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Kinetic Study of Rh(III) Catalyzed Oxidation of Sucrose by Sodium Periodate in Acidic Medium

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The kinetics of rhodium(III) catalyzed oxidation of sucrose by sodium periodate in acidic medium has been studied in the temperature range 30-50 ºC. The reaction is carried out in the presence of mercuric acetate as a scavenger for bromide ion. The rate shows first order kinetics with respect to the oxidant *i.e.*, sodium periodate and Rh(III) for sucrose. Negligible effect of mercuric acetate and ionic strength of the medium was observed and the reaction showed no effect of [Cl^-] and [H^+] on the reaction rate for sucrose. A suitable mechanism in conformity with the kinetic observations has been proposed and the thermodynamic parameters computed.

Key Words: Rh(III) Catalysis, Sucrose, Sodium periodate, Kinetic study.

INTRODUCTION

N-Bromoacetamide[1-3], N-bromosuccinamide[4-7] and potassium bromate[8-16], *etc.* have been earlier used in oxidation of various compounds. A scant attention has been paid to sodium periodate[17-20] as an oxidant in various catalyzed reactions. The use of rhodium(III) chloride as a catalyst has been reported by several workers[21,22], but no work has been reported on Rh(III) catalyzed oxidation of sodium periodate in acidic medium. This prompted us to undertake the present investigation which consists of Rh(III) catalyzed oxidation of sucrose by periodate in acidic medium.

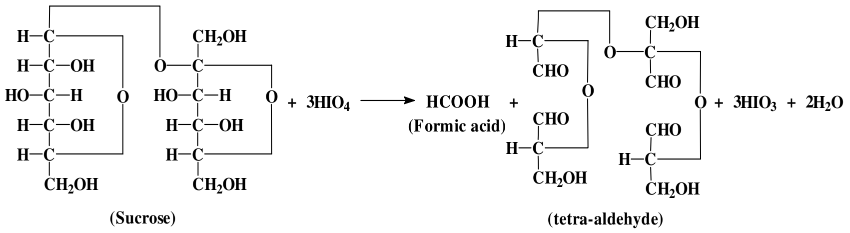
EXPERIMENTAL

An Aqueous solutions of sucrose (S.D. Fine), sodium periodate (S.D. Fine, A.R.), mercuric acetate and sodium perchlorate (all E. Merck) were prepared by dissolving the weighed amount of sample in triple distilled water. Perchloric acid (E. Merck, 60 %) was used as a source of hydrogen ions. Rhodium(III) chloride (Johnson Matthey) was prepared by dissolving the sample in hydrochloric acid of known strength. All other reagents of analytical grade were available. Sodium perchlorate (E. Merck) was used to maintain the ionic strength of the medium. The reaction stills were blackened from outside to prevent photochemical effects.

All the reagents except the oxidant ($NaIO_4$) were allowed to mix in a reaction vessel and thermostated at 35 ºC for thermal equilibrium. A measured volume of sodium periodate solution equilibrated separately at the same temperature was rapidly poured into the reaction vessel. The progress of the reaction was monitored by determining unconsumed $NaIO_4$ iodometrically at regular time intervals using starch as an indicator.

RESULTS AND DISCUSSION

The stoichiometry of the reaction was determined by equilibrating varying ratios of sodium periodate to sucrose at 35 ºC for 48 h under kinetic conditions. Estimation of unconsumed $NaIO_4$ revealed that, 1 mole of sucrose consumed three moles of periodate. This result showed 1:3 stoichiometry, according to the following equation:



The oxidation products were detected by conventional method[23].

The kinetic results were collected at several initial reactants concentration (Table-1). First order kinetics was observed with respect to the oxidant sodium periodate in the case of sucrose. Insignificant effect on the rate was observed on increasing the concentration of the substrate, indicating zero order in substrate *i.e.*, sucrose.Variation of KCl did not influence the value of (-dc/dt) appreciably, showing zero order dependence in [Cl^-] (Table-1). A plot of (-dc/dt) *vs.* [Rh(III)] (Fig. 1) gives a slope 3.75×10^{-3}, which is close to the average value of first order rate constants *i.e.*, $k_1 = 3.39 \times 10^{-3}$ s^{-1} for sucrose at 35 ºC. A fair degree of closeness in the first order rate constants obtained graphically and obtained values of {(-dc/dt)/[Rh(III)] = k_1} clearly confirm the first order dependence on [Rh(III)].

