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Kinetics of Os(VIII) and Mn(VII) Catalysed Oxidation of Thiocyanate by Periodate in Alkaline Medium

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The kinetics of oxidation of thiocyanate with periodate in presence of permanganate and Os (VIII) as catalysts has been studied. The reactions are found to be zero order in oxidant, first order in MnO_4^-/Os(VIII), first order in substrate, independent of alkali in MnO_4^- catalysed reactions, while it is of fractional order in alkali in Os(VIII) catalysed reactions. Os(VIII) is more effective as catalyst than MnO_4^- under catalytic conditions. Suitable mechanisms have been postulated to explain the kinetics observed in both the cases.

INTRODUCTION

Oxidation of thiocyanate ion by different oxidising agents has been studied extensively[1–7]. Sulphate, cyanate and cyanide ions have been postulated as products depending upon the nature of the oxidant and other experimental conditions. Even kinetic orders have been differently reported. Hence, it is thought worthwhile to study the oxidation of thiocyanate ion in alkaline medium by periodate under uncatalysed and catalysed conditions using catalytic amounts of permanganate and Os(VIII).

EXPERIMENTAL

All the chemicals used were of analytical reagent grade. Thiocyanate solution was standardised by argentometry. Permanganate solution was estimated by iodometric method. Osmium(VIII) solution was prepared from OsO_4 (Johnson and Matthey Co., London) in 0.5 M NaOH to minimise the volatility of the metal ion[8]. The Os(VIII) was determined iodometrically to the starch end point. Necessary dilutions were made from this stock Os(VIII) solution for the kinetic runs. Due allowance was given to the already present alkalinity.

The following method was adopted to estimate IO_4^- quantitatively in neutral/alkaline medium: 5.0 mL of the periodate solution was pipetted out into an iodine flask containing 100 mL of distilled water, suitable amount of 10% aqueous solution of KH_2PO_4 was added so that the pH of the resulting solution was 5 to 5.5 and 5 mL of 5% potassium iodide solution, the liberated iodine was titrated after three minutes against a standard solution of sodium thiosulphate to the end point of starch indicator.

There is no reaction between liberated iodine and thiocyanate under these conditions. This has been checked experimentally. Kinetics has also been followed by alternative procedure in completely acid medium by iodometry. The reaction stopped at 25% completion of the reaction indicating that the oxidation sequence has stopped at the IO_3^- stage. Both the methods yielded identical results.

IO_4^- is quantitatively reduced to IO_3^- as per the reaction:

$$KIO_4 \rightarrow KIO_3 + O$$

$$2KI + O \rightarrow K_2O + I_2$$

$$K_2O + KH_2PO_4 \rightarrow H_2O + K_3PO_4$$

and IO_3^- is without any effect on the added I^-. In the pH range of 5.0 to 5.5, the observed concentration of periodate differs from the theoretical concentration by only ±1%.

Stoichiometry

Experiments on stoichiometry in the presence of five times molar excess of periodate established that the stoichiometric ratio is 3 : 1 (iodine: thiocyanate) in alkaline medium with Os(VIII) as a catalyst amounting to a six electron oxidation of the substrate.

$$3\ IO_4^- + SCN^- + 2\ OH^- + 3\ Os(VIII) \rightarrow SO_4^{2-} + CN^- + 3\ IO_3^- + 3\ Os(VIII) + H_2O$$

The cyanide and sulphate ions are the products of oxidation as identified by their qualitative tests. Similar stoichiometry has been observed with Mn(VII) as catalyst.

RESULTS AND DISCUSSION

Reactions with periodate catalysed by permanganate:

Under the conditions of low temperature upto 40°C there is no perceptible oxidation of thiocyanate ion by periodate under alkaline conditions of 0.02 to 0.04 M hydroxide ion. Hence, the study has been made in the presence of catalysts like Os(VIII) and MnO_4^- in the range 10^{-6}.

