

# MECHANISM OF OXIDATION OF *n*-HEXANOL BY ALKALINE HEXACYANOFERRATE (III) IN PRESENCE OF OSMIUM TETROXIDE AS A HOMOGENEOUS CATALYST

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(Communicated by Prof. S. K. Bhattacharyya, F.N.A.)

(Received 1 August 1973; after revision 28 November 1974)

In order to elucidate the actual mechanistic path of the reaction, kinetics of oxidation of *n*-hexanol in aqueous alkaline medium with hexacyanoferrate (III) in presence of osmium tetroxide as catalyst is reported. The reaction rate shows the zero order kinetics in hexacyanoferrate (III) ion concentration even upto tenfold variation. The order of reaction with respect to *n*-hexanol is unity even upto very high concentration of the substrate. The effect of hydroxide ion on the velocity of the reaction leads a slight complicated feature. The velocity of the reaction which follows nearly first order kinetics at low hydroxide ion concentration, tends to zero order at higher concentrations. The effect of variation of osmium tetroxide concentration on the reaction rate also shows the direct proportionality. On the basis of these results the following probable rate law might be proposed :

$$\frac{-d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{K[\text{S}][\text{Os}(\text{VIII})]_0[\text{OH}^-]}{k_a + k_b[\text{OH}^-]}$$

## INTRODUCTION

Studies in homogeneously catalysed oxidation kinetics of organic compounds in liquid phase are considerably limited and, therefore, the mechanistic exposition of such reactions have valuable contributions to the knowledge of Chemistry. An interesting system comprising of Os (VIII)—hexacyanoferrate(III) (Solymosi 1957; and Munemor 1962) has recently been found to be highly effective in oxidizing organic and inorganic compounds in aqueous alkaline medium. The oxidation mechanism of some organic compounds (Singh, H. S. 1967; Krishna & Singh 1966; Singh, N. P. *et al.* 1968; Singh, V. N. *et al.* 1969, 70; Lal *et al.* 1972; Pandey 1968; Singh, B. N. 1970; and Singh, Lallu 1971) by this system has recently been reported from our laboratory. On the basis of the limited account of the data, however, a general oxidative feature of this system has also been derived. Owing to the greater importance of the oxidation of alcohols, an attempt has been made to work out the kinetics and mechanism of oxidation of *n*-hexanol.

## RESULTS AND DISCUSSION

In the osmium tetroxide catalysed oxidation of *n*-hexanol by alkaline hexacyanoferrate(III), the reaction has been studied with respect to hexacyanoferrate(III) ion, keeping the concentration of other reactions constant. The ionic strength of the medium was kept constant with the help of standard solution of potassium chloride. The last column of Table I indicates the perfect zero order velocity

TABLE I

(Temp. 20°C)

$[K_3Fe(CN)_6]$	$= 1.00 \times 10^{-3} M$
$[n\text{-Hexanol}]$	$= 1.00 \times 10^{-2} M$
$[NaOH]$	$= 2.50 \times 10^{-2} M$
$[OsO_4]$	$= 7.86 \times 10^{-5} M$
$[KCl]$	$= 2.49 \times 10^{-1} M$
$\mu$	$= 0.28 M$

Time (min)	Ce(SO <sub>4</sub> ) ( $1.53 \times 10^{-2} M$ ) ml	$\frac{\Delta x}{\Delta t} \times 10$ ml/min
0	0.00	—
10	0.38	0.38
20	0.66	0.28
30	0.96	0.30
40	1.24	0.28
50	1.52	0.28
65	1.94	0.28
80	2.36	0.28
90	2.62	0.26
105	3.02	0.27
T <sup>∞</sup>	3.28	—

Average value ( $k_o$ )(neglecting 1st constant) =  $0.28 \times 10^{-1}$  ml/min $k_s = 0.85 \times 10^{-5}$  mole lit<sup>-1</sup> min<sup>-1</sup>.

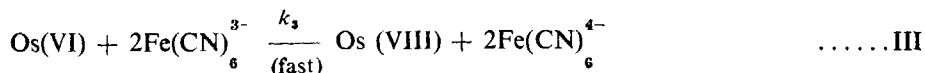
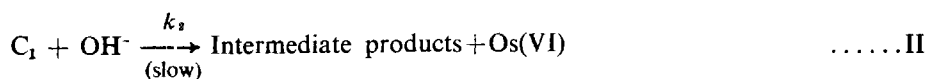
constant from beginning to the end except the first constant. The  $k_s$  values are constant even upto ten fold variation of hexacyanoferrate(III) and this clearly substantiates the zero order dependence of the reaction rate with respect to it (Table II). The fourteen-fold variation of *n*-hexanol confirms the pseudo first order kinetics with respect to the organic substrate (Fig. 1). The hydroxyl ion variation on the reaction rate leads to the conclusion that rate follows first order kinetics at its lower concentrations and tends towards zero order kinetics at higher hydroxyl ion concentrations (Fig. 2). The results presented in Fig. 3 demonstrates that the reaction velocity follows first order kinetics even up to a wide range of the catalyst concentration. A positive cut in the rate axis also indicates the small fraction of the reaction occurring without catalyst. In fact this part of the reaction is very small and therefore it might be assumed at this stage that the measure part of the reaction is taking place with the catalyst, osmium tetroxide.

