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Kinetics of Oxidation of Some Cycloalkanones by Alkaline Hexacyanoferrate(III)

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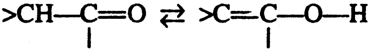
The oxidation of cyclopentanone, cyclohexanone, cycloheptanone and cyclooctanone, by alkaline hexacyanoferrate(III) follows the same kinetics in the absence of any catalyst. The study indicated that: (i) even the uncatalysed oxidations of cycloalkanones by aqueous alkaline hexacyanoferrate(III) are fast reactions, (ii) the order of the reactivity is cyclohexanone ≥ cyclopentanone ≥ cyclooctanone ≥ cycloheptanone.

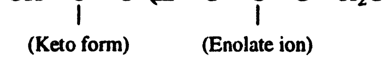
INTRODUCTION

The well known keto-enol tautomerism[1] is represented by equilibrium (1). But it is more probable especially in base catalysis[2(a)] that an enol anion (enolate ion) intermediate forms which rapidly reacts with the halogen[2(b)]. Therefore, in the present study it was postulated that the enolate ion forms directly from the keto form in the alkaline medium (Equilibrium (2)). However, this enolate ion does not react rapidly with the hexacyanoferrate(III) ion but forms another intermediate >C═C—O• in the slow step (eqn. 3). This new intermediate has been postulated to be very reactive.



$$>\underset{}{CH}—\underset{|}{C}=O \rightleftarrows >C=\underset{|}{C}—O—H \qquad (1)$$

(Keto form) (Enol form)



$$>CH—\underset{|}{C}=O \rightleftarrows >C=\underset{|}{C}—O—H_2O \qquad (2)$$

(Keto form) (Enolate ion)

$$>C=\underset{|}{C}—O^- + Fe(CN)_6^{3-} \xrightarrow[\text{Slow}]{} >C=\underset{|}{C}—O^\bullet + Fe(CN)_6^{4-} \qquad (3)$$

Equilibrium (2) seems to be valid as a higher [OH—] has been kept in the present study in comparison to the Os(VIII) catalysed oxidation of some of these compounds[3(a)].

EXPERIMENTAL

Reagents: All the reagents were prepared as reported earlier[3(b)].

Cycloalkanones used were of Aldrich Chemical company, while all the other chemicals used were of the same make as reported earlier by this laboratory[3(b)].

Product Analysis: α-Hydroxy cyclohexanone is the first oxidation product by using Littler's method[4] while adipic acid (identified by I.R. and m.p. of the product) was found to be the final oxidation product of cyclohexanone. This could be generalised for all the cyclic-ketones undertaken for the study.

Rate Measurements: The kinetics of the uncatalysed oxidation of the cycloalkanones by alkaline hexacyanoferrate(III) was studied at constant ionic strength (sodium chloride was used for this purpose). The reaction rate was monitored by measuring the absorbance of the unreacted [Fe(CN)$_6^{3-}$] at 420 nm