The reaction has been found to be zero order in oxidant in the range studied. The reaction has been found to be first order in permanganate in the range 5×10^{-6} to 25×10^{-6}. Further increase in the concentration of MnO_4^- does not result in increase in the kinetic rate indicating that the catalysis is specific in the concentration range (5×10^{-6} to 50×10^{-6} of MnO_4^-)

In the range of alkali variation studied (5×10^{-3} to 40×10^{-3}) the reaction rate decreases with increase in alkali concentration though the decrease is not pronounced. Variation of thiocyanate concentration in the range 5×10^{-3} to 30×10^{-3} shows first order dependence on substrate. The reaction has been studied at different temperatures and the reaction rate is enhanced with increase in temperature. The results were incorporated in Table-1.

Plots of log k *vs* $1/T$ are linear. Various thermodynamic parameters have been computed and they are quite compatible with those of bimolecular reactions. The parameters ΔE, ΔH, $\log_{10} p_z$ and ΔS are found to be 41 KJ / mole; 39 KJ / mole; 1.608 and –214.4 $JK^{-1}\ mol^{-1}$ respectively.

The most probable reason for high negative entropy of activation is the cumulative effect of

(a) Endothermic function of a complex prior to the reaction proper.

(b) The necessity for the ionization of either or both of the reactants.

(c) Deactivation by the solvent molecules.

(d) Stringent conditions of orientation or of internal phase of the reacting molecules at the moment of impact and

(e) The existence of strong forces of repulsion.

TABLE-1

OXIDATION OF THIOCYANATE BY PERIODATE CATALYSED BY PERMANGANATE

Variant	Concentration of non-variant M	Concentration of variant M	$k_0 \times 10^6$ M. min^{-1}
IO_4^-	$MnO_4^- = 10 \times 10^{-6}$	3.58×10^{-4}	2.79
	$SCN^- = 10 \times 10^{-3}$	5.70×10^{-4}	2.94
	$OH^- = 20 \times 10^{-3}$	8.04×10^{-4}	3.14
	Temp. = 40°C	10.70×10^{-4}	2.85
MnO_4^-	$IO_4^- = 5.7 \times 10^{-4}$	5.0×10^{-6}	1.13
	$SCN^- = 10 \times 10^{-3}$	7.0×10^{-6}	1.35
	$OH^- = 20 \times 10^{-3}$	10.0×10^{-6}	2.94
	Temp. = 40°C	15.0×10^{-6}	4.16
		20.0×10^{-6}	6.07
		25.0×10^{-6}	8.15
OH^-	$IO_4^- = 5.7 \times 10^{-4}$	5.0×10^{-3}	3.35
	$SCN^- = 10 \times 10^{-3}$	10.0×10^{-3}	3.01
	$MnO_4^- = 10 \times 10^{-6}$	20.0×10^{-3}	2.94
	Temp. = 40°C	40.0×10^{-3}	2.26
SCN^-	$IO_4^- = 5.7 \times 10^{-4}$	5.0×10^{-3}	0.95
	$MnO_4^- = 10 \times 10^{-6}$	10.0×10^{-3}	2.94
	$OH^- = 20 \times 10^{-3}$	20.0×10^{-3}	4.72
	Temp. = 40°C	30.0×10^{-3}	8.05
Temperature	$IO_4^- = 5.7 \times 10^{-4}$	40°C	2.94
	$MnO_4^- = 10 \times 10^{-6}$	50°C	4.57
	$OH^- = 20 \times 10^{-3}$	60°C	7.76
	$SCN^- = 10 \times 10^{-3}$		