The negligible effect of mercuric acetate excludes the possibility of its involvement either as a catalyst or as an oxidant because it dose not help the reaction proceed without periodate. Hence the function of mercuric acetate is to act as scavenger[24] for any bromide ion formed in the reaction. Experimental data showed negligible effect of ionic strength of the medium on the rate and the reaction is unaffected by H^+ concentration (Table-2). The kinetic studies were also made in the 30-45 ºC range

TABLE-1
EFFECT OF VARIATION OF REACTANTS ON
THE REACTION RATE AT 35 ºC

$[IO_4^-] \times 10^3$ (mol dm^{-3})	$[S] \times 10^3$ (mol dm^{-3})	$[KCl] \times 10^3$ (mol dm^{-3})	$[-dc/dt] \times 10^7$ (mol dm^{-3} s^{-1})
0.83	5.00	1.00	1.42
1.00	5.00	1.00	1.81
1.25	5.00	1.00	2.22
1.67	5.00	1.00	3.00
2.50	5.00	1.00	4.46
5.00	5.00	1.00	8.68
1.00	1.66	1.00	2.00
1.00	2.00	1.00	1.87
1.00	2.50	1.00	1.80
1.00	3.33	1.00	1.75
1.00	5.00	1.00	1.81
1.00	10.00	1.00	2.00
1.00	5.00	0.83	1.75
1.00	5.00	1.00	1.81
1.00	5.00	1.25	2.00
1.00	5.00	1.67	2.00
1.00	5.00	2.50	1.77
1.00	5.00	5.00	1.81

$[Hg(OAc)_2] = 1.67 \times 10^{-3}$ mol dm^{-3}, $[Rh(III)] = 5.72 \times 10^{-5}$ mol dm^{-3}
$[HClO_4] = 5.00 \times 10^{-3}$ mol dm^{-3}, [S] = Substrate

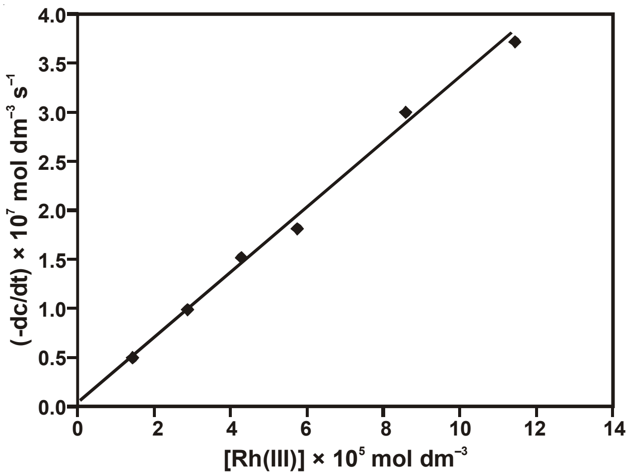


Fig. 1. Plot between (-dc/dt) *vs.* [Rh(III) in oxidation of sucrose at 35 ºC

TABLE-2
EFFECT OF VARIATION OF MERCURIC ACETATE, PERCHLORIC ACID AND IONIC STRENGTH (μ) AT 35 ºC

$[Hg(OAc)_2] \times 10^3$ (mol dm^{-3})	$[HClO_4] \times 10^3$ (mol dm^{-3})	$\mu \times 10^3$ (mol dm^{-3})	$[-dc/dt] \times 10^7$ (mol dm^{-3} s^{-1})
0.83	5.00	–	1.55
1.00	5.00	–	1.75
1.25	5.00	–	1.61
1.67	5.00	–	1.81
2.50	5.00	–	1.50
5.00	5.00	–	1.50
1.67	0.83	–	1.80
1.67	1.00	–	1.75
1.67	1.25	–	2.00
1.67	1.67	–	1.60
1.67	2.50	–	2.00
1.67	5.00	–	1.81
1.67	5.00	0.83	1.70
1.67	5.00	1.00	1.66
1.67	5.00	1.25	1.61
1.67	5.00	1.67	1.81
1.67	5.00	2.50	1.75
1.67	5.00	5.00	1.60

[Rh(III)] = 5.72×10^{-5} mol dm^{-3}, $[NaIO_4] = 1.00 \times 10^{-3}$ mol dm^{-3},
[KCl] = 1.00×10^{-3} mol dm^{-3}, [S] = 5.00×10^{-3} mol dm^{-3}

