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# Kinetics and Mechanism of Oxidation of Some Cycloalkanols by Alkaline Hexacyanoferrate(III)

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The kinetics of oxidation of cyclohexanol, cyclopentanol, cycloheptanol and cyclooctanol by alkaline hexacyanoferrate(III) was studied in the 40°–60°C temperature range, in the absence of any catalyst. The following mechanism was suggested.

$$>CHOH + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} >CHO^- + H_2O \quad (I)$$

$$>CHO^- + Fe(CN)_6^{3-} \xrightarrow[Slow]{k_2} >CHO^{\bullet} + Fe(CN)_6^{4-} \quad (II)$$

$$>CHO^{\bullet} + Fe(CN)_6^{3-} \xrightarrow[Fast]{} >C{=}O + Fe(CN)_6^{4-} + H^+ \quad (III)$$

$$>C{=}O + 6\,Fe(CN)_6^{3-} + 6\,OH^- \xrightarrow[Fast]{} \text{Final Oxidation Product} + 6\,Fe(CN)_6^{4-} + 3\,H_2O \quad (IV)$$

based on which the rate law derived was:

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = \frac{8k_1k_2[>CHOH]_{total}\,[OH^-][Fe(CN)_6^{3-}]}{k_{-1} + k_1[OH^-] + k_2[Fe(CN)_6^{3-}]}$$

## INTRODUCTION

Equilibrium (1) between alcohol and alkoxide ion in alkaline medium[1] is usually attained immediately. A low [$OH^-$] was kept to ensure that the equilibrium is not completely shifted to the right as reported earlier also for the oxidation of these compounds in the presence of Os(VIII) catalyst.[2]

$$ROH + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RO^- \quad (1)$$

The kinetics of oxidation of cyclopentanol, cyclohexanol, cycloheptanol and cyclooctanol by alkaline hexacyanoferrate(III) has been attempted with the aim to compare the uncatalysed oxidation of these compounds with the Os(VIII) catalysed oxidation, using the same oxidant.

## EXPERIMENTAL

All the solutions were prepared as reported earlier[2]. Cycloheptanol (Aldrich) was also prepared by the same method.

The corresponding ketones were identified to be the first oxidation products

as reported for the Os(VIII) catalysed oxidation of these compounds. Glutaric acid (m.p. 100°C) and adipic acid (m.p. 151°C) were found to be the final oxidation products of cyclopentanol and cyclohexanol respectively.

*Rate Measurements:* The kinetic study was undertaken under the condition that [Cycloalkanol] $\gg$ [$Fe(CN)_6^{3-}$]. [$OH^-$] was varied in 0.003–0.015 mol $dm^{-3}$ range. Ionic strength ($\mu$) of the reaction mixtures was kept 1.00 mol $dm^{-3}$.

The reaction rate was monitored by measuring the absorbance of the underacted [$Fe(CN)_6^{3-}$] of 420 nm using a Spectrochem Digital Mk II Spectrophotometer. The log (absorbance) *vs.* time plots were linear and indicated a first order dependence on the oxidant. The pseudo first order rate constants ($k_{obs}$) were reproducible within a maximum error of ± 5%.

*Stoichiometry:* The stoichiometry of the reaction under the condition [Cycloalkanol] $\ll$ [$Fe(CN)_6^{3-}$] was determined. The stoichiometric equation based upon the products identified is given by equation (2).

$$\underset{\text{(Cycloalknol)}}{C_nH_{2n-1}OH} + 8\,Fe(CN)_6^{3-} + 8\,OH^- \rightarrow \underset{\text{(Dicarboxylic acid)}}{nH_{2n-2}O_4} + 8\,Fe(CN)_6^{4-} + 5\,H_2O \quad (2)$$

## RESULTS AND DISCUSSION

A low [$OH^-$] ensured that equilibrium (1) did not completely shift to the right. The $k_{obs}^{-1}$ *vs.* [cyclohexanol]$^{-1}$ plot (Fig. 1) ruled out the possibility of oxidant-substrate complex. The $k_{obs}$ *vs.* [$OH^-$] plots (Fig. 2) with a (+)ve intercept on the $k_{obs}$-axis indicated that (i) the reaction occurs even in the absence of $OH^-$ ions, (ii) the rate $\propto$ [$OH^-$]. These results of the uncatalysed reaction were at variance with the Os(VIII) catalysed oxidation of the cycloalkanols[2], where (i) no reaction was reported to be taking place in the absence of $OH^-$ ions, (ii) a complex formed between the substrate and Os(VIII), the effective oxidant.

