

CHAPTER IV

**KINETICS AND MECHANISM OF OXIDATION
OF TERTIARY AMINO ALCOHOLS BY CAT
IN ACID MEDIUM USING Ru(III) AS CATALYST**

SECTION 4.1

INTRODUCTION

2-dimethylamino ethanol (DMAE) and 3-dimethylamino-1 -propanol (DMAP) are important derivatives of tertiary amino alcohols. These compounds behave like primary alcohols and are oxidised to the respective aldehydes, by mild oxidants.

2-dimethylamino ethanol :

This is a colourless liquid with a molecular weight of 103.17 ($d = 0.872$). The boiling range of the liquid is 163 - 164°. The compound is miscible with water and other solvents.

3-dimethylamino-1-propanol :

This is a colourless, irritating liquid of molecular weight 89.14 ($d = 0.887$). The boiling range of the liquid is 133- 134°. The compound dissolves in water and other solvents.

These compounds have a number of pharmacological applications, while reports on chemical application are scanty. However 2-dimethylamino ethanol (DMAE) is used as a potential volatile amine^{257a} for boiler water treatment and was investigated for their complexation behaviour with copper. Its P^{K_b} value is 4.52 at 25°. DMAE forms coloured complexes with absorption in the range of 5 10 nm. In the pH range 8 - 10.5, the Cu • DMAE complex established $2e^-$ reduction and the species $[Cu(DMAE)_2]$ was identified, with a stability constant of 1020.39.

Chloride and iodide complexes of lead (II) with 2-dimethylamino ethanol is obtained by direct synthesis.^{257b}

A review of literature shows that there is no report on the kinetics of oxidation of DMAE and DMAP by any oxidant. Hence in the present investigation, a detailed study is made on the kinetic and mechanistic aspects of the oxidation of these two alcohols by CAT in HCl medium with Ru(III) as catalyst at 45°.

SECTION 4.2

OXIDATION : A REVIEW

A review of literature shows little information on the kinetics of oxidation of primary alcohols by N-haloamines. Mahadevappa and Naidu²⁵⁸⁻²⁶⁰ and Herlihy²⁶¹ have reported on the oxidation of conjugated alcohols, allyl, cinnamyl and crotyl alcohols by CAT in HCl medium. The rate is found to be first order each in [CAT], [H⁺] and [Cl⁻]. Similar results have been obtained²⁶² with CAB. Mahadevappa and co-workers have also carried out the oxidation of primary alcohols by BAB²⁶³ and of allyl crotyl alcohols by BAT catalysed by OsO₄.²⁶⁴

Mushran et al²⁶⁵ have oxidised n-butanol, iso-butanol and iso-pentanol by CAT in acid medium. The rate is first order in each [CAT]₀ and [H⁺] but shows a zero order dependence in [Alcohol]₀. The proposed mechanism involves HOCl as the reactive species.

Uma and Mayanna²⁶⁶ have reported the oxidation of primary alcohols by CAT in alkaline medium, catalysed by OsO₄. The proposed mechanism indicates formation of an activated complex between the substrate and OsO₄ which slowly decomposes in a rate limiting step in to the aldehyde and Os (VI) formed is oxidised rapidly to Os (VIII) with the anion of CAT.

Mukherji and Banerji²⁶⁷ have reported on the oxidation of nine primary alcohols by CAB in presence of HClO₄. The rate is first order each with respect to the [ox], [alcohol] and [H⁺] ions. The primary kinetic isotope effect using deuterated alcohol and the solvent isotope effect in

D_2O medium have been studied. The reaction exhibits a reaction constant $\rho^\ddagger = 2.2$ at 298 K. The probable oxidising species is $PhSO_2NHCl$. A mechanism involving transfer of hydride ion to the oxidant is suggested.

Singh et al²⁶⁸ have reported on the mechanism of Ru(III) catalysed oxidation of methanol and ethanol by BAT in acid medium. The rate shows a first-order each with respect to [BAT], [substrate], [H⁺] and [Ru(III)] and inverse first-order on [Cl⁻]. Kinetic results point to a mechanism involving interaction between a reactive species of BAT and a transient complex formed between the substrate and ruthenium (III) species. Similar results²⁶⁹ were obtained in the oxidation of n-propanol and n-butanol by BAT.

Mittal et al²⁷⁰ have reported on the kinetics and mechanism of the oxidation of primary alcohols by sodium N-chloro ethyl carbamate in acid medium. The reaction is first order each with respect to the [ox]_o and [alcohol]_o. The rate increase with an increase in acidity (H_o) and the value of solvent isotope effect $k(H_2O) / k(D_2O) = 2.23$ at 298 K. Plots of $(\log k_2 + H_s)$ vs $(H_s + \log [H^+])$ are linear and a concerted mechanism involving transfer of a hydride ion from C-H bond of the alcohol to the oxidant and removal of a proton from the OH group by a water molecule has been proposed.

Neg et al²⁷¹ have reported on the kinetics and mechanism of the oxidation of aliphatic alcohols by sodium hypobromite in alkaline medium. The reaction is first order each with [ox] and [alcohol] and inverse order with respect to [OH⁻] ion. The primary kinetic isotope effect has been studied using deuterated alcohol.