TABLE II  
(Temp 20°C)

[ <i>n</i> -Hexanol]	= 1.00 × 10 <sup>-2</sup> M
[NaOH]	= 2.50 × 10 <sup>-2</sup> M
[OsO <sub>4</sub> ]	= 7.86 × 10 <sup>-5</sup> M
μ	= 0.28 M

(K <sub>4</sub> Fe(CN) <sub>6</sub> ) × 10 <sup>3</sup> M	k <sub>2</sub> × 10 <sup>5</sup> mole lit <sup>-1</sup> min <sup>-1</sup>
1.00	0.85
2.00	0.88
3.00	0.88
4.00	0.92
5.00	0.92
6.00	0.85
8.00	0.92
9.00	0.92
10.00	0.92

On the basis of the aforesaid results the following scheme of oxidation might be proposed :



where *S* represents *n*-hexanol.

The rate law might be formulated in terms of decreasing hexacyanoferrate(III) concentration or in terms of the rate of formation Os(VI). So

$$\frac{-d[\text{Fe(CN)}_6^{3-}]}{dt} = \frac{2d[(\text{Os(VI)})]}{dt} = 2k_2(\text{C}_1)(\text{OH}^-) \quad \dots\dots(1)$$

Concentration of C<sub>1</sub> from the steps I and II at steady state condition will be given as :

$$[\text{C}_1] = \frac{k_1[\text{S}][\text{Os(VIII)}]_T}{k_{-1} + k_2[\text{OH}^-] + k_1[\text{S}]} \quad \dots\dots(2)$$

where [Os(VIII)]<sub>T</sub> represents the total concentration of the osmium taken according to equation (3).

$$[\text{Os(VIII)}]_T = [\text{Os(VIII)}] + \text{C}_1 \quad \dots\dots(3)$$

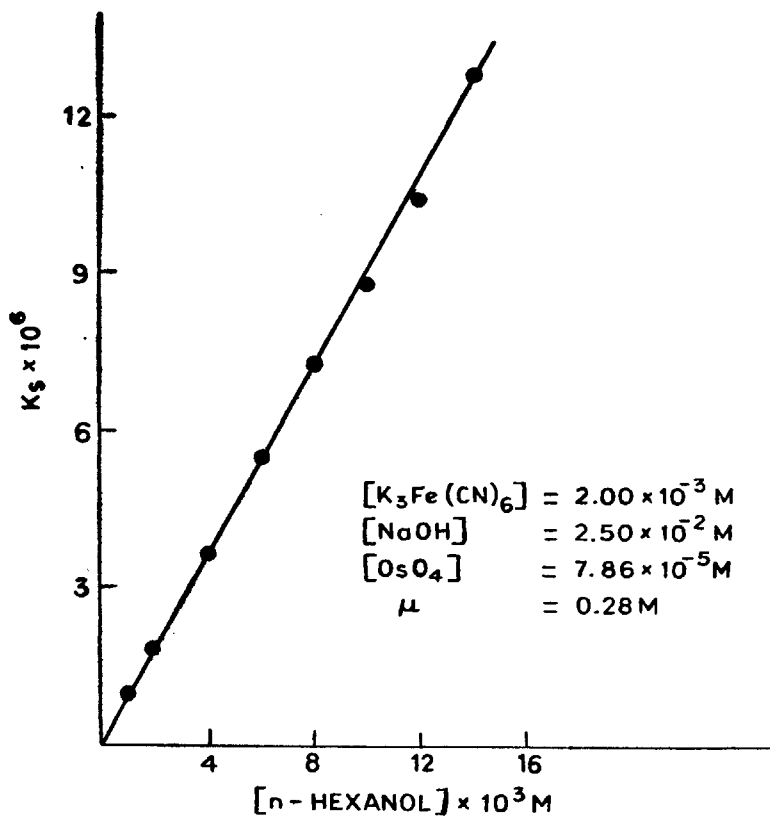


FIG. 1

From eqn. (1) and (2), the final rate law comes out to be :

$$\frac{-d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{2 k_1 k_2 [\text{S}] [\text{OH}^-] [\text{Os}(\text{VIII})]_T}{k_{-1} + k_2 [\text{OH}^-] + k_1 [\text{S}]} \quad \dots(4)$$

