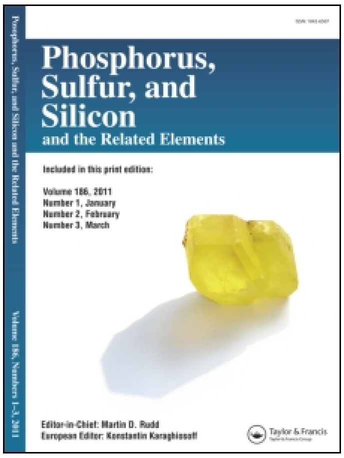

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KINETICS AND MECHANISM OF THE OXIDATION OF 1-BUTANETHIOL AND 2-BUTANETHIOL BY HEXACYANOFERRATE (III) ION IN METHANOL-WATER MEDIUM

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The kinetics of the oxidation of 1-butanethiol and 2-butanethiol by hexacyanoferrate (III) ion in methanol-water medium and in presence of hydroxyl ions have been studied. The reactions show a first order dependence on hexacyanoferrate (III) ion and a zero order in thiol when great excess is used (15–60 times). In the oxidation of 1-butanethiol (1-BT), the order in hydroxyl ions shows a transition from zero towards unity whereas in the case of 2-BT, the first order rate constant increases linearly with increasing hydroxyl ion concentration. The reaction follows second order kinetics at low concentrations of thiol (ca. $<6.0 \times 10^{-3}$ M), and the second order rate constant decreases with increasing thiol concentration. The kinetic data indicate that the accumulation of hexacyanoferrate (II) ions is responsible for the change of kinetics. This possibility has been further explored, and the results are presented in Part II of the present communication. The rate increases with increasing ionic strength, and dielectric constant of the medium. Activation parameters have been evaluated and discussed on the basis of kinetic and steric effects.

In our earlier studies, we have reported the steric influence of the sulfhydryl substrates on the kinetics of the oxidation of such compounds by 2,6-dichlorophenolindophenol (a coenzyme Q model). The substrates investigated include 2-mercaptopropionic and 3-mercaptopropionic acids,[1,2] 1-propanethiol and 2-propanethiol,[3–5] thiobenzoic and o-mercaptobenzoic acids.[6–7] We have also reported the kinetics of the oxidation of 2-butanethiol by 2,6-dichlorophenolindophenol,[8] and in the light of these studies, we felt a necessity to eliminate various side reactions involving the oxidant molecule in order to understand the structural influence of thiol compounds in these reactions. We therefore employed hexacyanoferrate (III) ion as the oxidant which has been extensively used in such systems.[9–13] Our investigations have, however, revealed some new features, and thus, the reactions of 1- butanethiol and 2-butanethiol with alkaline hexacyanoferrate (III) ion in the absence and the presence of hexacyanoferrate (II) ions have been reported in this communication.

EXPERIMENTAL

Reagents and Procedure

The solutions of 1-butanethiol and 2-butanethiol (obtained from Fluka, Switzerland and abbreviated as 1-BT, 2-BT respectively) were prepared in methanol (E. Merck, GR) and standardized against a

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standard iodine solution.[14] The solutions of hexacyanoferrate (III and II) ions were prepared by dissolving an exactly weighted quantity of BDH AnalaR grade samples in double distilled water. Fresh solutions were prepared to avoid the photo-chemical reactions, and the runs were made in aqueous methanol of known compositions. The disulfide was prepared by oxidizing thiol with iodine.[15] All other reagents used in the investigations were analytical grade samples.

The reaction was studied colorimetrically by measuring the decrease in concentration of hexacyanoferrate (III) ion with time. A Klett-Summerson Photoelectric colorimeter fitted with a light filter No. 42 (spectral range 400–465 nm) was employed to follow the progress of the reaction. The use of this light filter is justified because the hexacyanoferrate (III) ion shows a maximum absorbance at 420 nm. The spectra were recorded on a Pye Unicam Spectrophotometer SP 8-100, using silica cells with 1 cm light path. The concentration of hexacyanoferrate (III) ion in each kinetic run was calculated from the plots according to Beer's law.