Banerji²⁷² has reported the oxidation of aliphatic alcohols by pyridinium fluoro chromate in dimethyl sulphoxide medium. The reaction is first order with respect of $[Ox]_0$ but the order with respect to the $[Alcohol]_0$ is less than one. The primary kinetic isotope effect and the formation constant of the alcohol-oxidant complex have been studied.

Mahadevappa et al²⁷³ have oxidised substituted ethanols by BAB in the presence of HCl medium. The rate shows a first-order on $[BAB]$ and is fractional in $[alcohol]$, $[H^+]$ and $[Cl^-]$. The solvent isotope effect and the rates do not correlate satisfactorily with Taft's substituent constants is suggested.

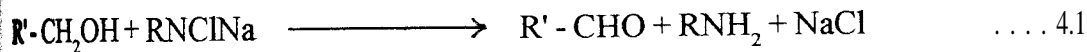
SECTION 4.3

Kinetics and mechanism of oxidation of tertiary aminoalcohols by CAT in HCl medium using Ru(III) as catalyst

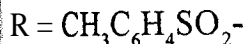
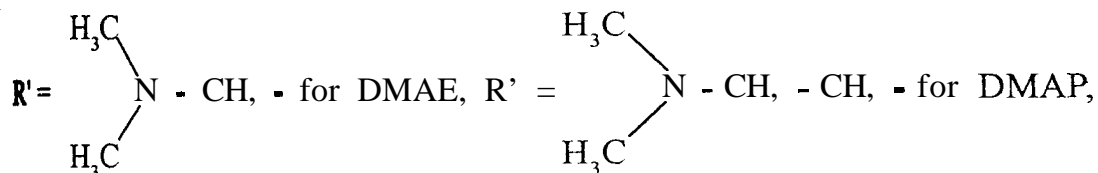
In this section, the kinetics and mechanism of oxidation of tertiary amino alcohols namely 2-dimethylamino ethanol and 3-dimethylamino- 1 -propanol by CAT in hydrochloric acid medium using RuCl_3 as catalyst at 45° has been reported. Experiments have been designed to determine the kinetic order with respect to the oxidant, the substrate, medium, catalyst etc. The effects of dielectric constant, addition of reaction product, p-toluenesulphonamide (PTS) and addition of neutral salts have been studied. Kinetic and thermodynamic parameters have been evaluated by determining the rate constant of the reaction at different temperatures. A suitable mechanism with respect to two substrates have been proposed to account for the observed rate law.

Stoichiometry :

Reaction mixtures containing various ratios of oxidant to substrate were equilibrated in $0.08 \text{ mol dm}^{-3} \text{ HCl}$ at 45° for about 24 hours with $[\text{oxid}]_0 > [\text{S}]$. The excess unreacted oxidant was estimated by iodometric titration with standard sodium thiosulphate. It was found that one mole of substrate consumed one mole of the oxidant to yield the corresponding aldehyde, confirming to equation (4.1)



Where



Product Analysis :

The aldehyde formed in the reaction was extracted into ether, followed by washing with dilute NaOH to eliminate the interfering PTS. Evaporation of the solvent yielded a small amount of oily material which gave positive test with 2,4-DNP. Confirming the corresponding aldehyde. These materials were compared with the authentic samples.

RESULTS

Effect of varying reactant concentration on the rate :

The kinetics of oxidation of tertiary aminoalcohols by CAT were investigated at several initial concentrations of reactants in hydrochloric acid medium using RuCl_3 as catalyst at 45° . With the [substrate] in excess and at constant $[\text{HCl}]$ and $[\text{RuCl}_3]$, plots of $\log [\text{CAT}]$ versus time were linear (Table 4.1, Fig 4.1, $r > 0.9990$, $s \leq 0.01$) for each $[\text{CAT}]_0$. The reaction showed a first order dependence of rate on $[\text{CAT}]$ (Table 4.2). Values of the k_{obs} increased with increase in $[\text{S}]_0$ for DMAE while the values were constant for DMAP indicating a zero order dependence on the latter. The plots of $\log k_{\text{obs}}$ vs $\log [\text{DMAE}]_0$ were linear ($r = 0.9900$, $s < 0.05$) with fractional slope (Table 4.3, Figure 4.2).

Effect of $[\text{HCl}]$:

The rate decreases with increase in $[\text{HCl}]$ and the plot of $\log k_{\text{obs}}$ vs $\log [\text{HCl}]$ is linear (Figure 4.3, $r > 0.9989$, $s < 0.04$ Table 4.3(a)) with a fractional slope of (-0.5).

Effect of ionic strength :

Variation of the ionic strength of the medium by adding NaClO_4 ($0.3 - 1.2 \text{ mol dm}^{-3}$) had no effect on the reaction rate (Table 4.7), thus showing the involvement of non-ionic species in the rate limiting step.

Effect of $[\text{RuCl}_3]$:

The rate increases with increase in $[\text{RuCl}_3]$ and plots of $\log k$ vs $\log [\text{RuCl}_3]$ were linear ($r > 0.9999$, $s \leq 0.01$) with unit slopes (Table 4.6, Figure 4.5) for both alcohols, indicating a fractional order dependence on the [catalyst].

Effect of $[\text{H}^+]$:

At constant $[\text{Cl}^-] = 0.6 \text{ mol dm}^{-3}$ maintained by adding NaCl, increase in $[\text{H}^+]$ had no effect on the rate (Table 4.4).