Mechanism

MnO_4^- ion reacts with thiocyanate forming an intermediate which decomposes to give CN^-, SO and Mn(V). The catalyst is regenerated and is recycled catalytically. SO that is formed is rapidly oxidised by periodate to give sulphate as final product. The sequence of reactions is

$$SCN^- + MnO_4^- \overset{K_1}{\rightleftharpoons} \text{Complex}$$

$$\text{Complex} \xrightarrow[\text{slow}]{k} CN^- + SO + Mn(V)$$

$$Mn(V) + IO_4^- \xrightarrow{\text{fast}} MnO_4^- + IO_3^-$$

$$SO + 2IO_4^- \xrightarrow{\text{fast}} SO_3 + 2IO_3^-$$

$$SO_3 + 2H_2O \xrightarrow{\text{fast}} H_2SO_4$$

$$H_2SO_4 + 2OH^- \xrightarrow{\text{fast}} SO_4^{2-} + 2H_2O$$

The conversion of Mn(V) to Mn(VII) can also be routed by the following pathway

$$Mn(V) + Mn(VII) \rightarrow 2Mn(VI)$$

$$2Mn(VI) + IO_4^- \rightarrow 2Mn(VII)$$

The overall reaction is

$$3\ IO_4^- + SCN^- + 2\ OH^- \rightarrow SO_4^{2-} + CN^- + 3\ IO_3^- + H_2O$$

Broadly the rate is equal to $kK_1 \times MnO_4^- \times SCN^-$ neglecting the negligible dependence on alkali as observed. This explains zero order in oxidant IO_4^-, first order in MnO_4^- and first order in substrate.

It has been earlier stated that reaction rate decreases with increase in alkali concentration though slightly. But if the pH is varied from pH 12 to 10, there is increase in rate indicating that the dependence is really inverse in alkali though it is not abundantly clear in the narrow range studied. This is explainable as the MnO_4^- ion tends to become more reactive as the pH is made relatively less alkaline.

Catalysed Oxidation with Os (VIII)

As a parallel investigation, the reaction has been studied with varying amounts of Os(VIII) in the presence of alkali and IO_4^- as the oxidant. The reaction is found to be of zero order in IO_4^-. The reaction is first order in Os(VIII) and first order in substrate. The reaction is directly influenced by increase in alkali as increase in OH^- concentration increases the rate. The reaction is found to be fractional order in alkali (0.7). The reactions are carried out at different temperatures and the results are presented in Table-2

TABLE-2
OXIDATION OF THIOCYANATE BY PERIODATE CATALYSED BY Os(VIII)

Variant	Concentration of non-variant M	Concentration of variant M	$k_O \times 10^6$ M min^{-1}
IO_4^-	Os(VIII) = 3.2×10^{-6}	3.20×10^{-4}	14.80
	$SCN^- = 10 \times 10^{-3}$	5.15×10^{-4}	10.35
	$OH^- = 20 \times 10^{-3}$	10.60×10^{-4}	13.15
	Temp. = 40°C	17.50×10^{-4}	13.70
Os (VIII)	$IO_4^- = 5.15 \times 10^{-4}$	1.6×10^{-6}	4.49
	$SCN^- = 10 \times 10^{-3}$	3.2×10^{-6}	10.35
	$OH^- = 20 \times 10^{-3}$	6.4×10^{-6}	19.08
	Temp. = 40°C		

Variant	Concentration of non-variant M	Concentration of variant M	$k_0 \times 10^6$ M min^{-1}
SCN^-	$IO_4^- = 5.15 \times 10^{-4}$	2.6×10^{-3}	2.44
	$Os(VIII) = 3.2 \times 10^{-6}$	5.0×10^{-3}	4.53
	$OH^- = 20 \times 10^{-3}$	10.0×10^{-3}	10.35
	Temp. = 40°C	20.0×10^{-3}	21.46
OH^-	$IO_4^- = 5.15 \times 10^{-4}$	5.0×10^{-3}	3.84
	$SCN^- = 10 \times 10^{-3}$	10.0×10^{-3}	6.26
	$Os(VIII) = 3.2 \times 10^{-6}$	20.0×10^{-3}	10.35
	Temp. = 40°C	40.0×10^{-3}	12.20
		80.0×10^{-3}	12.20
Temperature	$IO_4^- = 5.15 \times 10^{-4}$	35°C	6.96
	$SCN^- = 10 \times 10^{-3}$	40°C	10.35
	$Os(VIII) = 3.2 \times 10^{-6}$	45°C	13.22
	$OH^- = 20 \times 10^{-3}$		

The derived parameters are found, *viz.*, ΔE, ΔH, $\log_{10} p_z$ and ΔS are 41 KJ/mole; 39 KJ/mole; 2.15 and -204 JK^{-1} mol^{-1} respectively.