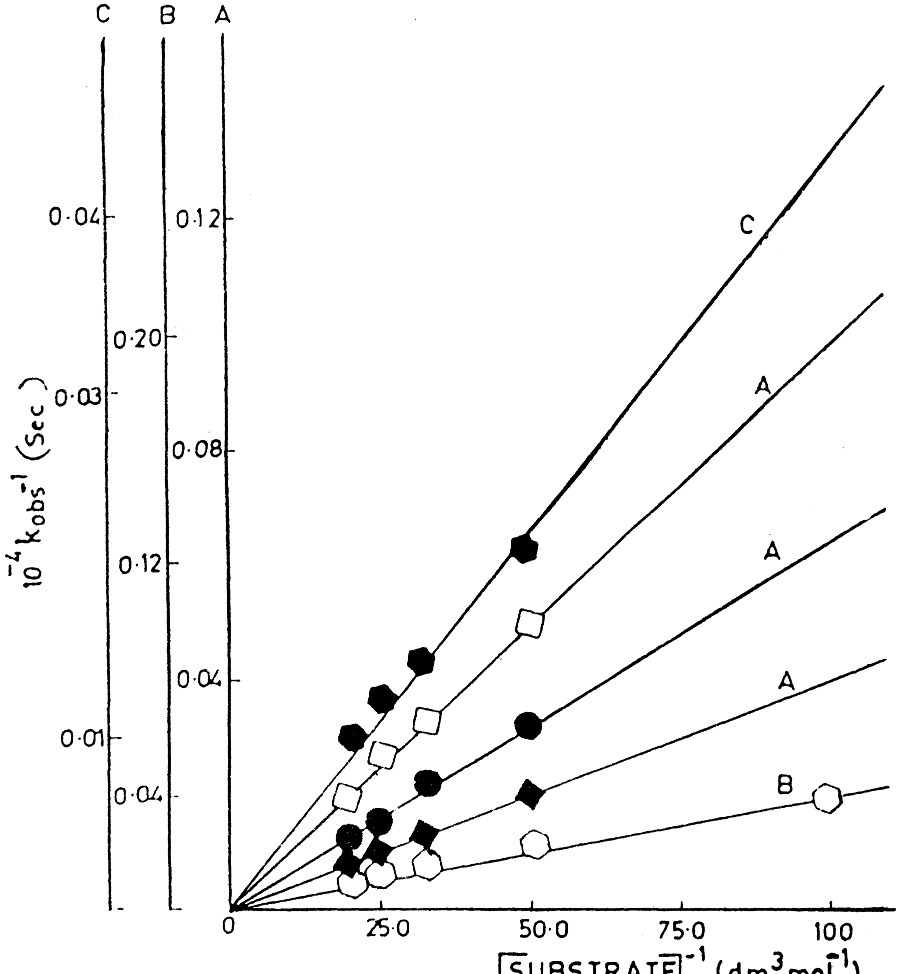


FIG. 1 PLOTS OF k_{obs}^{-1} AGAINST [SUBSTRATE]$^{-1}$ FOR THE OXIDATION OF CYCLOHEXANONE AT (◇)20°, (●) 25°, (○)30°, (⬢)35° AND (◆) 40°C.

using a Spectrochem Digital Mk II Spectrophotometer. The first order dependence on the oxidant was indicated by the linear log (absorbance) versus time plots. The reproducibility of the k_{obs} values was within a maximum error of ± 5.0%.

Stoichiometry: The stoichiometry of the oxidation reaction was determined under the condition [substrate] << [hexacyanoferrate(III)] and can be given with the help of Eq. (4) based on the products identified.

$$\underset{\text{(Cycloalkanone)}}{C_nH_{2n-2}O} + 6Fe(CN)_6^{3-} + 6OH^- \longrightarrow \underset{\text{(Dicarboxylic acid)}}{C_nH_{2n-2}O_4} + 6Fe(CN)_6^{4-} + 3H_2O \quad (4)$$

RESULTS AND DISCUSSION

The observed kinetics of the uncatalysed oxidation of the cycloalkanones by alkaline hexacyanoferrate(III) were almost similar to that observed in the uncatalysed oxidation of cycloalkanols by the same oxidant[5]. The k_{obs}^{-1} versus $[\text{cycloalkanone}]^{-1}$ linear plot (Fig. 1) passes through the origin indicating that the complex formation between the substrate and the oxidant is unlikely. The k_{obs} versus $[OH^-]$ plots (Fig. 2) are linear indicating that $k_{obs} \propto [OH^-]$. However,

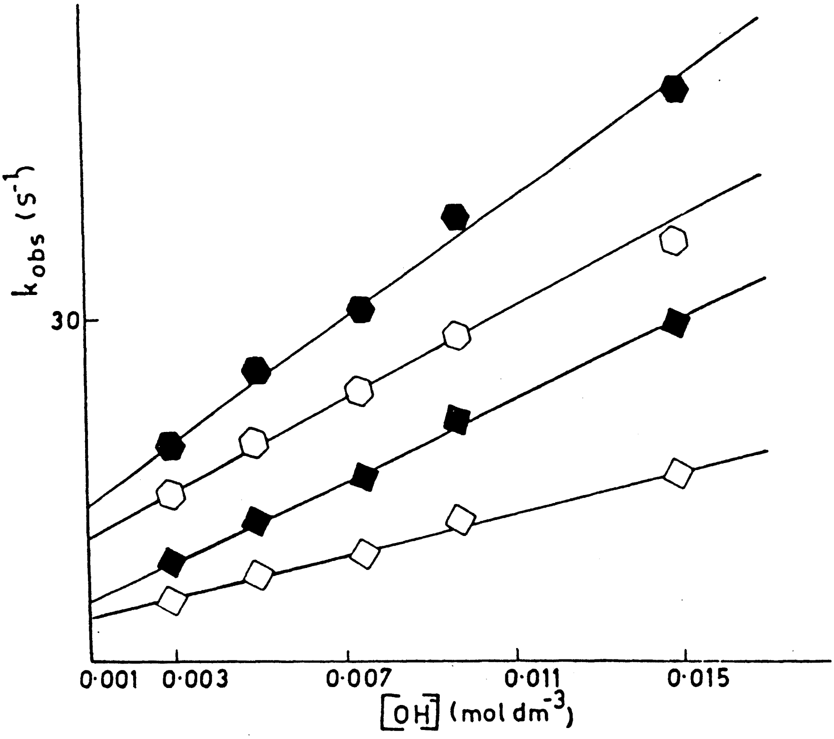


FIG. 2 PLOTS OF k_{obs} AGAINST $[OH^-]$ FOR THE OXIDATION OF (⬢) CYCLOHEXANONE, (⬡) CYCLOOCTANONE, (◆) CYCLOPENTANONE, (◇) CYCLOHEPTANONE.

k_{obs}^{-1} versus $[OH^-]^{-1}$ plots were found to be linear with (+)ve intercepts on the k_{obs}^{-1} axis.