Effect of $[\text{Cl}^-]$:

Addition of Cl^- ions in the form of NaCl ($0.1 - 0.8 \text{ mol dm}^{-3}$) at fixed $[\text{H}^+]$ decreases the rate with increasing $[\text{Cl}^-]$ and a plot of $\log k_{\text{obs}}$ vs $\log [\text{Cl}^-]$ was found to be linear ($r > 0.9890$, $s < 0.06$, Table 4.5, Figure 4.4) with a fractional slope of -0.50.

Effect of *p*-toluenesulphonamide $[\text{RNH}_2]$:

The rate decreased with the addition of RNH_2 . Plots of $\log k_{\text{obs}}$ vs $\log [\text{RNH}_2]$ was linear ($r > 0.9990$, $s < 0.04$, Table 4.9, Figure 4.7) with a small negative fractional slope of -0.33.

Effect of varying the solvent composition :

The solvent composition of the reaction medium was varied by the addition of methanol (0 - 40% v/v). The rate decreased with increase in methanol content (Table 4.8, Fig 4.6) plots of $\log k_{\text{obs}}$ vs $1/D$ (where 'D' is the dielectric constant of the medium) were linear (Figure 4.6,

$r > 0.9890$, $s \leq 0.06$) with a negative slope. Blank experiments performed showed that methanol is not oxidized by CAT under the experimental conditions.

Effect of Temperature :

The reaction was studied at different temperatures (**308 - 323 K**). From the linear Arrhenius plots of $\log k_{\text{obs}}$ vs $1/T$ (Table 4.9(a) Fig 4.8, $r > 0.9998$, $s \leq 0.01$), the activation energy E_a was calculated. Values of the other activation parameters, ΔH^\ddagger , ΔS^\ddagger , ΔG^\ddagger and $\log A$ were computed from the measured E_a values (Table 4.9(b)).

Test for free radicals :

Addition of the reaction mixture to aqueous acrylamide solution did not initiate polymerization showing the absence of free radical species.

Table 4.1, Fig 4.1**Effect of [CAT] on the rate of oxidation of tertiary amino alcohols (representative runs)**

$[\text{CAT}]_0 = 0.003 \text{ mol dm}^{-3}$, $[\text{S}]_0 = 0.02 \text{ mol dm}^{-3}$, $[\text{HCl}] = 0.08 \text{ mol dm}^{-3}$,
 $[\text{RuCl}_3] = 10 \times 10^{-5} \text{ mol dm}^{-3}$, $T = 45^\circ$.

2-dimethyl amino ethanol			3 -dimethyl amino- 1 -propanol		
Time	Titre	log [CAT]	Time	Titre	log [CAT]
mill.	ml.		min.	ml.	
0	30.2	1.48	0	29.5	1.47
10	27.0	1.31	10	26.1	1.41
20	23.3	1.37	20	23.0	1.36
30	20.2	1.31	30	19.9	1.29
40	17.2	1.24	40	16.7	1.22
50	15.4	1.19	50	14.4	1.16
60	14.5	1.16	60	12.0	1.10
70	12.7	1.10	70	10.1	1.00
80	11.6	1.06	80	9.0	0.95
90	10.1	1.00	90	7.5	0.88
100	9.4	0.97	100	7.0	0.85
110	8.1	0.91			
120	7.0	0.85			

$$k_{\text{obs}} = 2.021 \times 10^{-4} \text{ s}^{-1}$$

$$k_{\text{obs}} = 2.482 \times 10^{-4} \text{ s}^{-1}$$

Table 4.2

Effect of varying $[\text{CAT}]_0$ on the rate of oxidation of tertiary amino alcohols

$[\text{S}]_0 = 0.02 \text{ mol dm}^{-3}$, $[\text{HCl}] = 0.08 \text{ mol dm}^{-3}$, $[\text{RuCl}_3] = 10.0 \times 10^{-5} \text{ mol dm}^{-3}$, $T = 45^\circ$

$10^3 [\text{CAT}]_0$ mol dm^{-3}	$10^4 k_{\text{obs}} (\text{s}^{-1})$	
	3-dimethyl amino- 1 -propanol	2-dimethyl amino ethanol
2.0	2.75	2.33
2.5	2.60	2.20
3.0	2.48	2.02
3.5	2.53	2.10
4.0	2.39	2.06
4.5	2.45	2.03
5.0	2.40	2.00
5.5	2.36	1.98
6.0	2.30	1.90

Table 4.3, Fig 4.2**Effect of varying the substrate on the rate**

$$[\text{CAT}]_0 = 0.003 \text{ mol dm}^{-3}, [\text{HCl}] = 0.08 \text{ mol dm}^{-3}, [\text{RuCl}_3] = 10.0 \times 10^{-5} \text{ mol dm}^{-3}, T = 45^\circ$$

$10^2 [\text{S}]_0$ mol dm ⁻³	$10^3 k_{\text{obs}} (\text{s}^{-1})$	
	3-dimethyl amino- 1-propanol	2-dimethyl aminoethanol
0.8	2.20	1.30
1.0	2.22	1.50
2.0	2.48	2.02
3.0	2.33	2.58
4.0	2.20	3.11
5.0	2.35	3.33
6.0	2.46	3.66