PART I

RESULTS

Both analytical and spectrophotometric methods[16] were employed to determine the stoichiometry of the reaction and they conform to the equation

$$2\text{RSH} + 2[\text{Fe(CN)}_6]^{3-} \rightarrow \text{RSSR} + 2[\text{Fe(CN)}_6]^{4-} + 2\text{H}^+$$

The reaction between the sulfhydryl substrates and hexacyanoferrate (III) ion obeys a first order rate dependence in the oxidant. A number of runs varying between 15 to 60 times excess of thiol over hexacyanoferrate (III) ion were made while keeping other parameters constant. The calculated pseudo first order rate constants are given in Table I. The order in the oxidant was also determined by the initial rate measurement method. The results shown in Table I suggest that the rate constant remains practically unchanged on varying thiol concentration and thus, the order in the substrate is zero in this concentration range. The ionic strength of the system was maintained at a constant level by adjusting with KCl.

TABLE I

Rate constants at different concentrations of RSH

	$k_1 \times 10^4$ sec^{-1}	
[RSH] × 10^2 M	(1-BT)	(2-BT)
0.90	12.5	16.4
1.20	12.1	17.0
1.80	12.1	16.5
2.40	12.5	16.6
3.00	—	16.6
3.60	13.8	16.7

6.0×10^{-4} M—hexacyanoferrate (III) ion, temp. = 30°.

	1-BT	2-BT
Sodium hydroxide	3.8×10^{-3} M	2.2×10^{-3} M
Methanol	65% (v/v)	50% (v/v)
Ionic strength	0.01 M	0.015 M

In the next series of experiments, the concentration of hexacyanoferrate (III) ion was varied while keeping the other variables unchanged. The rate decreases with increasing $[Fe(CN)_6]^{3-}$, as already noticed by earlier investigators. In the oxidation of 1-BT, the relationship between the rate constant and the initial concentration of the oxidant is linear but in case of 2-BT, the relation is less simple. The rate constants obtained at different oxidant concentrations are given in Table II.

TABLE II

Rate constants at different $[K_3Fe(CN)_6]$

$[Fe(CN)_6^{3-}] \times 10^4$ M	$k_1 \times 10^4$ sec^{-1}	$[Fe(CN)_6^{3-}] \times 10^4$ M	$k_1 \times 10^4$ sec^{-1}
4.00	16.8	3.50	21.0
5.00	14.9	4.00	19.9
5.50	14.3	4.50	18.7
6.00	12.1	5.00	17.6
6.50	11.8	6.00	17.0
6.75	10.6	6.50	14.6
—	—	7.00	13.7

1-BT 1.2×10^{-2} M
NaOH 3.8×10^{-3} M
Ionic strength 0.01 M
Methanol-65% (v/v); temp. = 30°

2-BT 1.2×10^{-2} M
NaOH 2.2×10^{-3} M
Ionic strength 0.015 M
Methanol-50% (v/v); temp. = 30°

The rate increases with increasing $[OH^-]$ in the oxidation of 2-BT. A plot of $\log k_1$ against $\log[OH^-]$ gives a straight line with a slope equal to 0.8. Here too, the ionic strength of the system was maintained constant at 0.015 M. In case of 1-BT, however, the rate is not influenced by variation in $[OH^-]$ (Table III).

TABLE III

Rate constants at different $[OH^-]$

$[OH^-] \times 10^3$ M	$k_1 \times 10^4$ sec^{-1}	$[OH^-] \times 10^3$ M	$k_1 \times 10^4$ sec^{-1}
2.0	12.6	6.40	26.7
3.0	12.6	4.40	24.1
4.0	12.9	3.30	20.7
5.0	13.0	2.75	18.7
6.0	12.9	2.20	16.5
		1.65	12.5
		1.10	10.6
		0.55	6.5

1-BT 1.2×10^{-2} M
$K_3Fe(CN)_6$ 6.0×10^{-4} M
Ionic strength 0.01 M
Methanol-65% (v/v); temp. = 30°

2-BT 1.2×10^{-2} M
$K_3Fe(CN)_6$ 6.0×10^{-4} M
Ionic strength 0.015 M
Methanol-50% (v/v); temp. = 30°

The rate increases on increasing the ionic strength of the medium, which could be varied only by adding uni-univalent and uni-bivalent electrolytes because higher valent cations are precipitated in presence of sodium hydroxide. A specific cation effect on the rate has been observed. Incidentally, such a behaviour has also been noticed earlier in the oxidation of phosphorothioate by the same oxidant.[17]

The increase in dielectric constant accelerates the rate. The runs were made by varying the methanol-water composition of the medium while keeping all other parameters constant. The plots of $\log k_1$ against $1/D$ gave a straight line with a negative slope, which again indicates the participation of ions with similar charge in the rate determining step.

