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Kinetics of Oxidation of Hexahydroxycyclohexane by Os(VIII) Continuously Regenerated by Hexacyanoferrate(III) ions

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The kinetics of oxidation of hexahydroxycyclohexane (meso-form) by alkaline Os(VIII) which was continuously regenerated by $Fe(CN)_6^{3-}$ was studied in the 1.0 M–10.0 M [OH^-] and 293 K–313 K temperature range. The rate of the reaction was found to be one each with respect to Os(VIII) and $Fe(CN)_6^{3-}$. Suitable mechanism consistent with the observed kinetics has been proposed.

INTRODUCTION

$C_6H_6(OH)_6$ *i.e.* hexahydroxycyclohexane (*hhch*) can exist in eight geometrical isomeric forms[1] of which only one is optically active. The (+)- and (–)-forms of this isomer occur in plants as the hexahyroxyphosphoric ester, which is known as phytin. Some of the optically inactive forms also occur as their hexaphosphoric esters. One of the optically inactive forms is present in vitamin B complex; it appears to have growth-promoting properties in chicks and is an anti-alopecia factor (antibaldness) in mice. The oxidation of *meso*-form of *hhch* which occur naturally would therefore be interesting.

EXPERIMENTAL

Fresh standard solutions of *hhch* (*meso*-form) were prepared in double distilled conductivity H_2O by direct weighing. Other reagents were prepared as reported earlier[2].

Kinetic study: As the [Os(VIII)] was kept low, the kinetics of the oxidation of *hhch* by alkaline Os(VIII) was studied by measuring the absorbance of the unreacted [$Fe(CN)_6^{3-}$] at 420 nm on a speetrochem digital MK(II) spectrophotometer.

Product analysis: Inosose was identified as the final oxidation product by its IR spectral studies and its 2,4-dinitrophenylhydrazone, which is in accord with the oxidation product of *hhch* by V(V).[3]

Stoichiometry:

$$\underset{\text{(hhch)}}{C_6H_6(OH)_6} + Os(VIII) + 2Fe(CN)_6^{3-} + 2OH^- \longrightarrow \underset{\text{(Inosose)}}{C_5H_5(OH)_5C{=}O} + Os(VIII) + 2Fe(CN)_6^{4-} + 2H_2O \qquad (1)$$

RESULTS AND DISCUSSION

A low Os(VIII) ensured that it was regenerated during the reaction and therefore could be considered as a catalyst for the oxidation of *hhch* by alkaline $Fe(CN)_6^{3-}$. In the present study an almost different kinetics was observed in comparison to the kinetics reported earlier.[4] k_0 *versus* [Os(VIII)] plot (Fig. 1) was linear and passed through the origin, while k_0 versus [OH^-] plot (Fig. 2) though linear but did not pass through the origin.

Results have been given in Tables 1–3.

TABLE-1
DEPENDENCE OF k_0 ON [OH^-] FOR THE OXIDATION OF *hhch* BY Os(VIII) AT DIFFERENT TEMPERATURES

Temp. (K)	10 [OH^-] (mol dm^{-3})				
	1.0	2.5	5.0	7.5	10.0
			10^6 k_0 (mol dm^{-3} s^{-1})		
293	1.23	2.10	3.49	4.90	6.30
298	1.72	2.71	4.40	6.00	7.71
303	3.20	4.30	6.33	8.30	10.30
308	4.30	5.60	7.70	9.80	12.00
313	5.90	7.30	9.80	13.60	14.80

10^2 [*hhch*] = 5.0 mol dm^{-3}, 10^3 [$Fe(CN)_6^{3-}$] = 1.4 mol dm^{-3},
10^5 Os [VIII] = 1.0 mol dm^{-3} and μ = 1.5 mol dm^{-3}

TABLE-2
DEPENDENCE OF k_0 ON THE INITIAL [*hhch*] AT DIFFERENT TEMPERATURES

Temp. (K)	10^2 [*hhch*] (mol dm^{-3})				
	3.0	5.0	9.0	12.0	15.0
			10^6 k_0 (mol dm^{-3} s^{-1})		
293	2.20	3.49	4.92	6.05	8.32
298	3.00	4.40	7.05	9.51	10.56
303	4.33	6.33	9.85	12.40	13.80
308	4.80	7.70	10.00	13.10	16.80
313	6.50	9.80	14.00	16.50	20.22

10^3 [$Fe(CN)_6^{3-}$] = 1.4 mol dm^{-3}, 10^5 Os [VIII] = 1.0 mol dm^{-3}
10 [OH^-] = 5.0 mol dm^{-3} and μ = 1.5 mol dm^{-3}