Mechanism

OsO_4 interacts with SCN^- through an inner sphere redox mechanism probably. An inner sphere redox reaction is one involving a multistage process in which one of the stages is rate determining such as the precursor complex formation[9], electron transfer in which the precursor complex is converted to successor complex and the disintegration of the successor complex.

$$[OsO_4(OH)H_2O]^- + OH^- \xrightleftharpoons{K_1} [OsO_4(OH)_2]^{2-}$$

$$[OsO_4(OH)_2]^{2-} + SCN^- \xrightleftharpoons{K_2} \text{Complex}$$

$$\text{Complex} \xrightarrow{k} SO + CN^- + [OsO_3(OH)_2]^{2-}$$

$$[OsO_3(OH)_2]^{2-} + IO_4^- \xrightarrow{\text{fast}} [OsO_4(OH)_2]^{2-} + IO_3^-$$

$$[OsO_4(OH)_2]^{2-} + H_2O \longrightarrow [OsO_4(OH)H_2O]^- + OH^-$$

$$SO + 2\,IO_4^- \longrightarrow SO_3 + 2\,IO_3^-$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$H_2\,SO_4 + 2\,OH^- \longrightarrow SO_4^{2-} + 2\,H_2O$$

The mechanism envisages a slow and rate determining breakdown of the complex formed in step II resulting in Os(VI) and the intermediate product. The Os(VIII) is represented by fast oxidation of Os(VI) by IO_4^- and by making either electron transfer or oxygen atom transfer. The latter possibility is more likely as IO_4^- is known to function through oxygen atom transfer[10]

The rate law is derived as follows:

There always exists an equilibrium between $[OsO_4(OH)H_2O]^-$ and $[OsO_4(OH)_2]^{2-}$ in alkaline medium.

The rate of oxidation obviously would be given by the rate of decomposition of the complex.

$$\frac{d[\text{complex}]}{dt} = k[\text{complex}] = \frac{d[\text{Os(VIII)}]}{dt}$$

But the rate has been measured in terms of decreasing concentrations of IO_4^- and hence the observed rate would be

$$\frac{-d[IO_4^-]}{dt} = \frac{d[\text{Os(VIII)}]}{dt} = k[\text{complex}]$$

$$[\text{Os(VIII)}]_T = [OsO(OH)H_2O]^- + [OsO_4(OH)_2]^{2-} + [\text{complex}]$$

Solving for the complex in terms of $[\text{Os(VIII)}]_T$

$$\text{complex} = \frac{K_1K_2[\text{Os(VIII)}]_T[OH^-]\,[S]}{\{1 + K_1[OH^-]\}\{1 + K_2[S]\}}$$

$$\frac{-d[IO_4^-]}{dt} = \frac{kK_1K_2[\text{Os(VIII)}]_T[OH^-][S]}{\{1 + K_1[OH^-]\}\{1 + K_2[S]\}}$$

This rate law explains first order in Os(VIII), first order in substrate and fractional order in OH^-. It also explains the independence to alkali at higher alkali concentrations. Since there is first order dependence in substrate it appears $K_2[S]$ is negligible in the denominator and the rate law takes the form

$$\frac{-d[IO_4^-]}{dt} = \frac{kK_1K_2[\text{Os(VIII)}]_T[OH^-][S]}{1 + K_1[OH^-]}$$

It can be summarised from the observed kinetic results that Os(VIII) is a better catalyst than permanganate under the experimental conditions.

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