The external addition of the corresponding disulfide in the reaction mixture does not influence the rate, but the hexacyanoferrate (II) ion retards the rate in a linear manner.

The runs were made at different temperatures in the region between 20° and 40°C, and the rate constants were used to calculate the activation parameters:

	1-BT	2-BT
ΔH^*	9.5	38.2 kJ mol^{-1}
ΔS^*	−196.4	−98.8 J deg^{-1} mol^{-1}
ΔF^*	69.0	68.1 kJ mol^{-1}

DISCUSSION

As mentioned earlier, the reaction of hexacyanoferrate (III) ion with a variety of sulfhydryl substrates has already been investigated by different authors and the kinetic observations have been mostly explained on the basis of mechanisms analogous to Scheme I which assumes the formation of a transient species (c) as a consequence of the extension of coordination sphere of the oxidant molecule.[18]

SCHEME I

$$\mathrm{Fe(CN)_6^{3-} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C} \tag{1}$$

$$\mathrm{C + RS^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} RS^{\cdot} + Fe(CN)_6^{4-} + H_2O} \tag{2}$$

$$\mathrm{RS^{\cdot} \xrightarrow{k_3} \tfrac{1}{2}RSSR} \tag{3}$$

Assuming steady state for C and RS$^{\cdot}$, the rate of reaction is given by:

$$-\frac{d[\mathrm{Fe(CN)_6^{3-}}]}{dt} = \frac{k_1k_2k_3[\mathrm{Fe(CN)_6^{3-}}][\mathrm{RSH}][\mathrm{OH^-}]}{k_2k_3[\mathrm{RSH}] + k_{-1}k^*_{-2}[\mathrm{Fe(CN)_6^{4-}}] + k_{-1}k_3} \tag{4}$$

(where $k^*_{-2} = k_{-2}[\mathrm{H_2O}]$).

This reaction scheme, therefore, predicts a first order dependence in the oxidant as well as in sodium hydroxide, and a transition in order of reaction from zero to unity with respect to thiol on decreasing its concentration below a particular level. In fact, such a transition for 1-BT as well as 2-BT has been observed at lower concentrations of the substrate (Table IV). It is noticed that the rate of 2-BT shows an inverse linear relationship whereas the rate of 1-BT shows a fractional dependence.

TABLE IV

Rate constants at low concentrations of 1-BT and 2-BT

$[1\text{-BT}] \times 10^3$ M	k_2, lit. mol^{-1} sec^{-1}	$k_2 \times [RSH]^{\frac{1}{2}} \times 10^{3/2}$	$[2\text{-BT}] \times 10^3$ M	k_2, lit mol^{-1} sec^{-1}	$(k_2 \times [RSH]) \times 10^3$
0.6	1.73	1.34	0.6	1.96	1.17
1.2	1.02	1.11	1.8	0.72	1.29
2.4	0.56	0.86	3.0	0.44	1.32
3.6	0.40	0.75	4.2	0.26	1.09
4.8	0.39	0.85			
6.0	0.36	0.88	4.8	0.24	1.15

$[Fe(CN)_6^{3-}]$ 6.0×10^{-4} M	$[Fe(CN)_6^{3-}]$ 6.0×10^{-4} M
NaOH 3.8×10^{-3} M	NaOH 2.2×10^{-3} M
CH_3OH 65% (v/v)	CH_3OH 50% (v/v)
μ 0.013 M	μ 0.015 M
Temp. 30°	Temp. 30°

Thus, the above scheme apparently explains the kinetic observations for the oxidation of 2-BT but fails to explain the zero order dependence of rate on OH^- in the oxidation of 1-BT, as well as the inverse proportionality of the second order rate constant on the concentrations of 1-BT and 2-BT (Table IV). Accordingly, Scheme II has been proposed as an alternative.