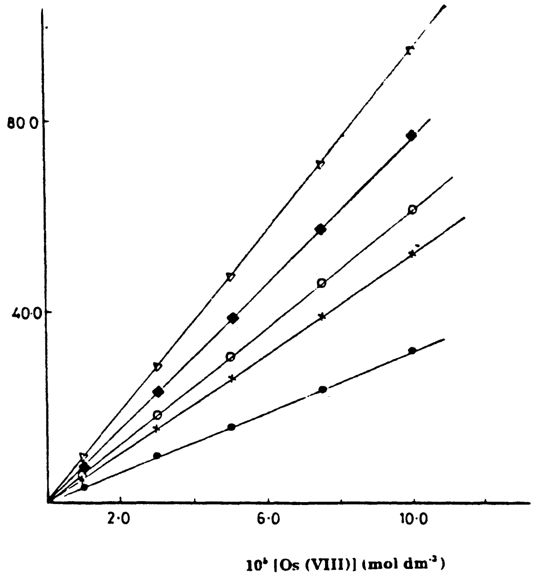

Fig. 1. k_0 *versus* [Os(VIII)] plots for the oxidation of hexahydroxycyclohexane at (•) 20°, (×) 25°, (O) 30°, (■) 35° and (Δ) 40°C

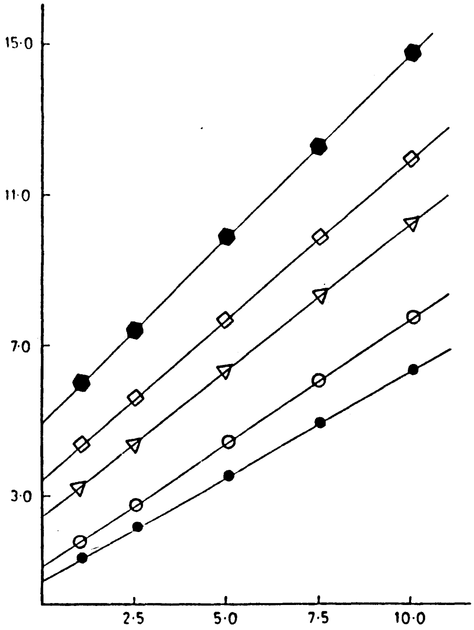

Fig. 2. k_0 *versus* [OH$^-$] plots for the oxidation of hexahydroxycyclohexane at (•) 20°, (O) 25°, (Δ) 30°, (□) 35° and (⬢) 40°C

TABLE-3
DEPENDENCE OF k_0 ON THE INITIAL [Os (VIII)] AT DIFFERENT TEMPERATURES

Temp. (K)	10^5 [Os(VIII)] (mol dm^{-3})				
	1.0	3.0	5.0	7.5	10.0
	$10^6\ k_0$ (mol dm^{-3} s^{-1})				
293	3.49	10.47	16.04	24.00	32.02
298	4.40	13.21	26.40	39.61	52.62
303	6.33	18.00	31.21	44.40	66.50
308	7.70	23.11	38.20	57.90	77.00
313	9.81	29.43	47.04	71.20	95.11

$10^3 [Fe(CN)_6^{3-}] = 1.4$ mol dm^{-3}, 10^2[*hhch*] = 5.0 mol dm^{-3},
10 [OH^-] = 5.0 mol dm^{-3} and $\mu = 1.5$ mol dm^{-3}

The equilbrium between an alcohol and alkoxide ion which involves a proton transfer can be represented by Eq. (2).

$$\text{Alcohol} + OH^- \rightleftharpoons \text{Alkoxide ion} + H_2O \qquad (2)$$

Species of Os(VIII) in alkaline medium are well known[5,6]. Assuming that equilibrium (2) is operative for *hhch*, the mechanism of the oxidation of *hhch* by Os(VIII) continuously regenerated by $Fe(CN)_6^{3-}$ in alkaline medium can be given as follows:

$$\underset{(hhch)}{C_6H_6(OH)_6} + OH^- \overset{K}{\rightleftharpoons} \underset{\text{(Alkoxide ion)}}{C_5H_5(OH)_5CHO^-} + H_2O \qquad (3)$$

$$[OsO_3(OH)_3]^- + OH^- \overset{K_1}{\rightleftharpoons} [OsO_4(OH)_2]^{2-} + H_2O \qquad (4)$$