Evidently the rate law (4) accounts for the variation of the order of reaction with respect to hydroxide and substrate concentration. But the region in which the experimental work was performed, no retarding effect of the substrate concentration was observed. Thus, the inequality  $[k_{-1} + k_2 [\text{OH}^-]] \gg k_1 [\text{S}]$  might be taken as valid. Under these conditions, the rate law (4) reduces to (5).

$$\frac{-d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{2k_1 k_2 [\text{S}] [\text{OH}^-] [\text{Os}(\text{VIII})]_T}{k_{-1} + k_2 [\text{OH}^-]} \quad \dots(5)$$

At very low concentrations of hydroxyl ion the inequality  $k_{-1} \gg k_2 [\text{OH}^-]$  might hold good and so  $k_2 [\text{OH}^-]$  can be neglected against  $k_{-1}$  and eq. (5) reduces to eq. (6).

$$\frac{-d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = 2 K k_2 [\text{S}] [\text{OH}^-] [\text{Os}(\text{VIII})]_T \quad \dots(6)$$

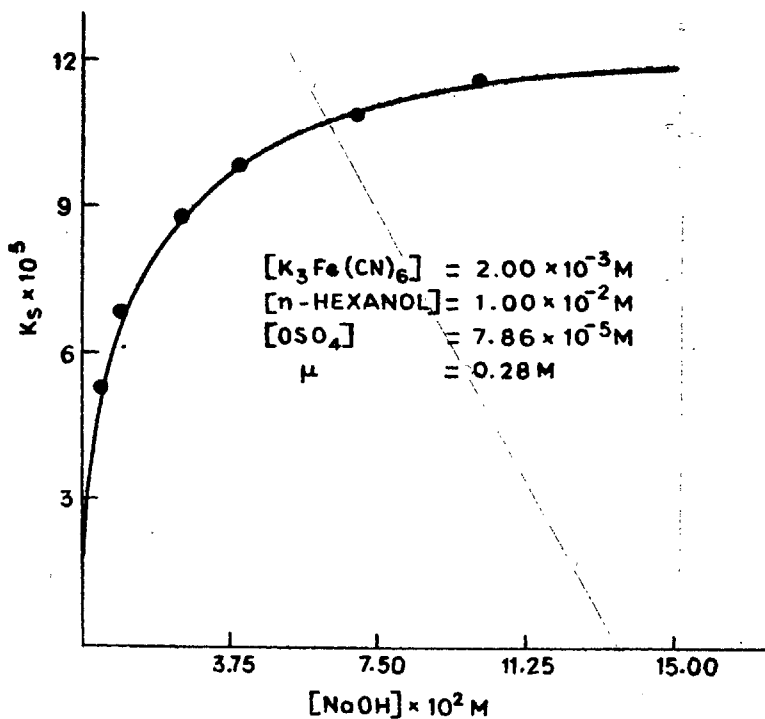


FIG. 2

$$\text{where } K = \frac{k_1}{k_{-1}}$$

Therefore, eq. (6) clearly substantiates that at lower hydroxyl ion concentration, the reaction order with respect to each *n*-hexanol, hydroxyl ion and osmium tetroxide is unity. The above equation also indicates that the rate is independent to the hexacyanoferrate(III) concentration.

Further, at very high hydroxyl ion concentration the inequality  $k_2 [OH^-] \gg k_{-1}$  might be assumed and the eqn (5) will take the form :

$$\frac{-d [Fe(CN)_6^{3-}]}{dt} = 2k_1 [S] [Os(VIII)]_0 \quad \dots (7)$$

This equation again proves beyond doubt that the velocity of the reaction varies independent to the concentration of hydroxyl ion and hexacyanoferrate (III) ion.

During the course of osmium tetroxide catalyzed oxidation of organic compounds with alkaline hexacyanoferrate (III) the formation of Os(VI) species has been fully confirmed (Singh *et al.* 1968; 1969, 1970; Lal *et al.* 1972; Pandey (1968), Singh (1970), Singh, Lallu (1971); and Mayell (1968). Not only this, it is also reported that osmium (VI) is rapidly oxidized with alkaline hexacyanoferrate(III) in agreement with the step (III) shown in the scheme of oxidation. Thus, the way of participation of osmium tetroxide in the hexacyanoferrate (III) oxidation of *n*-hexanol in alkaline medium is