SCHEME II

$$Fe^{III} + OH^- \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} Fe^{II} + OH^{\cdot} \tag{5}$$

$$RS^- + OH^{\cdot} \underset{k'_{-2}}{\overset{k'_2}{\rightleftharpoons}} (RSOH^{-\cdot}) \tag{6}$$

$$(RSOH^{-\cdot}) \underset{k'_{-3}}{\overset{k'_3}{\rightleftharpoons}} RS^{\cdot} + OH^- \tag{7}$$

$$RS^{\cdot} \xrightarrow{k'_4} \tfrac{1}{2}RSSR \tag{8}$$

(Here Fe^{III} and Fe^{II} denote hexacyanoferrate (III), and (II) ions respectively).

Kinetics of the interaction of hexacyanoferrate (III) ion with hydroxyl ion to give hydroxyl radical has been reported by Rao and coworkers.[19] Moreover, a transition state involving addition of hydroxyl radical to sulfur atom in aliphatic thiols has also been reported recently by Semmes and coworkers.[20] The decomposition of the transient species $(RSOH^{-\cdot})$ to produce $RS^{\cdot}$ is also in agreement with the mechanistic interpretations of elimination reactions where steric rearrangements in the transition state have been shown.[21]

The kinetic results obtained for the two thiol isomers are best explained by assuming that step (6) is rate limiting. Thus,

$$-\frac{d[Fe^{III}]}{dt} = k'_2[RS^-][OH^{\cdot}] - k'_{-2}[RSOH^{-\cdot}] \tag{9}$$

Applying steady-state treatment for $OH^{\cdot}$, $RSOH^{-\cdot}$ and $RS^{\cdot}$ gives:

$$-\frac{d[\mathrm{Fe^{III}}]}{dt}=\frac{k'_1k'_2k'_3k'_4[\mathrm{RS^-}][\mathrm{Fe^{III}}][\mathrm{OH^-}]}{k'_{-1}k'_3k'_4[\mathrm{Fe^{II}}]+k'_2k'_3k'_4[\mathrm{RS^-}]+k'_2k'_{-2}[\mathrm{RS^-}](k'_{-3}[\mathrm{OH^-}]+k'_4)}\times\left\{1-\frac{k'_{-2}(k'_{-3}[\mathrm{OH^-}]+k'_4)}{k'_3k'_4}\right\} \quad (10)$$

If

$$\frac{k'_{-2}(k'_{-3}[\mathrm{OH^-}]+k'_4)}{k'_3k'_4}\ll 1;$$

then

$$-\frac{d[\mathrm{Fe^{III}}]}{dt}=\frac{k'_1k'_2k'_3k'_4[\mathrm{RS^-}][\mathrm{Fe^{III}}][\mathrm{OH^-}]}{k'_{-1}k'_3k'_4[\mathrm{Fe^{II}}]+k'_2k'_3k'_4[\mathrm{RS^-}]+k'_2k'_{-2}[\mathrm{RS^-}](k'_{-3}[\mathrm{OH^-}]+k'_4)} \quad (11)$$

When $[\mathrm{RS^-}]$ is large and $[\mathrm{Fe^{II}}]$ is negligibly small, the rate will be independent of $[\mathrm{RS^-}]$ as shown below.

$$-\frac{d[\mathrm{Fe^{III}}]}{dt}=\frac{k'_1k'_3k'_4[\mathrm{Fe^{III}}][\mathrm{OH^-}]}{k'_3k'_4+k'_{-2}k'_{-3}[\mathrm{OH^-}]+k'_4} \quad (12)$$

Further, if $k'_3k'_4$ is larger in denominator in Equation (12); the rate will show a nearly linear relationship with $[\mathrm{OH^-}]$ as observed for 2-BT. Thus,

$$-\frac{d[\mathrm{Fe^{III}}]}{dt}=k'_1[\mathrm{Fe^{III}}][\mathrm{OH^-}] \quad (13)$$

But if $k'_{-2}k'_{-3}[\mathrm{OH^-}]$ is comparatively larger, then the rate will be independent of $[\mathrm{OH^-}]$ as found in the oxidation of 1-BT.