TABLE-1
DEPENDENCE OF k_{obs} ON THE INITIAL $[OH^-]$ AT DIFFERENT TEMPERATURES

Temp. (°C)	$10^3 [OH^-]$ (mol dm^{-3})				
	3.0	5.0	7.5	10.0	15.0
10^2 [Cyclohexanone] = 1.0 mol dm^{-3}				10^4 k_{obs} (s^{-1})	
20	9.2	13.5	18.3	23.2	30.5
25	15.6	20.9	27.0	36.9	42.6
30	18.45	25.8	30.9	39.0	52.8
35	26.1	32.5	42.0	51.8	66.0
40	33.3	44.1	49.9	62.3	77.3
10^2 [Cyclopentanone] = 1.0 mol dm^{-3}					
20	8.5	12.4	16.8	21.6	29.0
25	14.2	18.0	24.5	34.0	40.8
30	16.9	21.3	28.3	37.5	48.5
35	22.0	28.3	37.5	48.0	59.1
40	24.5	30.5	44.0	54.1	60.0
10^2 [Cycloheptanone] = 1.0 mol dm^{-3}					
20	1.35	1.80	2.85	4.05	6.00
25	1.95	2.85	4.10	5.90	8.30
30	5.10	7.60	9.80	12.80	16.00
35	7.50	10.29	13.10	16.20	21.90
40	16.40	21.50	24.90	29.80	36.80
10^2 [Cyclooctanone] = 1.0 mol dm^{-3}					
20	5.60	7.70	9.20	12.00	15.90
25	7.60	10.18	13.10	16.20	21.50
30	13.88	16.90	20.00	24.20	28.90
35	15.40	19.80	23.80	28.70	31.90
40	22.10	25.00	29.50	36.00	41.10

$10^4 [Fe(CN)_6^{3-}] = 16.0$ mol dm^{-3} and $\mu = 1.0$ mol dm^{-3}

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

Temp. (°C)	10^2 [Cycloalkanone] (mol dm^{-3})				
	1.0	2.0	3.0	4.0	5.0
[Cyclohexanone]				10^4 k_{obs} (s^{-1})	
20	13.5	20.1	30.3	34.9	49.0
25	20.9	30.5	43.5	65.0	80.1
30	25.8	34.5	61.1	72.8	91.2
35	32.5	47.2	69.1	79.9	98.0
40	44.1	50.1	75.4	89.8	102.1
[Cyclopentanone]					
20	12.4	18.3	29.0	33.5	45.1
25	18.0	29.1	41.1	60.3	77.1
30	21.3	32.5	50.25	65.6	80.0
35	28.3	45.0	64.0	74.6	87.1
40	30.5	48.0	72.3	84.2	95.2
[Cycloheptanone]					
20	1.8	3.52	4.9	6.9	8.8
25	2.8	3.90	5.25	8.74	10.95
30	7.6	11.96	15.8	19.81	23.3
35	10.3	13.10	18.0	22.1	25.9
40	21.5	26.3	31.5	40.2	48.4
[Cyclooctanone]					
20	7.7	13.9	20.1	25.8	32.5
25	10.2	19.2	25.6	33.2	41.1
30	16.9	25.3	34.6	41.2	51.2
35	19.8	30.2	41.6	48.6	55.5
40	25.0	35.8	44.1	59.2	65.9

$10^4[Fe(CN)_6^{3-}] = 16.0$ mol dm^{-3}, $10^3[OH^-] = 5.0$ mol dm^{-3} and $\mu = 1.0$ mol dm^{-3}

Utilising equilibrium (2) and eqn. (3), a general mechanism as represented below seems to be appropriate. (>C═O represents the cycloalkanone where the actual ring on the left side of >C═O has been omitted for simplicity)

$$\underset{\substack{\text{(Cycloalkanone)}\\ \text{Keto form}}}{>C{=}O} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{(Enolate ion)}}{>C{=}O^-} + H_2O \tag{5}$$

$$>C{=}O^- + Fe(CN)_6^{3-} \xrightarrow[\text{Slow}]{k_2} >C{=}O^{\bullet} + Fe(CN)_6^{4-} \tag{6}$$

$$>C{=}O^{\bullet} + Fe(CN)_6^{3-} \xrightarrow[\text{Fast}]{} \text{Product (I)} + Fe(CN)_6^{4-} \tag{7}$$

$$\text{Product (I)} + 4\,Fe(CN)_6^{3-} + 8\,OH^- \xrightarrow[\text{Fast}]{} \text{Final product} + 4\,Fe(CN)_6^{4-} + 4\,H_2O \tag{8}$$

The rate of the reaction is determined by the rate of disappearance of hexacyanoferrate(III).