A general mechanism as follows, where >CHOH represents the cycloalkanol, applies to all the cycloalkanols undertaken for the study.

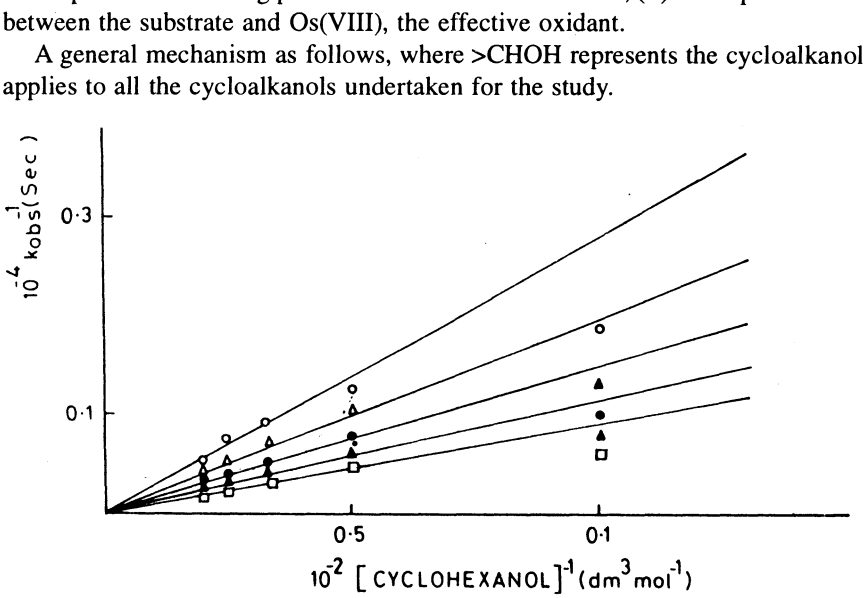


Fig. 1 $k_{obs}^{-1}$ *vs.* [cyclohexanol]$^{-1}$ plots at (○) 40°C, (△) 45°C, (●) 50°C, (▲) 55°C, (□) 60°C

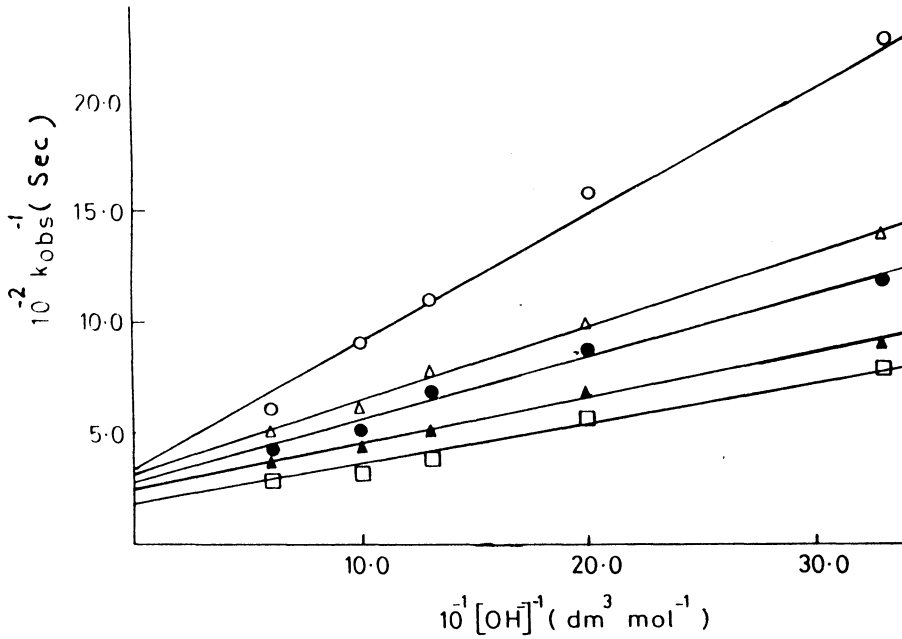


Fig. 2 $k_{obs}$ *vs.* $[OH^-]$ plots for cylohexanol at (○) 40°C, (Δ ) 45°C, (●) 50°C, (▲) 55°C, (□) 60°C