$$-\frac{d[\mathrm{Fe^{III}}]}{dt}=\frac{k'_1k'_3k'_4[\mathrm{Fe^{III}}]}{k'_{-2}k'_{-3}} \quad (14)$$

The assumptions regarding the relative magnitudes of $k'_3k'_4$ and $k'_{-2}k'_{-3}[\mathrm{OH^-}]$ seem justified in the light of the fact that the concentration of hydroxyl ions is larger in kinetic runs made for 1-BT. Further, 2-BT is expected to be more strained as compared to 1-BT due to steric hindrance and consequently, its participation in step (6) would be more facilitated giving larger values of k'_3 and k'_4. These assumptions could be checked by varying $[\mathrm{OH^-}]$ in the oxidation of 1-BT because Equation (12) predicts a first order dependence in hydroxyl ions at low concentrations. This possibility was checked by following the runs at low concentrations of 1-BT (Table V).

The proposed mechanism is, therefore, in accordance with the kinetic features of the reactions of 1-BT and 2-BT with hexacyanoferrate (III) ion at large concentrations of the substrate. Equation (11) also predicts a transition in order from zero to unity with respect to thiol at low concentrations because the terms involving $[\mathrm{RS^-}]$ are expected to be negligibly small under such conditions. This will lead to the rate expression:

$$-\frac{d[\mathrm{Fe^{III}}]}{dt}=\frac{k'_1k'_2[\mathrm{RS^-}][\mathrm{Fe^{III}}][\mathrm{OH^-}]}{k'_{-1}[\mathrm{Fe^{II}}]} \quad (15)$$

TABLE V

Rate constants at different $[OH^-]$ at low concentrations of 1-BT

$[OH^-] \times 10^3$ M	$k_1 \times 10^4\ sec^{-1}$	$\frac{k_1 \times 10}{[OH^-]}$
2.5	11.7	4.67
3.0	13.8	4.61
3.8	14.6	3.83
5.0	21.3	4.26
6.0	21.8	—
8.0	19.9	—

1-BT 3.6×10^{-3} M; $[Fe(CN)_6^{3-}]$ – 6.0×10^{-4} M; CH_3OH 65% (v/v); $\mu = 0.013$ M; Temp.–30°

at a constant $[OH^-]$

$$-\frac{d[Fe^{III}]}{dt} = k^{II}[RS^-][Fe^{III}] \tag{16}$$

Where

$$k^{II} = \frac{k_1' k_2' [OH^-]}{k_{-1}'[Fe^{II}]} \tag{17}$$

(and is the observed second order rate constant).

It has already been shown in Table IV that the second order rate constants decrease linearly with increasing [RSH] which may be ascribed to the accumulation of Fe^{II} in the reaction system as suggested by Equation (17). This presumption further prompted us to investigate the kinetic runs at low [RSH] in presence of externally added Fe^{II} because an excess $[Fe^{II}]$ is expected to have a limiting inhibitory effect on the rate and thus, under these conditions an increase in [RSH] will increase the rate linearly. Our investigations have confirmed this view and have also revealed some interesting features of these reactions. In the light of these findings, the results obtained for the oxidation of 1-BT and 2-BT in presence of externally added hexacyanoferrate (II) ions have been reported in Part II of this communication.

PART II

It has already been mentioned earlier (Part I) that the second order rate constant decreases on increasing [RSH] in the low concentration region and this may be ascribed to the accumulation of hexacyanoferrate (II) ion in the reaction system. In order to verify this hypothesis, the runs at low 1-BT and 2-BT concentrations were made on adding an excess of hexacyanoferrate (II) ion to the reaction system (ca. 6.0×10^{-3} and 7.0×10^{-3} M respectively). Under these conditions, the over-all order of reaction again changes from two to unity in both cases and the first order rate constant increases linearly with increasing [RSH] as predicted by the proposed mechanism (Table VI).