$$[OsO_3(OH)_3]^- + C_5H_5(OH)_5\,CHO^- \overset{K_2}{\rightleftharpoons} [OsO_4(OH)C_5H_5(OH)_5CHO]^{2-} + H_2O \qquad (5)$$

$$[OsO_4(OH)_2]^{2-} + C_6H_6(OH)_6 \overset{K_3}{\rightleftharpoons} [OsO_4(OH)C_5H_5(OH)_5CHO]^{2-} + H_2O \qquad (6)$$

$$[OsO_4(OH)C_5H_5(OH)_5CHO]^{2-} + H_2O \xrightarrow[\text{slow}]{k} [OsO_2(OH)_4]^{2-} + C_5H_5(OH)_5C=O \qquad (7)$$

$$[OsO_2(OH)_4]^{2-} + 2Fe(CN)_6^{3-} \xrightarrow[\text{fast}]{} [OsO_4(H_2O)_2] + 2Fe\,(CN)_6^{4-} \qquad (8)$$

In view of reactions (2) to (8), the rate of the reaction can be given in terms of the disappearance of Os(VIII).

Hence,

$$-\frac{d[\mathrm{Os(VIII)}]}{dt} = k[\mathrm{OsO_4(OH)C_5H_5(OH)_5CHO}]^{2-} \tag{9}$$

Since,

$$[\mathrm{OsO_3(OH)_3}]^- = \frac{[\mathrm{Os(VIII)}]_{\mathrm{Total}}}{1 + K_1[\mathrm{OH^-}] + (K_1K_3 + KK_2)[\mathrm{C_6H_6(OH)_6}][\mathrm{OH^-}]} \tag{10}$$

Hence,

$$-\frac{d[\mathrm{Os(VIII)}]}{dt} = \frac{k(KK_2 + K_1K_3)[\mathrm{C_6H_6(OH)_6}][\mathrm{OH^-}][\mathrm{Os(VIII)}]_{\mathrm{Total}}}{1 + K_1[\mathrm{OH^-}] + (K_1K_3 + KK_2)[\mathrm{C_6H_6(OH)_6}][\mathrm{OH^-}]} \tag{11}$$

In view of the results obtained, it can be presumed that,

$$\{1 + K_1K_3[\mathrm{C_3H_6(OH)_6}][\mathrm{OH^-}]\} \gg K_1[\mathrm{OH^-}] \text{ and } K_1K_3 \gg KK_2$$

Hence, Eq. (11) can be written as

$$-\frac{d[\mathrm{Os(VIII)}]}{dt} = \frac{kK_1K_3[\mathrm{C_6H_6(OH)_6}][\mathrm{OH^-}][\mathrm{Os\ (VIII)}]_{\mathrm{Total}}}{1 + K_1K_3[\mathrm{C_6H_6(OH)_6}][\mathrm{OH^-}]} \tag{12}$$

Utilizing Eq. (8), Eq. (12) can be written as,

$$k_0 = -\frac{d[\mathrm{Fe\ (CN)_6^{3-}}]}{dt} = \frac{2kK_1K_3[\mathrm{C_6H_6(OH)_6}][\mathrm{OH^-}][\mathrm{Os(VIII)}]_{\mathrm{Total}}}{1 + K_1K_3[\mathrm{C_6H_6(OH)_6}][\mathrm{OH^-}]} \tag{13}$$

where k_0 is the pseudo zero order rate constant with respect to $\mathrm{Fe(CN)_6^{3-}}$.

K_3 and k values could be calculated by plotting k_0^{-1} *versus* $[hhch]^{-1}$. The K_3, k values and the respective thermodynamic parameters have been given in Tables 4 and 5.

TABLE-4
TEMPERATURE DEPENDENT K_3 VALUES

Temp. (K)	293	298	303	308	313
$10^2\ K_3\ (\mathrm{dm^3\ mol^{-1}})$	49.265	34.36	40.09	38.80	39.65

TABLE-5
RATE CONSTANT k AND RELATED ACTIVATION PARAMETERS

Temp. (K)	293	298	303	308	313
$k\ (\mathrm{s^{-1}})$	0–85	1.342	1.523	1.626	1.844

$\Delta H\ (\mathrm{kJ\ mol^{-1}}) = 26.896$, $\Delta S\ (\mathrm{J\ K^{-1}\ mol^{-1}}) = -215.461$

The results obtained are in fair agreement with the view that osmium(VIII) is continuously regenerated during the oxidation reaction. The study may be useful for the oxidation of the compounds of biological importance.

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