mixed together. Aliquots of the reaction mixture were drawn at different time intervals, and their absorbance recorded immediately. The concentration of unreacted $Fe(CN)_6^{3-}$ was calculated from the absorbance with the help of a standard plot between concentration and optical density drawn earlier.

The equimolar reaction mixtures were generally used for following the kinetics. The second order rate constant ($k''$) was calculated from the slope of the linear plots between inverse concentration and time. This indicated a first order dependence of the rate both in $Fe(CN)_6^{3-}$ and the thiol. It was further supported by the results obtained by varying the concentration of one of the reactants at a constant concentration of the other. The similar values of the rate constant ($k''$), obtained by the two methods and calculated from the slope of the

linear plots obtained by using Eqs. (1) and (2), indicated a first order dependence in hexacyanoferrate(III) and the thiol respectively.

$$k'' = \frac{1}{t}\left(\frac{1}{a-x} - \frac{1}{a}\right) \qquad \ldots(1)$$

$$k'' = \frac{2 \cdot 303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)} \qquad \ldots(2)$$

where $a$ is the concentration of each of the reactant when equimolar reactants are used for the application of Eq. (1), and in Eq. (2) $a$ is the concentration of the reactant present in excess over the concentration ($b$) of the other reactant.

## Results and Discussion

The values of second order rate constant ($k''$), obtained by the two methods described above, are given in Table 1. An increase in [HCl] increased $k''$ (Table 2). The ionic strength was not controlled as the addition of NaCl or NaCN did not have any effect on $k''$. However, addition of $Fe(CN)_6^{4-}$, slightly but definitely retarded the rate (Table 3) though no retardation was noticeable in the individual run up to one half life of the reaction. The addition of disulphide did not affect the reaction rate. The increase in concentration of ethanol, i.e. decrease in dielectric constant of the medium, increased the rate (Table 4). The activation parameters are

TABLE 1 — VALUES OF SECOND ORDER RATE CONSTANT ($k''$) AT DIFFERENT CONCENTRATIONS OF THIOL AND HEXACYANOFERRATE(III) IN 70% AQ. ETHANOL AND 1$M$ HCl AT 30°

| $[Fe(CN)_6^{3-}] \times 10^4$ $M$ | $[Thiol] \times 10^4$ $M$ | $k''$ (litre mole$^{-1}$ sec$^{-1}$) | |
|---|---|---|---|
| | | (a) | (b) |
| 2·5 | 2·5 | 7·25 | 6·41 |
| 3·0 | 2·5 | 7·22 | 6·38 |
| 3·5 | 2·5 | 7·20 | 6·36 |
| 4·0 | 2·5 | 7·11 | 6·33 |
| 5·0 | 2·5 | 7·00 | 6·30 |
| 2·5 | 3·0 | 7·00 | 6·33 |
| 3·5 | 3·5 | 7·00 | 6·42 |
| 2·5 | 3·0 | 7·30 | 6·45 |
| 2·5 | 4·0 | 7·40 | 6·52 |
| 2·5 | 5·0 | 7·40 | 6·55 |

(a) 4-*tert*-Butylthiophenol.
(b) 2-Methyl-4-*tert*-butylthiophenol.

TABLE 2 — EFFECT OF VARYING [HCl] ON $k''$

$[10^4[Fe(CN)_6^{3-}] = 2 \cdot 5M$; $10^4[thiol] = 2 \cdot 5M$; ethanol = 70%; temp. = 30°]

| [HCl] $M$ | $k''$ (litre mole$^{-1}$ sec$^{-1}$) | |
|---|---|---|
| | (a) | (b) |
| 0·6 | 4·30 | 3·95 |
| 0·8 | 5·81 | 5·20 |
| 1·0 | 7·25 | 6·50 |
| 1·2 | 8·65 | 7·75 |
| 1·4 | 10·05 | 9·10 |

(a) 4-*tert*-Butylthiophenol.
(b) 2-Methyl-4-*tert*-butylthiophenol.

TABLE 3 — EFFECT OF VARYING INITIAL $[K_4Fe(CN)_6]$ ON $k''$

$[10^4[Fe(CN)_6^{3-}] = 2 \cdot 5M$; $10^4[thiol] = 2 \cdot 5M$; $[HCl] = 1M$; ethanol = 70%(v/v); temp.= 30°]

| $[K_4Fe(CN)_6] \times 10^4$ $M$ | $k''$ (litre mole$^{-1}$ sec$^{-1}$) | |
|---|---|---|
| | (a) | (b) |
| 0·0 | 7·25 | 6·41 |
| 0·5 | 7·00 | 6·38 |
| 1·0 | 6·90 | 6·35 |
| 1·5 | 6·80 | 6·33 |
| 2·0 | 6 71 | 6·30 |
| 2·5 | 6·62 | 6·28 |

(a) 4-tert-Butylthiophenol.
(b) 2-Methyl-4-tert-butylthiophenol.