TABLE VI

Rate constants at different [RSH] in presence of $Fe(CN)_6^{4-}$ ion

[1-BT] × 10^4 M	$k_1 \times 10^4\ sec^{-1}$	[2-BT] × 10^4 M	$k_1 \times 10^4\ sec^{-1}$
36	52.4	54	20.8
30	39.1	42	16.7
24	32.3	30	15.3
18	28.4	24	12.0
12	18.4	6	4.3
6	9.8	—	—

Hexacyanoferrate (III) ion	6.0×10^{-4} M; 6.0×10^{-4} M
Sodium hydroxide	3.8×10^{-3} M; 2.2×10^{-3} M
Hexacyanoferrate (II) ion	6.0×10^{-3} M; 7.0×10^{-3} M
Methanol	50% (v/v); 50% (v/v)
Ionic strength	0.07 M; 0.08 M
temp.	30°C; 30°C.

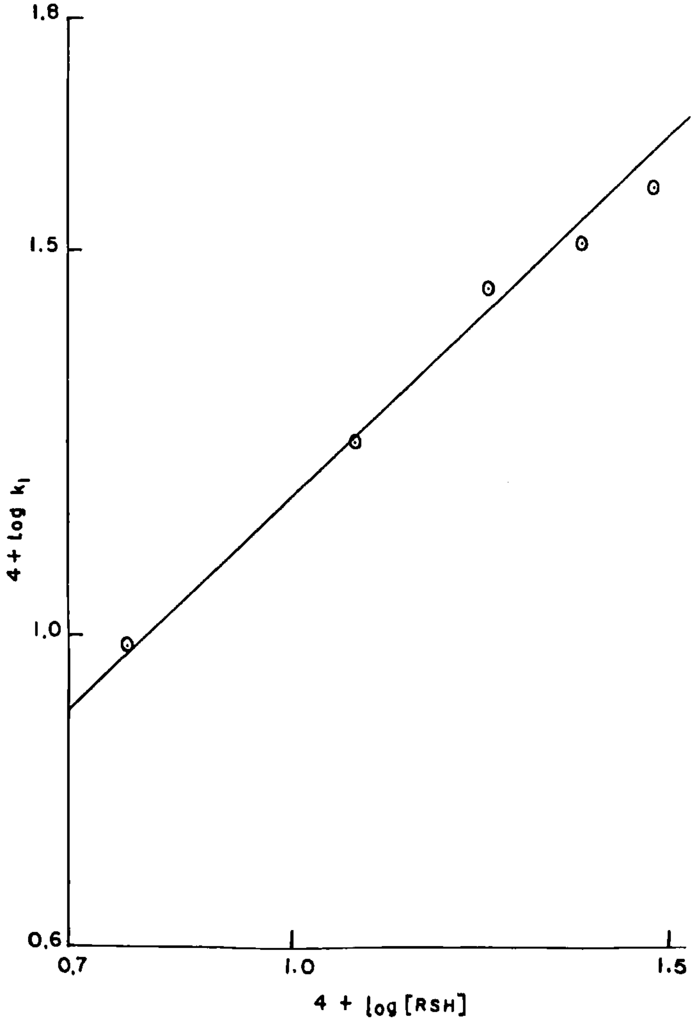

FIGURE 1 $[Fe(CN)_6^{3-}] = 6.0 \times 10^{-4}$ M; $[Fe(CN)_6^{4-}] = 6.0 \times 10^{-3}$ M; $[NaOH] = 3.8 \times 10^{-3}$ M; $CH_3OH = 50\%$ (v/v); $\mu = 0.07$ M; Temp. = 30°C.

The first order dependence of rate on [RSH] was also confirmed by drawing plots of log k_1 against log[1-BT] and log[2-BT] which give straight lines with the slopes of 0.93 and 0.71 respectively (Figure 1 and Figure 2). The first order rate constant remains practically unchanged on varying $[Fe^{III}]$ which suggests that the order in oxidant is zero (Table VII).