Hence,

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = k_2[>C{=}O^-][Fe(CN)_6^{3-}] \tag{9}$$

Since lower concentrations of the substrates have been used, assuming that the substrate is either free or is present as enolate ion as shown in the above mechanism,

$$[>C{=}O]_{\text{Total}} = [>C{=}O] + [>C{=}O^-] \tag{10}$$

where $[>C{=}O]_{\text{Total}}$ = Total concentration of the substrate,

$[>C{=}O]$ = Concentration of the free substrate,

$[>C{=}O^-]$ = Concentration of the enolate ion.

Hence, from eqn. (10),

$$[>C{=}O] = [>C{=}O]_{\text{Total}} - [>C{=}O^-] \tag{11}$$

Applying steady state treatment for $[>C{=}O^-]$

$$[>C{=}O^-] = \frac{k_1[>C{=}O]_{\text{Total}}[OH^-]}{k_1[OH^-] + k_{-1} + k_2[Fe(CN)_6^{3-}]} \tag{12}$$

Utilising stoichiometric ratio and eqn. (9) and (12).

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = \frac{6k_1k_2[OH^-][>C{=}O]_{\text{Total}}[Fe(CN)_6^{3-}]}{k_{-1} + k_1[OH^-] + k_2Fe(CN)_6^{3-}} \tag{13}$$

eqn. (13) represents that the reaction is first order with respect to hexacyanoferrate(III) ion.

If k_{obs} = pseudo first order rate constant with respect to hexacyanoferrate(III) ion,

$$k_{obs} = \frac{6k_1k_2[OH^-][>C{=}O]_{\text{Total}}}{k_{-1} + k_1[OH^-] + k_2Fe(CN)_6^{3-}} \tag{14}$$

As per results obtained, the assumption $k_1 + k_1[OH^-] \gg k_2[Fe(CN)_6^{3-}]$ should be valid. Hence

$$k_{obs} = \frac{6k_1k_2[OH^-][>C{=}O]_{\text{Total}}}{k_{-1} + k_1[OH^-]} \tag{15}$$

or,

$$\frac{1}{k_{obs}} = \frac{1}{6k_2[>C{=}O]_{\text{Total}}} + \frac{1}{8K[>C{=}O]_{\text{Total}}[OH^-]} \tag{16}$$

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

eqn. (16) is consistent with the observed results. The calculated values of K and k_2 and the related activation parameters have been reported in Tables 3 and 4.

TABLE-3
TEMPERATURE DEPENDENT K-VALUES

Temp. (°C)	20	25	30	35	40
Substrate			K ($dm^3 mol^{-1}$)		
Cyclohexanone	54.16	90.78	100.95	128.63	164.68
Cyclopentanone	51.79	84.31	95.09	103.15	107.98
Cycloheptanone	21.878	22.448	61.602	91.985	175.08
Cyclooctanone	102.33	98.45	208.14	185.32	273.1

TABLE-4
RATE CONSTANT k_2 AND RELATED ACTIVATION PARAMETERS

Temp. (°C)	20	25	30	35	40
Substrate			k_2 ($dm^3 mol^{-1} s^{-1}$)		
Cyclohexanone	67.79	74.01	81.27	93.99	103.01
Cyclopentanone	64.94	70.42	75.99	93.81	100.17
Cycloheptanone	21.78	31.39	33.84	35.36	48.80
Cyclooctanone	24.31	33.89	36.49	44.25	49.02

	Cyclohexanone	Cyclopentanone	Cycloheptanone	Cyclooctanone
ΔH ($kJ mol^{-1}$)	16.480	17.678	26.561	25.684
ΔS ($JK^{-1} mol^{-1}$)	-215.299	-213.732	-204.15	-205.136

Based on the k_2 values the order of the reactivity is:

cyclohexanone ≥ cyclopentanone > cyclooctanone ≥ cycloheptanone

The higher reactivity of cyclohexanone observed is consistent with the results reported by Radhakrishnamurti *et. al.*[6] for the oxidation of the cycloalkanones by hexacyanoferrate(III) in ethanol-water and pyridine-water mixtures. No significant change in the oxidation kinetics of these compounds in aqueous alkaline medium was observed in comparison to the oxidation kinetics reported earlier by Radhakrishnamurti *et. al.*[6]. It is therefore concluded that:

(i) even the uncatalysed oxidations of cycloalkanones by aqueous alkaline hexacyanoferrate(III) are fast reactions.

(ii) The order of the reactivity based on the k_2 values is
cyclopentanone ≥ cyclooctanone ≥ cyclohexanone ≥ cycloheptanone

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