TABLE 4 — THE EFFECT OF VARYING DIELECTRIC CONSTANT OF THE MEDIUM ON $k''$

{$10^4[Fe(CN)_6^{6-}] = 2 \cdot 5M$; $10^4[thiol] = 2 \cdot 5M$; $[HCl] = 1M$; temp.= 30°}

| Ethanol (%, v/v) | Dielectric constant[10] | $k''$ (litre mole$^{-1}$ sec$^{-1}$) | |
|---|---|---|---|
| | | (a) | (b) |
| 65 | 39·76 | 6·00 | 5·60 |
| 70 | 37·00 | 7·25 | 6·41 |
| 75 | 34·40 | 8·80 | 7·52 |
| 80 | 31·80 | 11·00 | 8·30 |

(a) 4-tert-Butylthiophenol.
(b) 2-Methyl-4-tert-butylthiophenol.

TABLE 5 — EFFECT OF TEMPERATURE ON $k''$

{$10^4[Fe(CN)_6^{3-}] = 2 \cdot 5M$; $10^4[thiol] = 2 \cdot 5M$; $[HCl] = 1M$; ethanol = 70%(v/v)}

| Temperature °C | $k''$ (litre mole$^{-1}$ sec$^{-1}$) | |
|---|---|---|
| | (a) | (b) |
| 30 | 7·25 | 6·41 |
| 35 | 9·50 | 7·95 |
| 40 | 12·50 | 10·80 |
| 45 | 16·20 | 12·60 |
| 50 | 21·30 | 13·20 |

(a) 4-tert-Butylthiophenol.
(b) 2-Methyl-4-tert-butylthiophenol.

$\Delta E^{\ddagger} = 10 \cdot 5$ kcal mole$^{-1}$ and $\Delta S^{\ddagger} = -22$ e.u. for 4-tert-butylthiophenol, and $\Delta E^{\ddagger} = 8$ kcal mole$^{-1}$ and $\Delta S^{\ddagger} = -30$ e.u. for 2-methyl-4-tert-butylthiophenol. The reaction rate increased with increasing temperature (Table 5).

The effects of ionic strength and dielectric constant of the medium on $k''$ suggest that the reaction takes place between a charged ion and a neutral molecule. The ionization of sulphydryl group of the thiol is likely to be reduced by the presence of highly electron releasing tertiary butyl group. It would therefore be correct to assume that the neutral reactant is the thiol molecule. The dependence of $k''$ on $[H^+]$ indicates that hydrogen ion is a part of the activated state. The first order dependence of the reaction in $Fe(CN)_6^{3-}$ and the thiol may indicate a bimolecular mechanism but it does not exclude the formation of an intermediate complex. This only indicates that the formation constant of the complex is not large and that the complex is only short-lived.

The formation of an inner sphere complex (Eq. 3) in which a ligand is replaced by the substrate[6] is certainly to be excluded because of the invariance of the rate with the added cyanide ion. However, the presence of an unpaired electron in $d$-orbital of Fe and that sulphur can expand its valence shell, force us to suppose a bond formation between $Fe(CN)_6^{3-}$ and sulphur. This would, however, mean an increase in the coordination number of iron from six to seven which is not to be considered as unusual because the same has been assumed earlier also in the oxidation of iodide by hexacyanoferrate(III)[7].
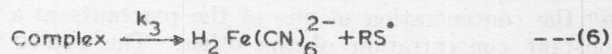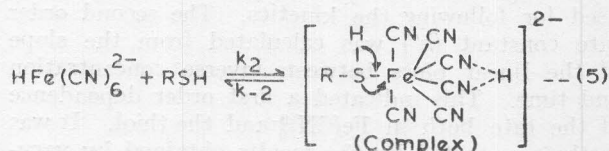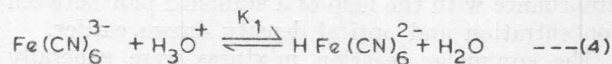
$$RSH + Fe(CN)_6^{3-} \rightarrow RSH.Fe(CN)_5^{2-} + CN^- \quad \ldots(3)$$
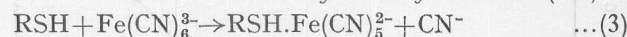
The linear dependence of $k''$ on $[H^+]$ indicates the presence of $H^+$ in the transition state. A further attempt to correlate $k''$ with the acidity showed that the plot of log $k''$ versus $-H_0$ (the Hammett acidity function[8]) was linear with a slope less than unity whereas the plot of log $k''$ versus log$[H^+]$ was also linear but with a unit slope. In terms of Zucker-Hammett hypothesis[9] the plot giving a unit slope is a better correlation between the rate and acidity and that a water molecule is involved in the rate limiting step.