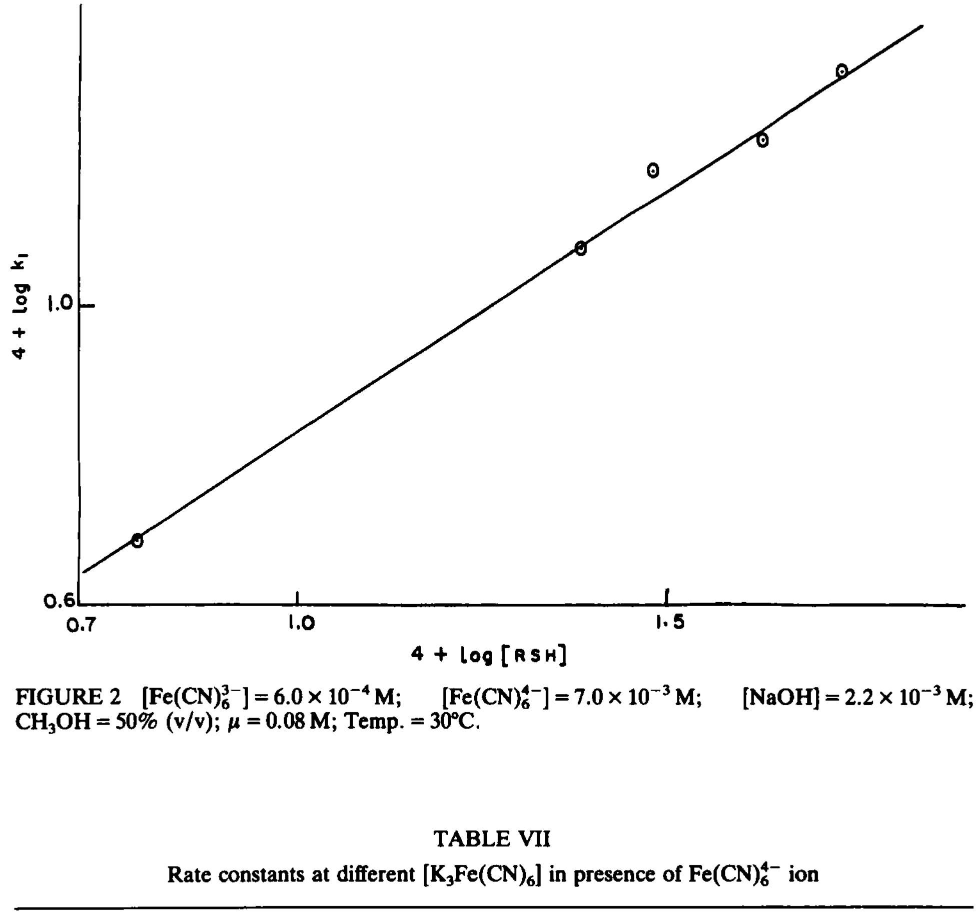

FIGURE 2 $[Fe(CN)_6^{3-}] = 6.0 \times 10^{-4}$ M; $[Fe(CN)_6^{4-}] = 7.0 \times 10^{-3}$ M; $[NaOH] = 2.2 \times 10^{-3}$ M; CH_3OH = 50% (v/v); $\mu = 0.08$ M; Temp. = 30°C.

TABLE VII

Rate constants at different $[K_3Fe(CN)_6]$ in presence of $Fe(CN)_6^{4-}$ ion

$[K_3Fe(CN)_6] \times 10^4$ M	$k_1 \times 10^4$ sec^{-1}	$[K_3Fe(CN)_6] \times 10^4$ M	$k_1 \times 10^4$ sec^{-1}
5.5	33.4	4.20	10.7
6.0	30.9	4.65	10.5
7.0	33.2	5.0	10.9
7.5	31.8	5.50	11.0
8.0	26.2	6.00	11.2
—	—	6.50	9.8

1-BT 1.8×10^{-3} M;
NaOH 3.8×10^{-3} M;
$K_4Fe(CN)_6$ 6.0×10^{-3} M
Methanol 50% (v/v)
$\mu = 0.07$ M
Temp. = 30°C

2-BT 3.0×10^{-3} M
NaOH 2.2×10^{-3} M
$K_4Fe(CN)_6$ 7×10^{-3} M
Methanol 50% (v/v)
$\mu = 0.08$ M
Temp. = 30°C