$$\underset{\text{(Cycloalkanol)}}{>CHOH} + OH^- \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} \underset{\text{(alkoxide ion)}}{>CHO^-} + H_2O \qquad (3)$$

$$>CHO^- + Fe(CN)_6^{3-} \xrightarrow[\text{Slow}]{k_2} >CHO^{\bullet} + Fe(CN)_6^{4-} \qquad (4)$$

$$>CHO^{\bullet} + Fe(CN)_6^{3-} \xrightarrow[\text{Fast}]{} \underset{\text{(Cycloalkanone)}}{>C{=}O} + Fe(CN)_6^{4-} + H^+ \qquad (5)$$

$$>C{=}O + 6\,Fe(CN)_6^{3-} + 6\,OH^- \xrightarrow[\text{Fast}]{} \text{Final product (a dicarboxylic acid)} + 6Fe(CN)_6^{4-} + 3H_2O$$

Hence

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = k_2[>CHO^-][Fe(CN)_6^{3-}] \qquad (7)$$

Assuming that the substrate (>CHOH) is either free or is present as the alkoxide ion,

$$[>CHOH]_{Total} = [>CHOH] + [>CHO^-] \qquad (8)$$

where

$[>CHOH]_{Total}$ = Total concentration of the cycloalkanol

[>CHOH ] = Concentration of the free cycloalkanol

[>CHO$^-$] = Concentration of the alkoxide ion

([>CHO$^-$] and [>C=O] have not been included while calculating $[>CHOH]_{Total}$, as both of these intermediate products are quickly converted into the final product in the fast steps).

TABLE-1
DEPENDENCE OF $k_{obs}$ ($s^{-1}$) ON THE INITIAL [$OH^-$] mol $dm^{-3}$
AT DIFFERENT TEMPERATURES

| Temperature (°C) | $10^3$ [$OH^-$] (mol $dm^{-3}$) | | | | |
|---|---|---|---|---|---|
| | 3.0 | 5.0 | 7.5 | 10.0 | 15.0 |
| | $10^2$ [Cyclohexanol] = 1.0 (mol $dm^{-3}$), $10^4$ $k_{obs}$ ($s^{-1}$) | | | | |
| 40 | 4.6 | 6.7 | 9.1 | 11.6 | 16.3 |
| 45 | 7.8 | 10.4 | 13.4 | 18.5 | 21.5 |
| 50 | 9.25 | 12.9 | 15.5 | 19.6 | 27.0 |
| 55 | 13.0 | 16.2 | 21.1 | 26.0 | 33.2 |
| 60 | 16.8 | 22.0 | 25.0 | 31.2 | 38.2 |
| | $10^2$ [Cyclopentanol] = 1.0 (mol $dm^{-3}$) | | | | |
| 40 | 4.2 | 6.1 | 8.5 | 10.7 | 14.6 |
| 45 | 7.0 | 9.1 | 12.2 | 17.1 | 20.5 |
| 50 | 8.4 | 10.6 | 14.3 | 18.6 | 24.7 |
| 55 | 11.2 | 14.1 | 18.7 | 24.0 | 28.6 |
| 60 | 12.2 | 15.3 | 22.1 | 27.0 | 30.2 |
| | $10^2$ [Cyclopentanol] = 1.0 (mol $dm^{-3}$) | | | | |
| 40 | 0.65 | 0.92 | 1.42 | 2.0 | 3.1 |
| 45 | 0.96 | 1.42 | 2.00 | 3.0 | 4.15 |
| 50 | 2.50 | 3.80 | 4.90 | 6.35 | 8.1 |
| 55 | 3.80 | 5.15 | 6.60 | 8.0 | 10.9 |
| 60 | 8.20 | 10.80 | 12.44 | 14.7 | 18.4 |
| | $10^2$ [Cyclooctanol] = 1.0 (mol $dm^{-3}$), $10^4$ $k_{obs}$ ($s^{-1}$) | | | | |
| 40 | 2.8 | 3.34 | 4.9 | 6.00 | 7.8 |
| 45 | 3.81 | 5,20 | 6.1 | 8.00 | 10.7 |
| 50 | 6.94 | 8.40 | 10.1 | 12.10 | 14.3 |
| 55 | 7.70 | 9.90 | 11.9 | 14.31 | 15.8 |
| 60 | 11.00 | 12.52 | 14.8 | 18.10 | 20.6 |