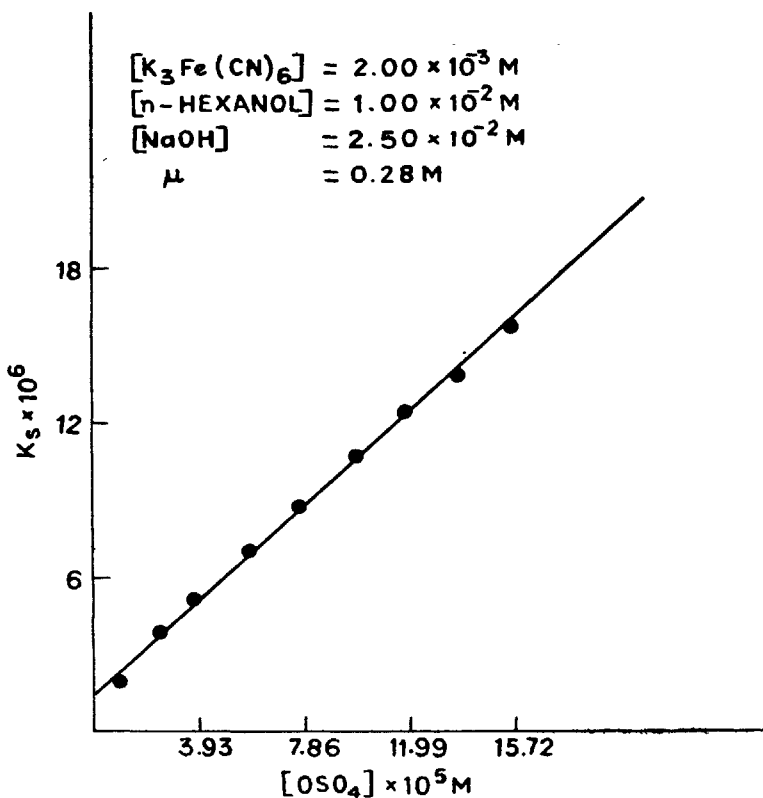
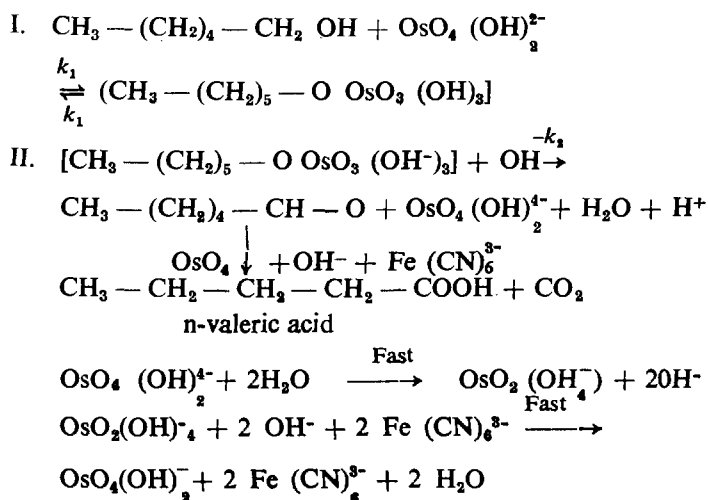


FIG. 3

fully explained. It is also confirmed that Os (VI) species in alkaline medium exists as  $OsO_2(OH)_4^{2-}$ . The details of the process occurring in the oxidation of *n*-hexanol might be described as follows :



The presence of *n*-valeric acid has been confirmed from the paper Chromatographic study. The equivalence measurement also lead to the same conclusion.

During the course of the study, it was observed that very small fraction of the reaction is taking place even in absence of the catalyst osmium tetroxide. It has been seen that this fraction is indeed very small and in fact will not effect the proposed mechanism.

Recently Steward and co-workers have reported that the oxidation of alcohols also occurs via their alkoxide form (Eq. 8).



It is also well known that transition metals like osmium has got excellent property of forming complexes with organic substrates. Thus, it is every possibility that at low hydroxide concentrations the oxidation will occur via complex and at higher concentration a very small fraction of the reaction may occur between alkoxide and osmium tetroxide. In the oxidation of glycols we have observed the 1 : 1 and 1 : 2 complexes of asmium tetroxide and glycol respectively.

The study was extended to four temperatures and the various thermodynamic parameters calculated are presented in Table III. A perusal of this table clearly reveals that these values are not abnormal for such type of reactions.

TABLE III

	kr (in sec)	$\Delta E^\ddagger$ k. cal/mole	$\Delta S^\ddagger$ e.u.	$\Delta F^\ddagger$ k. cal/mole	A
<i>n</i> -hexanol	$2.21 \times 10^1$	16	-4	-13	$3 \times 10^{13}$

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