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Kinetics of Oxidation of Cycloheptanol by Os(VIII) Continuously regenerated by Hexacyanoferrate(III) Ions

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The kinetics of oxidation of cycloheptanol by Os(VIII) continuously regenerated by hexaecyanofarrate (III) ions was studied in the 0.01 M–0.1 M [OH^-] range. The rate law derived on the basis of the mechanism suggested was:

$$-\frac{d[Os(VIII)]}{dt}=\frac{2kK_2K_4[\text{cycloheptanol}][OH^-][Os(VIII)]_{Total}}{1+K_2K_4[\text{cycloheptanol}][OH^-]}$$

INTRODUCTION

The equilibrium between an alcohol and alkoxide ion in alkaline medium[1] which is usually attained immediately is represented as:

$$\text{Alcohol} + OH^- \rightleftharpoons \text{Alkoxide ion}$$

Os(VIII) was continuously regenerated during the oxidation reaction by alkaline hexacyanoferrate(III).

EXPERIMENTAL

Reagents: All the solutions were prepared as reported earlier.[2, 3]

Product Analysis: Cycloheptanone as the final oxidation product was identified by the IR spectral studies and its 2,4-dinitrophenyl hydrazone.

Rate Measurements: As the [Os(VIII)] was kept low the kinetic study was done by measuring the absorbance of the unreacted [hexacyanoferrate(III)] at 420 nm using a spectochem digital MK(II) spectrophotometer.

Stoichiometry

$$(CH_2)_6CHOH + 2\,Fe(CN)_6^{3-} + Os(VIII) + 2OH^- \rightarrow (CH_2)_6C{=}O + 2\,Fe(CN)_6^{4-} + Os(VIII) + 2\,H_2O \quad (1)$$

RESULTS AND DISCUSSION

A low [Os(VIII)] ensured that it was continuously regnerated during the reaction and therefore could be considered as a catalyst for the oxidation of cycloheptanol by alkaline hexacyanoferrate(III). This presumption (Tables 1–3) was is in agreement with the results reported earlier.[3]

TABLE-1

DEPENDENCE OF k_0 (mol dm^{-3} s^{-1}) ON THE OXIDATION OF CYCLOHEPTANOL BY Os(VIII) AT DIFFERENT TEMPERATURES

Temperature (K)	10^2 [OH^-] (mol dm^{-3})				
	1.0	3.0	5.0	8.0	10.0
	$10^5 k_0$ (mol dm^{-3} s^{-1})				
298	0.50	0.90	1.50	1.90	2.20
303	0.70	1.20	1.80	2.70	3.20
308	0.80	1.70	2.50	3.65	4.50
313	1.30	2.20	3.40	5.10	6.30
318	1.60	2.50	3.60	5.80	7.81

10^2 [cycloheptanol] = 3.0 mol dm^{-3}, 10^3 [$Fe(CN)_6^{3-}$] = 1.4 mol dm^{-3}, 10^5 [Os(VIII) = 1.179 mol dm^{-3} and μ = 1.0 mol dm^{-3}].

TABLE-2

DEPENDENCE OF k_0 ON THE INITIAL [CYCLOHEPTANOL] AT DIFFERENT TEMPERATURES

Temperature (K)	10^2 [Cycloheptanol] (mol dm^{-3})				
	1.5	3.0	6.0	7.5	15.0
	$10^5 k_0$ (mol dm^{-3} s^{-1})				
298	0.39	0.51	0.80	1.10	1.75
303	0.48	0.78	1.00	1.38	1.81
308	0.56	0.98	1.21	1.71	2.29
313	1.10	1.61	2.00	2.78	3.56
318	1.51	2.01	2.54	3.02	3.88

10^3 [$Fe(CN)_6^{3-}$] = 1.4 mol dm^{-3}, 10^5 [Os(VIII)] = 1.179 mol dm^{-3}, 10^2 [OH^-] = 1.0 mol dm^{-3} and μ = 1.0 mol dm^{-3}.

TABLE-3

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

Temperature (K)	10^5 [Os (VIII)] (mol dm^{-3})				
	0.393	1.179	1.965	3.144	3.930
	$10^5 k_0$ (mol dm^{-3} s^{-1})				
298	0.20	0.51	0.90	1.42	1.60
303	0.31	0.80	1.31	2.00	2.41
308	0.41	1.00	1.90	3.01	3.71
313	0.60	1.61	2.60	4.01	5.11
318	0.70	2.01	3.81	5.70	7.31

10^3 [Fe $(CN)_6^{-3}$] = 1.4 mol dm^{-3}, 10^2 [cycloheptanol] = 3.0 mol dm^{-3}, 10^2 [OH^-] = 1.0 mol dm^{-3} and μ = 1.0 mol dm^{-3}.