$10^4$ [$Fe(CN)_6^{3-}$] = 14.0 mol $dm^{-3}$ and $\mu$ = 1.0 mol $dm^{-3}$

TABLE-2
DEPENDENCE OF $k_{obs}$ ON THE INITIAL [CYCLOALKANOL] AT DIFFERENT TEMPERATURES.

| Temperature (°C) | $10^2$ [Cyclohexanol] (mol $dm^{-3}$) | | | | |
|---|---|---|---|---|---|
| | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
| | $10^2$ [Cyclohexanol], $10^4$ $k_{obs}$ ($s^1$) | | | | |
| 40 | 6.7 | 10.0 | 15.1 | 17.4 | 24.5 |
| 45 | 10.5 | 15.2 | 21.8 | 33.0 | 40.1 |
| 50 | 12.9 | 17.22 | 31.0 | 36.4 | 45.6 |
| 55 | 16.2 | 23.6 | 34.5 | 39.0 | 49.1 |
| 60 | 22.1 | 25.0 | 38.0 | 44.9 | 51.5 |
| | $10^2$ [Cyclopentanol] $10^4k_{obs}(s^{-1})$ | | | | |
| 40 | 6.2 | 9.1 | 14.6 | 16.8 | 22.5 |
| 45 | 9.0 | 14.5 | 20.6 | 30.1 | 38.6 |
| 50 | 10.6 | 16.2 | 25.2 | 33.0 | 40.1 |
| 55 | 14.0 | 22.5 | 32.1 | 37.3 | 43.6 |
| 60 | 15.25 | 24.1 | 36.2 | 42.1 | 47.6 |
| | $10^2$ [Cycloheptanol] | | | | |
| 40 | 0.91 | 1.71 | 2.45 | 3.39 | 4.4 |
| 45 | 1.4 | 1.95 | 2.65 | 4.72 | 5.42 |
| 50 | 3.8 | 5.98 | 7.9 | 9.9 | 11.63 |
| 55 | 5.1 | 6.51 | 9.0 | 11.1 | 12.9 |
| 60 | 10.8 | 13.2 | 15.8 | 20.1 | 24.2 |
| | $10^2$ [Cyclooctanol] | | | | |
| 40 | 3.35 | 6.9 | 10.0 | 12.9 | 16.25 |
| 45 | 5.09 | 9.6 | 12.6 | 16.5 | 20.6 |
| 50 | 8.44 | 12.61 | 17.28 | 20.6 | 25.6 |
| 55 | 9.9 | 15.0 | 20.3 | 24.23 | 27.8 |
| 60 | 12.5 | 17.9 | 22.0 | 29.5 | 33.0 |

$10^4$ $[Fe(CN)_6^{3-}]$ = 14.0 mol $dm^{-3}$, $10^3$ $[OH^-]$ = 5.0 mol $dm^{-3}$ and $\mu$ = 1.0 mol $dm^{-3}$.

Hence from Eq. (8),

$$[>CHOH] = [>CHOH]_{Total} - [>CHO^-]$$

Applying steady state treatment for $>CHO^-$,

$$[>CHO^-] = \frac{k_1[>CHOH]_{Total}[OH^-]}{k_{-1} + k_1[OH^-] + k_2[Fe(CN)_6^{3-}]} \quad (9)$$

Hence,

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = \frac{k_1k_2[>CHOH)_{Total}[OH^-][Fe(CN)_6^{3-}]}{k_{-1} + k_1[OH^-] + k_2[Fe(CN)_6^{3-}]} \quad (10)$$

Utilizing Eq. (2), Eq. (10) can be written as:

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = \frac{8k_1k_2[>CHOH)_{Total}[OH^-][Fe(CN)_6^{3-}]}{k_{-1} + k_1[OH^-] + k_2[Fe(CN)_6^{3-}]} \quad (11)$$

Eq (11) indicates that the reaction is first order with respect to hexacynoferrate (III) ion.