The rate should be directly proportional to the water content in the binary solvent mixture if a water molecule participates in the rate limiting step. The analysis of the data in Table 4, however, indicated the plot of $k''$ versus $[H_2O]^{-1}$ to be linear. Thus there is an apparent contradiction between the expected and observed experimental results which need to be explained.

It is understood that the concentration of $HFe(CN)_6^{2-}$, the assumed reactive species (the assumption of $RSH_2^+$ is disfavoured because the slope of the plot between log $k''$ and $-H_0$ is less than unity), is expected to go up with the decreasing $[H_2O]$ because its dissociation $[HFe(CN)_6^{2-} + H_2O \rightleftharpoons Fe(CN)_6^{3-} + H_3O^+]$ is likely to be considerably checked with the increasing concentration of less basic ethanol. This, in our opinion, is the most plausible explanation for the increase in rate with a decrease in either $[H_2O]$ or dielectric constant of the binary solvent.

Consistent with these observations, reactions (4-7) are supposed to explain the kinetics of the oxidation where reaction (6) is the rate limiting reaction.

$$Fe(CN)_6^{3-} + H_3O^+ \underset{}{\overset{K_1}{\rightleftharpoons}} HFe(CN)_6^{2-} + H_2O \quad ---(4)$$

$$HFe(CN)_6^{2-} + RSH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \left[ \begin{array}{c} H\ CN\ CN \\ | \ | \ | \\ R-S-Fe-CN\cdots H \\ | \ | \\ CN\ CN \end{array} \right]^{2-} \quad ---(5)$$
(Complex)

$$Complex \overset{k_3}{\longrightarrow} H_2Fe(CN)_6^{2-} + RS^{\bullet} \quad ---(6)$$

$$2RS^{\bullet} \overset{fast}{\longrightarrow} RSSR \quad ---(7)$$

Eq. (8) could then be derived from reaction (4-7).

$$\frac{-d[\text{Fe(CN)}_6^{3-}]}{dt}$$

$$= \frac{k_3 k_2 K_1 [\text{Fe(CN)}_6^{3-}][\text{H}^+][\text{RSH}]}{(k_{-2}+k_3)(1+K_1[\text{H}^+])+K_2 K_1[\text{RSH}][\text{H}^+]} \quad \ldots(8)$$

The dissociation constant of $\text{HFe(CN)}_6^{2-}$ is reported to be very large and it is probably similar[6] to that of $\text{HP}_3\text{O}_9^{2-}$ ion[10]. As such the equilibrium constant $(K_1)$ for reaction (4) would be very small and therefore it could be assumed that $1 \gg K_1[\text{H}^+] + K_2 K_1[\text{RSH}][\text{H}^+]$ and that $k_{-2} \gg k_3$. Thus the rate law (8) is reduced to Eq. (9).

$$\frac{-d[\text{Fe(CN)}_6^{3-}]}{dt} = k_3 K_2 K_1 [\text{Fe(CN)}_6^{3-}][\text{RSH}][\text{H}^+] \quad \ldots(9)$$

The inclusion of $\text{H}^+$ in the transition state helps to induce an easier electron transfer from sulphur to Fe through the liberation of proton as a result of S-H cleavage. This mechanism also explains the slow rate of oxidation of 2-methyl-4-*tert*-butyl-thiophenol because the additional presence of electron releasing methyl group does not help in the easier liberation of proton from S-H cleavage. The crowded transition state having a more rigid structure than the initial states of the reactants is further supported by the appreciable negative value of the entropy of activation.

The electrostatic considerations indicate that the negatively charged trnasition complex would be preferentially surrounded by water molecules than by ethanol molecules. The disproportionation of the trnasition complex, therefore, takes place inside the water cage, and it is highly probable that the free radical RS· and $\text{H}_2\text{Fe(CN)}_6^{2-}$ might be reacting back to produce the transition complex unless these completely diffuse apart out of the solvent cage. Thus this helps to explain the slight retardation observed with ferrocyanide ion. The diffusion of the two species out of the water cage is rendered easier with decreasing water content in the binary solvent. Therefore the extent of the backward reaction leading to the regeneration of the transition complex decreases with the decreasing water content and thereby increasing the rate of the reaction.

## Acknowledgement

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