TABLE VIII

Rate constants at different $[OH^-]$ in presence of $Fe(CN)_6^{4-}$

$[OH^-] \times 10^3$ M	$k_1 \times 10^4$ sec^{-1}	$[OH^-] \times 10^3$ M	$k_1 \times 10^4$ sec^{-1}
1.0	7.4	1.6	7.0
2.0	15.5	2.53	10.9
3.0	22.2	3.2	12.9
3.8	23.9	4.0	15.6
4.2	25.8	4.8	18.4

1-BT 1.8×10^{-3} M
$Fe(CN)_6^{3-}$ 6.0×10^{-4} M
$Fe(CN)_6^{4-}$ 6.0×10^{-3} M
Methanol 50% (v/v)
Ionic strength 0.07 M
Temp. 30°C

2-BT 3.0×10^{-3} M
$Fe(CN)_6^{3-}$ 6.0×10^{-4} M
$Fe(CN)_6^{4-}$ 7.0×10^{-3} M
Methanol 50% (v/v)
Ionic strength 0.08 M
Temp. 30°C

The rate increases linearly on increasing $[OH^-]$ as is evident from Table VIII. It would be pertinent to recapitulate here that the rate is not influenced on varying $[OH^-]$ in the oxidation of 1-BT at higher concentrations of the substrate as pointed out in Part I but Scheme II expects a first order dependence in sodium hydroxide on decreasing its concentration below a particular level. A glimpse at Table VIII shows that the rate of 1-BT tends to attain a limiting value at higher concentrations of hydroxyl ions.

The external addition of hexacyanoferrate (II) ion to the reaction system is again found to retard the rate. The activation parameters were determined in the usual manner and the heat and entropy of activation are found to compensate each other to give a near constant value of the free energy of activation for these reactions. This indicates that the site of attack is common in these reactions when carried out in absence as well as in presence of hexacyanoferrate (II) ion.

The diversity in kinetic features at low concentrations of the substrate and in presence of hexacyanoferrate (II) ion prompted us to check the kinetic results obtained at higher concentrations of the substrate and in absence of hexacyanoferrate (II) ions. It has been described in Part I that the reaction follows a first order kinetics in hexacyanoferrate (III) ion and a zero order kinetics in the substrate under the pseudo conditions (Part I; Table I). In presence of an excess hexacyanoferrate (II) ion added externally to the reaction system, a similar behaviour has been noticed (Table IX). Since the kinetic features of the reaction remain unchanged on adding hexacyanoferrate (II) ion to the reaction mixture; the details of these studies have not been given here.

Thus, the results obtained for the oxidation of 1-BT and 2-BT in presence of externally added hexacyanoferrate (II) ion are in accordance with the expectations of Scheme II, already discussed in detail. The arguments given in Part I are further strengthened by the observations recorded in Table IX because at higher concentrations of thiol, the terms involving $[RS^-]$ in Equation (11) are again expected to be larger than $k'_{-1}k'_3k'_4$ $[Fe^{II}]$ and therefore, the kinetic features do not change when the runs are made in presence of hexacyanoferrate (II) ions. It has also been shown in Table VII that the rate of reaction is found to be practically unaffected on varying $[Fe^{III}]$ which can be qualitatively explained on the

TABLE IX

Rate constants at different [RSH] in presence of excess $[Fe(CN)_6^{4-}]$

$[1\text{-BT}] \times 10^3$ M	$k_1 \times 10^4$ sec^{-1}	$[2\text{-BT}] \times 10^3$ M	$k_1 \times 10^4$ sec^{-1}
12	25.9	12	20.0
18	27.2	18	20.0
24	26.8	24	22.7
36	26.0	30	20.8

Hexacyanoferrate (III) ion	6.0×10^{-4} M; 6.0×10^{-4} M
Sodium hydroxide	2.0×10^{-3} M; 2.2×10^{-3} M
Hexacyanoferrate (II) ion	6.0×10^{-3} M; 7.0×10^{-3} M
Methanol	50% (v/v); 50% (v/v)
ionic strength	0.0676 M; 0.08 M
Temp.	30°; 30°

basis of equilibrium given in step (1). It seems that hexacyanoferrate (III) ions have a limiting concentration in presence of excess ferrocyanide ions and thus the course of reaction remains unchanged on varying the concentration of the oxidant. In brief, therefore, Scheme II is amply verified by the observations summarized in Part II of this communication.

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