If $k_{obs}$ = pseudo first order rate constant with respect to hexacynoferrate (III) ion.

$$k_{obs} = \frac{8\ k_1k_2[>CHOH)_{Total}[OH^-]}{k_{-1} + k_1[OH^-] + k_2[Fe(CN)_6^{3-}]} \quad (12)$$

As per results obtained it is assumed that

$$k_{-1} + k_1[OH^-] \gg k_2[Fe(CN)_6^{3-}]$$

Hence,

$$k_{obs} = \frac{8\ k_1k_2[>CHOH]_{Total}[OH^-]}{k_{-1} + k_1[OH^-]} \quad (13)$$

or

$$\frac{1}{k_{obs}} = \frac{1}{8\ k_2[>CHOH]_{Total}} = \frac{k_{-1}}{8\ k_1k_2[>CHOH]_{Total}[OH^-]} \quad (14)$$

Eq. (14) is consistent with $k_{obs}^{-1}$ *vs.* $[OH^-]^{-1}$ linear plot (Fig. 2). The values of $K = \frac{k_1}{k_{-1}}$ and the values of $k_2$ were calculated using Eq. (14). These values and the related activation parameters have been given in Table-3 and Table-4.

TABLE-3
TEMPERATURE DEPENDENT K-VALUES

| Substrate | Temperature (°C) | | | | |
|---|---|---|---|---|---|
| | 40 | 45 | 50 | 55 | 60 |
| | K ($dm^3\ mol^{-1}$) | | | | |
| Cyclohexanol | 49.51 | 90.13 | 98.28 | 124.69 | 152.80 |
| Cyclopentanol | 48.60 | 79.43 | 91.01 | 114.19 | 106.43 |
| Cycloheptanol | 14.63 | 20.27 | 56.21 | 97.55 | 177.76 |
| Cyclooctanol | 96.39 | 108.83 | 208.96 | 188.22 | 266.31 |

TABLE-4
RATE CONSTANT $k_2$ AND RELATED ACTIVATION PARAMETERS

| Substrate | Temperature (°C) | | | | |
|---|---|---|---|---|---|
| | 40 | 45 | 50 | 55 | 60 |
| | $10^{-1}$ $k_2$ ($dm^3$ $mol^{-1}$ $s^{-1}$) | | | | |
| Cyclohexanol | 3.120 | 3.184 | 3.559 | 4.066 | 4.544 |
| Cyclopentanol | 2.901 | 3.129 | 3.348 | 3.782 | 4.360 |
| Cycloheptanol | 1.332 | 1.459 | 1.542 | 1.465 | 2.073 |
| Cyclooctanol | 1.057 | 1.349 | 1.559 | 1.879 | 2.121 |

| | Cyclohexanol | Cyclopentanol | Cyloheptanol | Cyclooctanol |
|---|---|---|---|---|
| $\Delta H$ (kJ $mol^{-1}$) | 17.326 | 17.469 | 19.179 | 30.120 |
| $\Delta S$ ($JK^{-1}$ $mol^{-1}$) | -218.840 | -218.840 | -219.300 | -202.430 |

A perusal of Table-3 and Table-4 indicates that the $k_2$ and $\Delta H$ values are almost same for the uncatalysed oxidations of cyclohexanol and cyclopentanol by alkaline hexacyanoferrate(III). These are in fair agreement with the reported[3] stability of the five and six membered ring based on the heat of combustion of $CH_2$ group. Similarly the $k_2$ and $\Delta H$ values are also in accord with the reported stability for the compounds containing carbon atoms in the ring[4].

On comparing the uncatalyzed oxidation of the cycloalkanols by alkaline hexacyanoferrate(III), with the Os(VIII) catalyzed oxidation of these compounds by alkaline hexacyanoferrate(III), the order of the reactivity is different based on $k_2$ values. The order of the reactivity observed in the present study was:

Cyclohexanol ≥ Cyclopentanol > Cycloheptanol ≥ Cyclooctanol.

Further studies are in progress.

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