The species of Os(VIII) are well known[4–6] in the alkaline medium. Hence the mechanism of the oxidation by Os(VIII) continuously regenerated by hexacyanoferrate(III) in alkaline medium can be given as follows:

$$\underset{\text{(Cycloheptanol)}}{(CH_2)_6CHOH} + OH^- \underset{}{\overset{K_1}{\rightleftharpoons}} \underset{\text{(Alkoxide ion)}}{(CH_2)_6CHO^-} + H_2O \qquad (2)$$

$$[OsO_4(OH)(H_2O)]^- + OH^- \overset{K_2}{\rightleftharpoons} [OsO_4(OH)_2]^{2-} + H_2O \qquad (3)$$

$$[OsO_4(OH)(H_2O)]^- + (CH_2)_6CHO^- \overset{K_3}{\rightleftharpoons} \underset{\text{(complex)}}{[OsO_4(OH)(CH_2)_6CHO]^{2-}} + H_2O \qquad (4)$$

$$[OsO_4(OH)_2]^{2-} + (CH_2)_6CHOH \overset{K_4}{\rightleftharpoons} [OsO_4(OH)(CH_2)_6CHO]^{2-} + H_2O \qquad (5)$$

$$[OsO_4(OH)(CH_2)_6CHO]^{2-} + H_2O \underset{\text{slow}}{\overset{k}{\rightleftharpoons}} [OsO_2(OH)_4]^{2-} + (CH_2)_6C{=}O \qquad (6)$$

$$[OsO_2(OH)_4]^{2-} + 2Fe(CN)_6^{3-} \underset{\text{Fast}}{\longrightarrow} [OsO_4(H_2O)_2] + 2Fe(CN)_6^{4-} \qquad (7)$$

In view of reactions (2) to (7), the rate of the reaction can be given in terms of the disappearance of Os(VIII).

Hence,

$$-\frac{d[Os(VIII)]}{dt} = k[OsO_4(OH)(CH_2)_6CHO]^{2-} \qquad (8)$$

Since,

$$[OsO_4(OH)(H_2O)]^- = \frac{[Os(VIII)]_{Total}}{1 + K_2[OH^-] + K_2K_4[(CH_2)_6CHOH][OH^-]} \qquad (9)$$

In view of the results obtained it is obvious that,

$$(1 + K_2K_4[(CH_2)_6CHOH][OH^-]) \gg K_2[OH^-] \quad \text{and} \quad K_2K_4 \gg K_1K_3.$$

Hence, utilizing Eq. (9) and the inequalities presumed Eq. (8) can be rearranged, to derive the rate law

$$-\frac{d[Os(VIII)]}{dt} = \frac{kK_2K_4[(CH_2)_6CHOH][OH^-][Os(VIII)]_{Total}}{1 + K_2K_4[(CH_2)_6CHOH][OH^-]} \qquad (10)$$

Utilizing Eq. (7), Eq. (10) can be written as

$$k_0 = -\frac{d[Fe(CN)_6^{3-}]}{dt} = \frac{2kK_2K_4[(CH_2)_6CHOH][OH^-][Os(VIII)]_{Total}}{1 + K_2K_4[(CH_2)_6CHOH][OH^-]} \qquad (11)$$

where k_0 is the pseudo zero order rate constant with respect to hexacyanoferrate(III). K_4 and k values could be calculated by plotting k_0^{-1} versus [cycloheptanol]$^{-1}$ [Fig. 1]. The K_4, k values and the respective thermodynamic parameters have been reported in Tables 4 and 5.