Table 4.3(a) Fig 4.3

Effect of $[\text{HCl}]$ on the rate of reaction $[\text{CAT}]_0 = 0.003 \text{ mol dm}^{-3}$, $[\text{S}]_0 = 0.02 \text{ mol dm}^{-3}$, $[\text{RuCl}_3] = 10.0 \times 10^{-5} \text{ mol dm}^{-3}$, $T = 45^\circ$

$10^2 [\text{HCl}]$ mol dm ⁻³	$10^4 k_{\text{obs}} (\text{s}^{-1})$	
	3-dimethyl amino- 1 -propanol	2-dimethyl aminoethanol
6.0	2.65	2.43
8.0	2.48	2.02
10.0	2.11	1.82
20.0	1.45	1.30
40.0	1.04	0.88
60.0	0.82	0.70

Table 4.4**Variation of [H⁺] (by adding NaCl) on the rate of Oxidation**

[CAT]₀ = 0.003 mol dm⁻³, [S]₀ = 0.02 mol dm⁻³, [RuCl₃] = 10.0 × 10⁻⁵ mol dm⁻³, T = 45°

10 ² [HCl] mol dm ⁻³	10 ³ k _{obs} (s ⁻¹)	
	3-dimethyl amino-1-propanol	2-dimethyl aminoethanol
6.0	2.50	2.08
8.0	2.48	2.02
10.0	2.25	1.98
20.0	2.20	1.93
40.0	2.18	1.89
60.0	2.16	1.86

Table 4.5 Fig 4.4

Variation of $[Cl^-]$ [at const $[H^+] = 0.0891$ on the rate of Oxidation

$$[CAT]_0 = 0.003 \text{ mol dm}^{-3}, [S]_0 = 0.02 \text{ mol dm}^{-3}, [HCl] = 0.08 \text{ mol dm}^{-3},$$

$$[RuCl_3] = 10.0 \times 10^{-5} \text{ mol dm}^{-3}, T = 45^\circ$$

$10^2 [NaCl]$ mol dm^{-3}	$10^4 k_{obs} (s^{-1})$	
	3-dimethyl amino- 1 -propanol	2-dimethyl aminoethanol
10.0	2.68	2.50
20.0	2.48	2.02
40.0	1.44	1.28
60.0	1.28	1.08
80.0	1.06	0.90

Table 4.6 Fig 4.5**Variation of $[\text{RuCl}_3]$ on the rate of Oxidation** $[\text{CAT}]_0 = 0.003 \text{ mol dm}^{-3}$, $[\text{S}]_0 = 0.02 \text{ mol dm}^{-3}$, $[\text{HCl}] = 0.08 \text{ mol dm}^{-3}$, $T = 45^\circ$

$10^5 [\text{RuCl}_3]_0$ mol dm ⁻³	$10^4 k_{\text{obs}} (\text{s}^{-1})$	
	3-dimethyl amino- 1 -propanol	2-dimethyl aminoethanol
3.0	0.67	0.62
4.0	0.90	0.82
6.0	1.40	1.26
8.0	1.98	1.66
10.0	2.48	2.02
12.0	2.85	2.50
14.0	3.58	2.83

Table 4.7**Effect of ionic strength on the rate of reaction**

$[\text{CAT}]_0 = 0.003 \text{ mol dm}^{-3}$, $[\text{S}]_0 = 0.02 \text{ mol dm}^{-3}$, $[\text{HCl}] = 0.08 \text{ mol dm}^{-3}$,
 $[\text{RuCl}_3] = 10.0 \times 10^{-5} \text{ mol dm}^{-3}$, $T = 45^\circ$

[I] mol dm ⁻³	$10^4 k_{\text{obs}} (\text{s}^{-1})$	
	3-dimethyl amino- 1 -propanol	2-dimethyl aminoethanol
0.3	2.45	2.02
0.5	2.60	2.20
0.7	2.55	2.33
0.9	2.48	2.08
1.2	2.40	2.18

Table 4.8 Fig 4.6**Effect of dielectric constant on the rate of oxidation**

$[\text{CAT}]_0 = 0.003 \text{ mol dm}^{-3}$, $[\text{S}]_0 = 0.02 \text{ mol dm}^{-3}$, $[\text{HCl}] = 0.08 \text{ mol dm}^{-3}$,
 $[\text{RuCl}_3] = 10.0 \times 10^{-5} \text{ mol dm}^{-3}$, $T = 45^\circ$

% MeOH	$10^4 k_{\text{obs}} (\text{s}^{-1})$	
	3-dimethyl amino- 1-propanol	2-dimethyl aminoethanol
00.0	2.48	2.02
10.0	2.20	1.78
20.0	1.95	1.60
30.0	0.90	1.40
40.0	0.66	1.16

Table 4.9, Fig 4.7**Effect of p-toluenesulphonamide on the rate of reaction**

$[\text{CAT}]_0 = 0.003 \text{ mol dm}^{-3}$, $[\text{S}]_0 = 0.02 \text{ mol dm}^{-3}$, $[\text{HCl}] = 0.08 \text{ mol dm}^{-3}$,

$[\text{RuCl}_3] = 10.0 \times 10^{-5} \text{ mol dm}^{-3}$, $T = 45^\circ$

$10^3 [\text{PTS}]$ mol dm^{-3}	$10^4 k_{\text{obs}} (\text{s}^{-1})$	
	3-dimethyl amino- 1 -propanol	2 -dimethyl aminoethanol
1.0	1.50	1.61
2.0	1.28	1.30
4.0	0.92	1.04
6.0	0.85	0.84
8.0	0.80	0.80