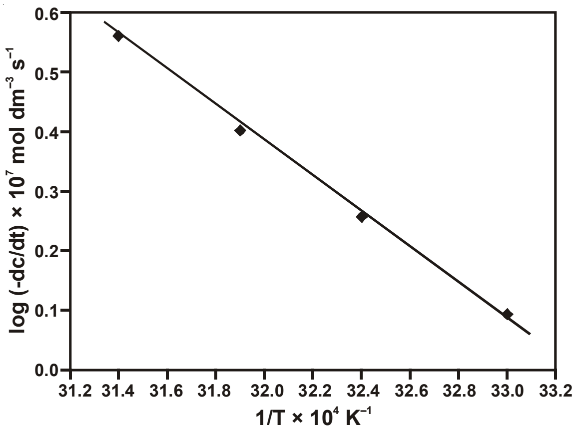


Fig. 2. Plot of (-dc/dt) *vs.* (1/T)
$[Hg(OAc)_2] = 1.67 \times 10^{-3}$ mol dm^{-3}, [KCl] = 1.00×10^{-3} mol dm^{-3}
$[HClO_4] = 5.00 \times 10^{-3}$ mol dm^{-3}, $[NaIO_4] = 1.00 \times 10^{-3}$ mol dm^{-3}
[S] = 5.00×10^{-3} mol dm^{-3}, [Rh(III)] = 5.72×10^{-5} mol dm^{-3}

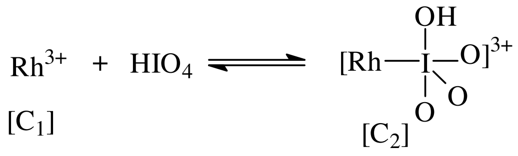
and specific rate constants obtained were used to draw a plot of log (-dc/dt) *vs.* 1/T (Fig. 2), which was linear. The values of activation parameters were calculated (Table-3).

TABLE-3
ACTIVATION PARAMETERS FOR ACID IODATE OXIDATION OF SUCROSE

Parameters	Temperature (ºC)	Sucrose
$-dc/dt \times 10^7$ mol dm^{-3} s^{-1}	30	1.24
$-dc/dt \times 10^7$ mol dm^{-3} s^{-1}	35	1.81
$-dc/dt \times 10^7$ mol dm^{-3} s^{-1}	40	2.52
$-dc/dt \times 10^7$ mol dm^{-3} s^{-1}	45	3.64
log A	–	11.06
ΔE^* (kJ mol^{-1})	–	63.77
ΔG^* (kJ mol^{-1})	–	75.18
ΔH^* (kJ mol^{-1})	–	72.45
ΔS^* (JK^{-1} mol^{-1})	–	-8.84

The following reaction steps are suggested on the basis of the above discussion for oxidation of sucrose by $NaIO_4$ in presence of rhodium(III) chloride as a catalyst.

$$H^+ + IO_4^- \rightleftharpoons HIO_4 \qquad (I)$$



$$\underset{[C_1]}{Rh^{3+}} + HIO_4 \rightleftharpoons \underset{[C_2]}{[Rh—\overset{OH}{\underset{O}{I}}(O)—O]^{3+}} \qquad (II)$$

$$[C_2] \xrightarrow[\text{Slow}]{k_2} [Rh—O]^{1+} + HIO_3 \qquad (III)$$

$$\underset{}{[Rh—O]^{1+}} + \underset{\text{(sucrose)}}{C_8H_{14}O_7(CHOH)_4} + HIO_4 + 3H_2O \longrightarrow$$

$$\underset{\text{(tetra-aldehyde)}}{C_7H_{12}O_6(CHO)_4} + [Rh—OH]^{2+} + HIO_3 + 3H_3O^+ + \underset{\text{(formic acid)}}{HCOOH} \qquad (IV)$$

$$[Rh—OH]^{2+} + HIO_4 + 3H_3O^+ \longrightarrow [Rh]^{3+} + HIO_3 + 5H_2O \qquad (V)$$

The species $[Rh—O]^{1+}$ and $[Rh—OH]^{2+}$ formed in step (iii), (iv) have already been established[22].

Considering the above reaction steps and applying the steady state treatment with reasonable approximation, the rate law may be written as eqn. (VI).

$$\text{Rate} = \frac{k_2K_1[Rh(III)]_T[HIO_4]}{[1+K_1[HIO_4]]} \qquad (VI)$$

where $K_1 = k_1/k_{-1}$

The value of K_1 [HIO_4] < < 1, therefore it can be neglected and final rate law can be written as

$$\text{Rate} = K_1\ k_2\ [Rh(III)]_T\ [HIO_4] \qquad \text{(VII)}$$

From the present investigation, it is concluded that $RhCl_3$ as such is the reactive species of the catalyst in acidic medium.

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