TABLE-4
TEMPERATURE DEPENDENT K_4 VALUES

Temp (K)	298	303	308	313	318
K_4 (dm^3 mol^{-1})	73.77	67.68	53.51	71.76	92.96

TABLE-5
RATE CONSTANT k AND RELATED ACTIVATION PARAMETERS

Temp. (K)	298	303	308	313	318
k (s^{-1})	0.743	0.938	1.227	1.634	1.675

ΔH (kJ mol^{-1}) = 34.685, ΔS (J K^{-1} mol^{-1}) = – 205.68

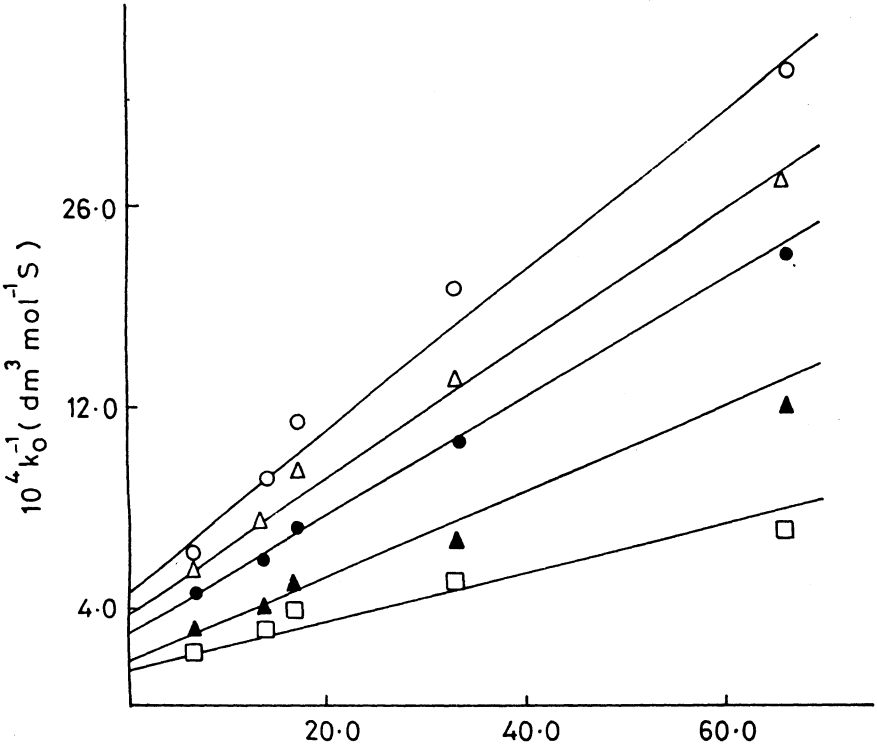

Fig. 1. k_0^{-1} Versus [Cycloheptanol]$^{-1}$ plots for O_s(VIII) Catalyzed Hexacyanoferrate(III) oxidation of cycloheptanol at (O) 25°C, (Δ) 30°C, (●) 35°C, (▲) 40°C and (□) 45°C.

A perusal of the results indicates that Os(VIII), the effective oxidant, is cntinuously regenerated during the oxidation reaction. Therefore it can also be concluded that Os(VIII) acts as a catalyst for the oxidation of cycloheptanol by hexacyanoferrate(III) in alkaline medium (Figs. 1 and 2).

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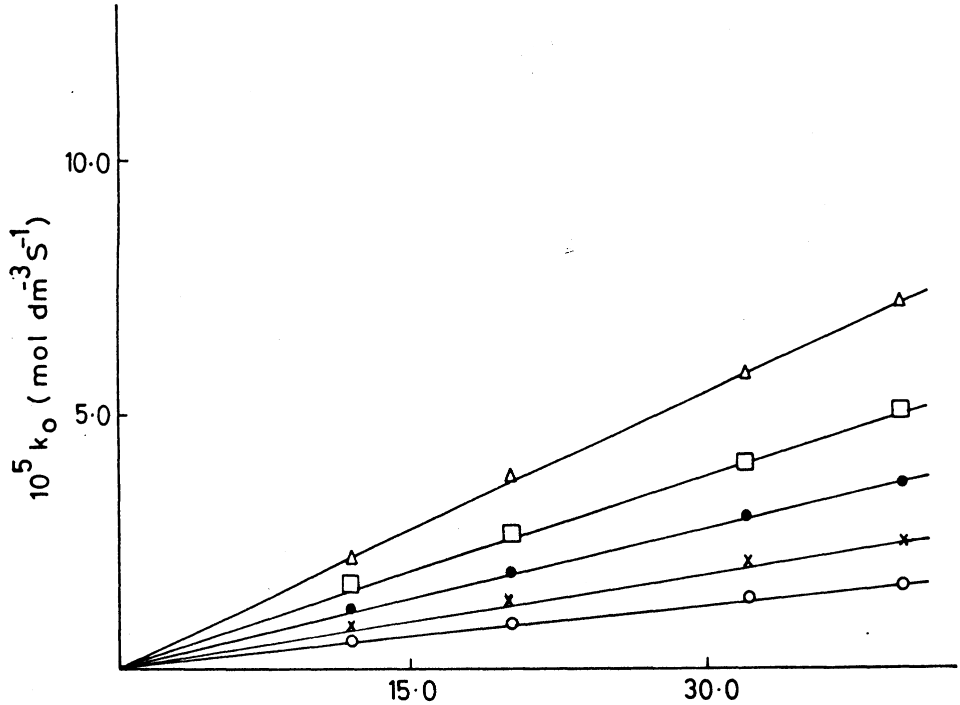

Fig. 2. k_0 Versus $[O_s(VIII)]$ plots for the $O_s(VIII)$ catalyzed hexacyanoferrate(III) oxidation of cycloheptanol at (O) 25°, (×) 30°C, (●) 35°C, (□) 40°C and (Δ) 45°C.

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