Table 4.9 (a), Fig 4.8**Effect of temperature on the rate of reaction** $[\text{CAT}]_0 = 0.003 \text{ mol dm}^{-3}$, $[\text{S}]_0 = 0.02 \text{ mol dm}^{-3}$, $[\text{HCl}] = 0.08 \text{ mol dm}^{-3}$, $[\text{RuCl}_3] = 10.0 \times 10^{-5} \text{ mol dm}^{-3}$

Temp (K)	$10^4 k_{\text{obs}} (\text{s}^{-1})$	
	3-dimethyl amino- 1 -propanol	2-dimethyl aminoethanol
308	0.72	0.58
313	1.03	0.90
318	2.48	2.02
323	3.26	2.88

Table 4.9 (b)**Activation parameters for the oxidation of tertiary amino alcohols in acid medium by CAT**

Tertiary amino alcohols	E_a (kJ mol ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	Log A
3dimethyl amino -1-propanol	82.5	79.8	100.0	-63.6	14.8
2dimethyl amino ethanol	90.3	87.7	100.6	-40.8	16.0

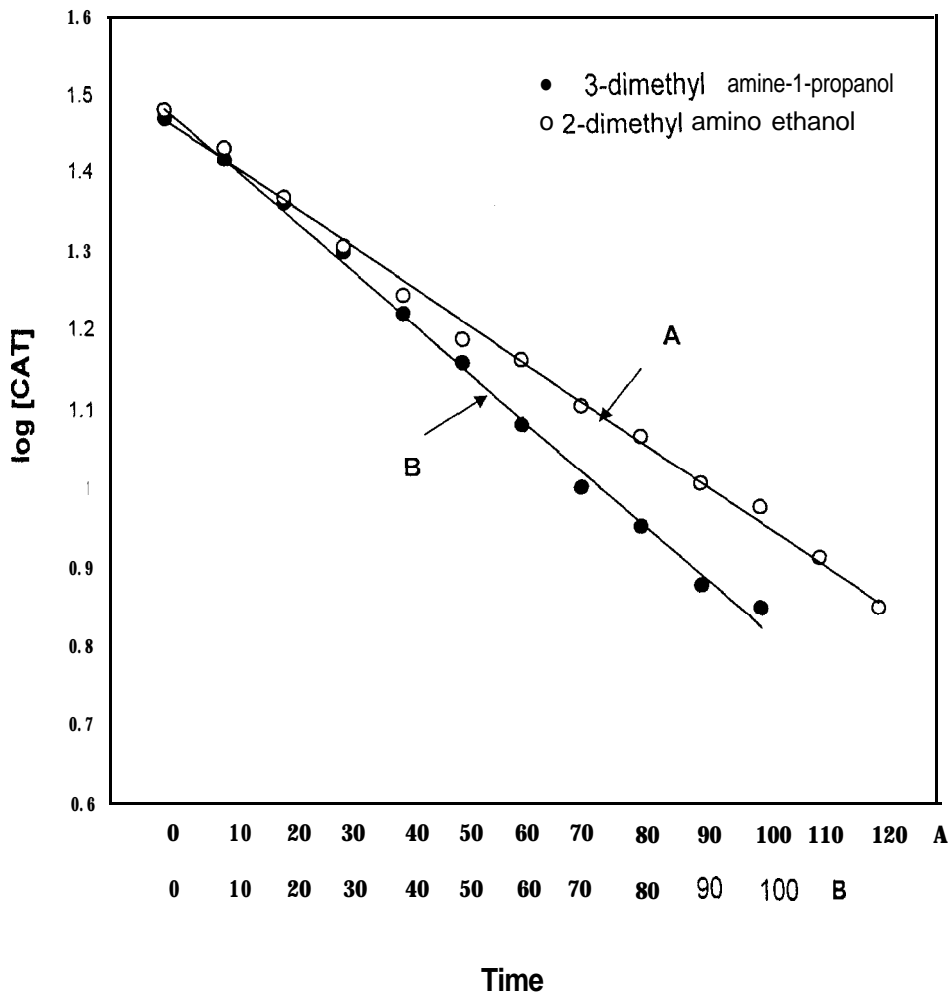


Fig. 4.1

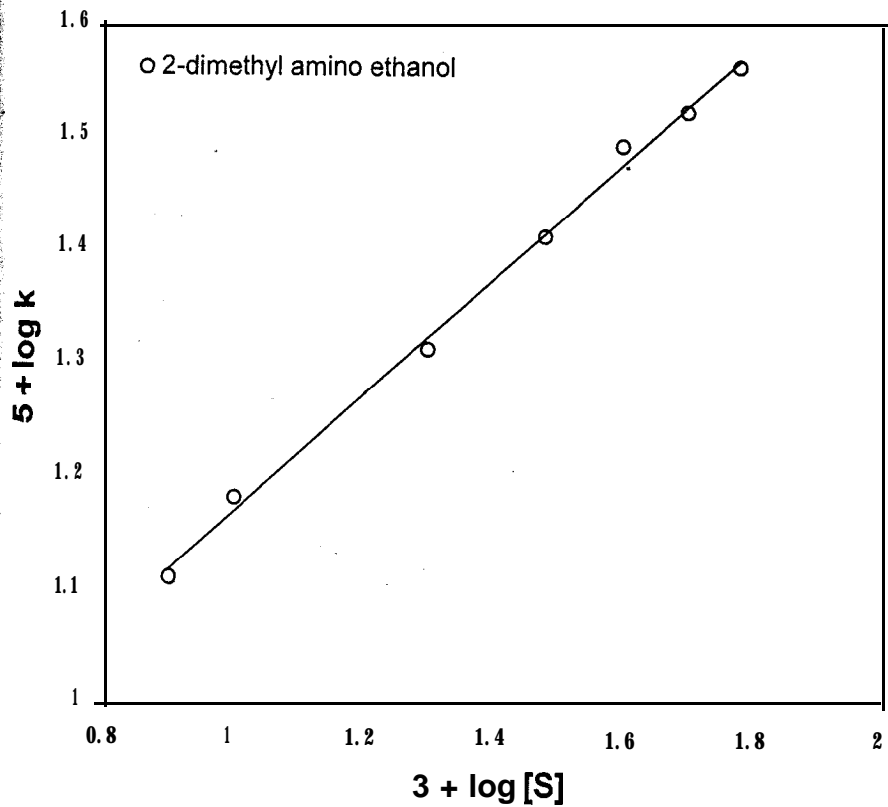


Fig. 4.2

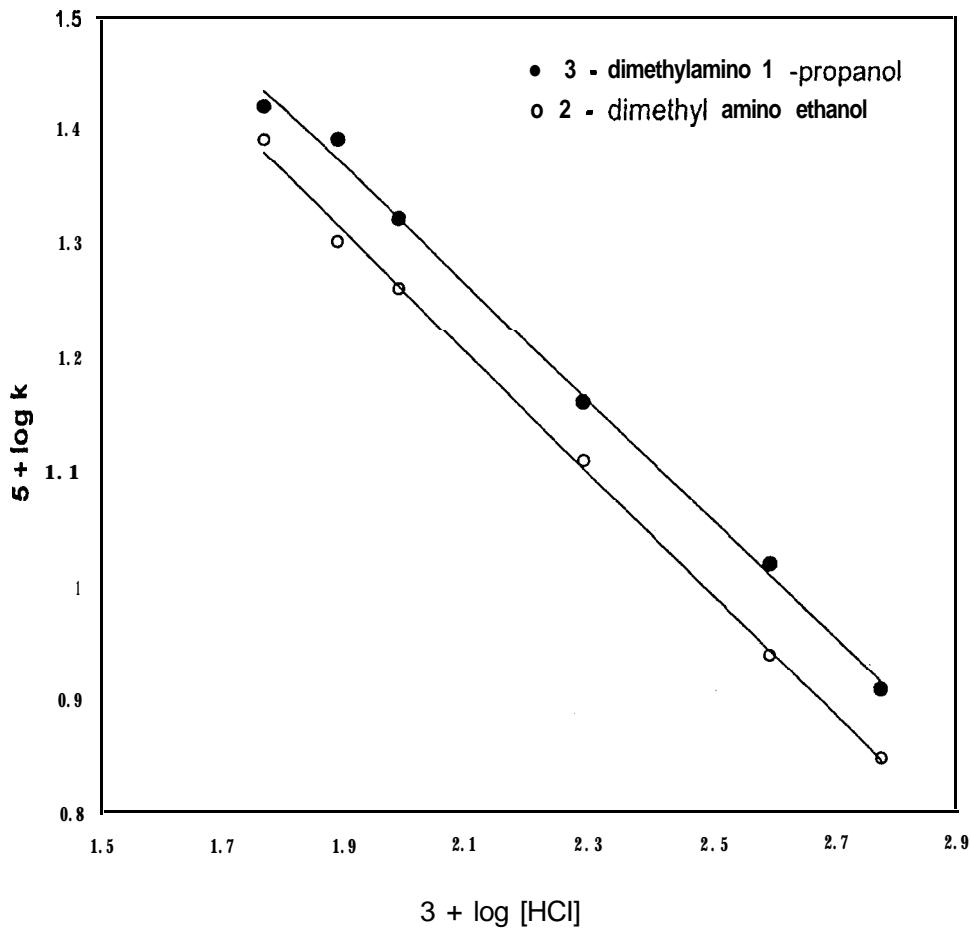


Fig 4.3

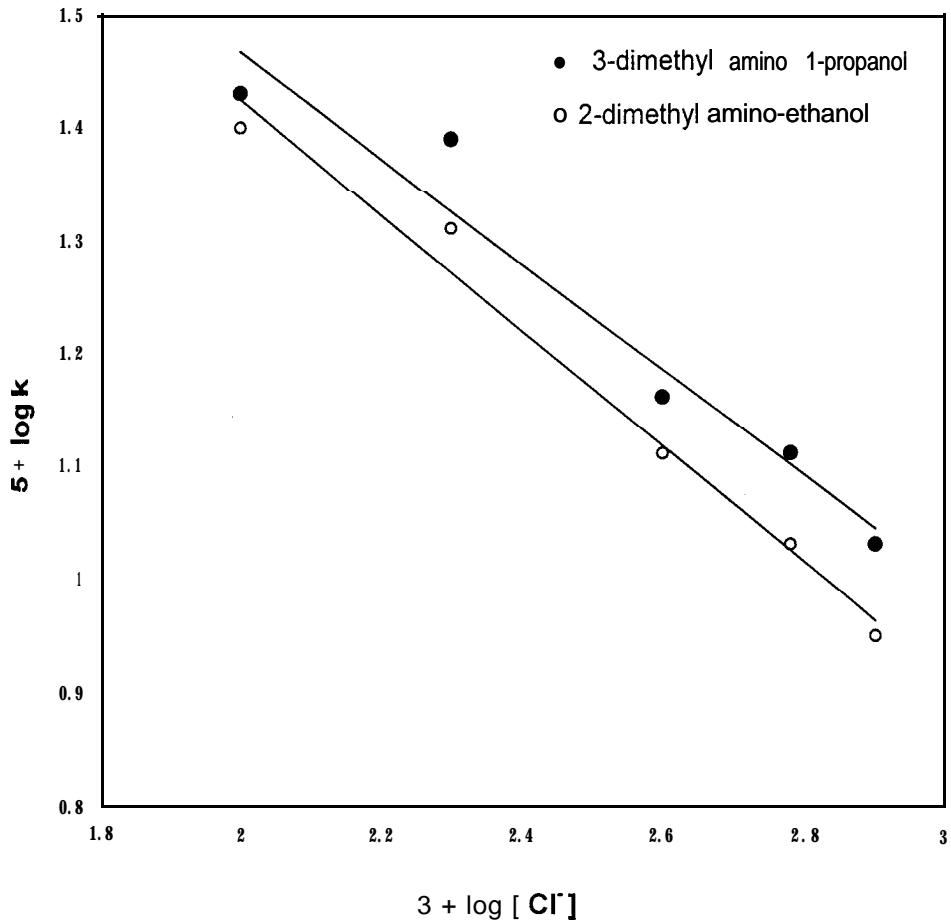


Fig. 4.4

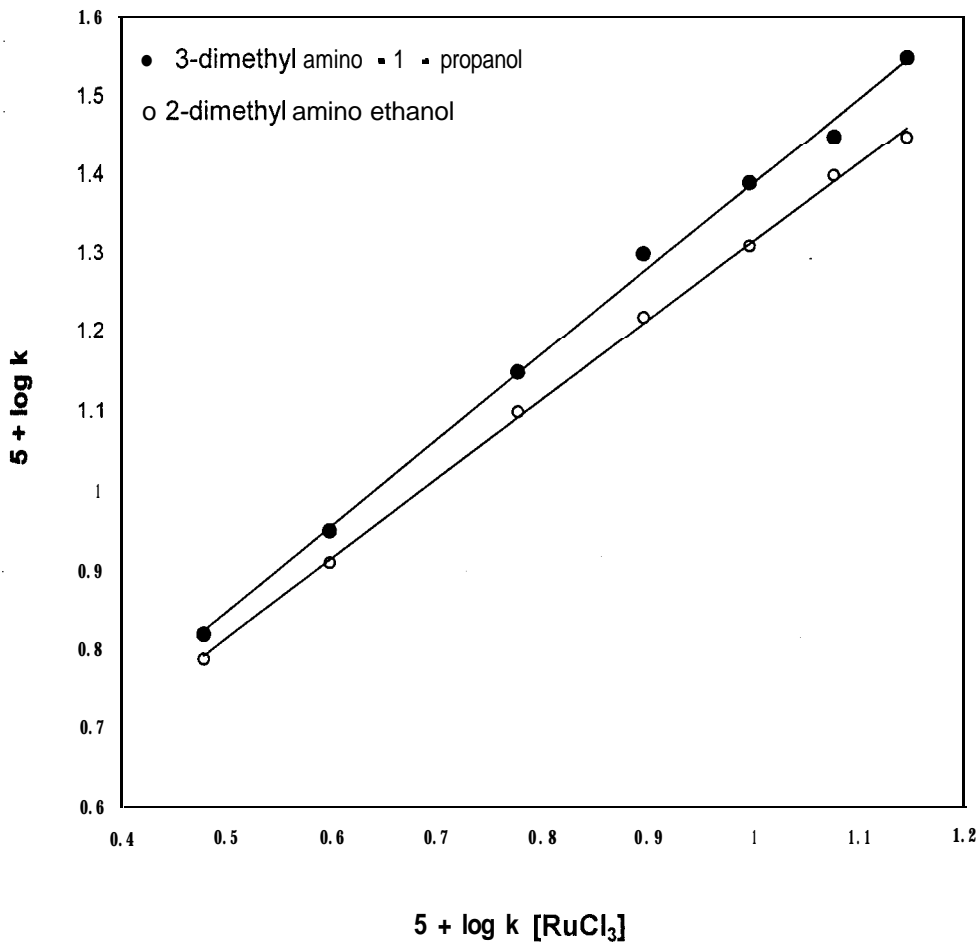


Fig. 4.5

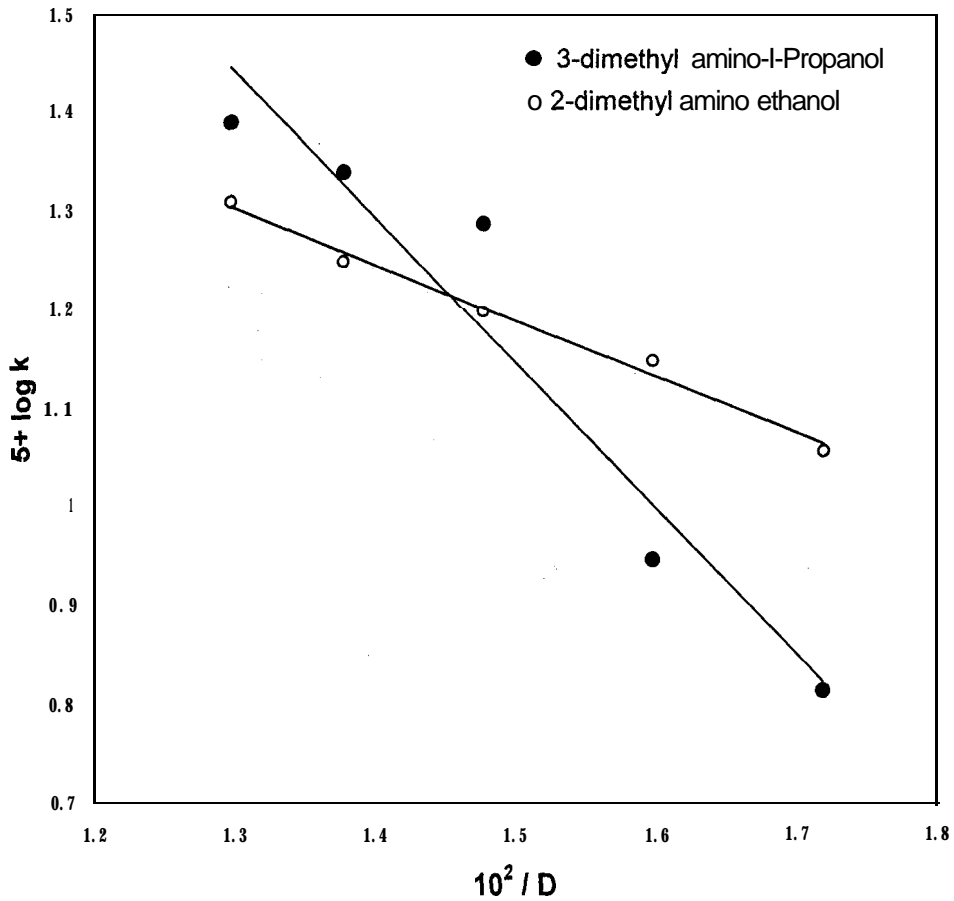


Fig. 4.6

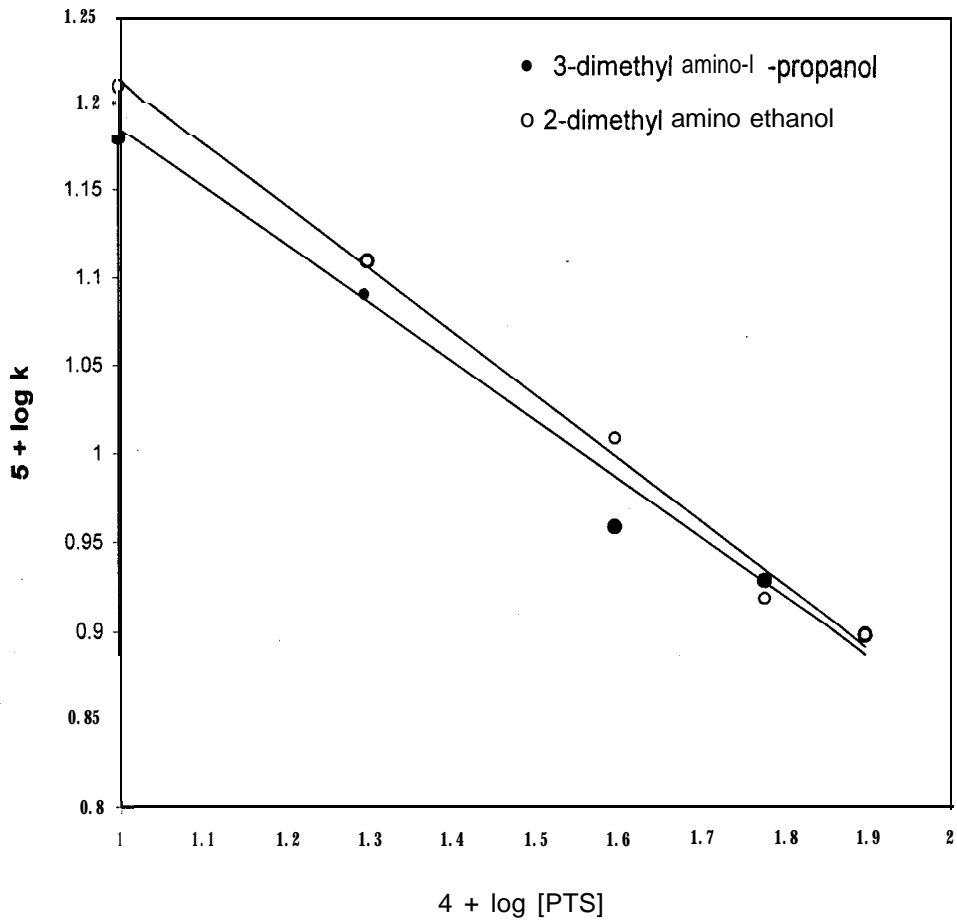


Fig. 4.7

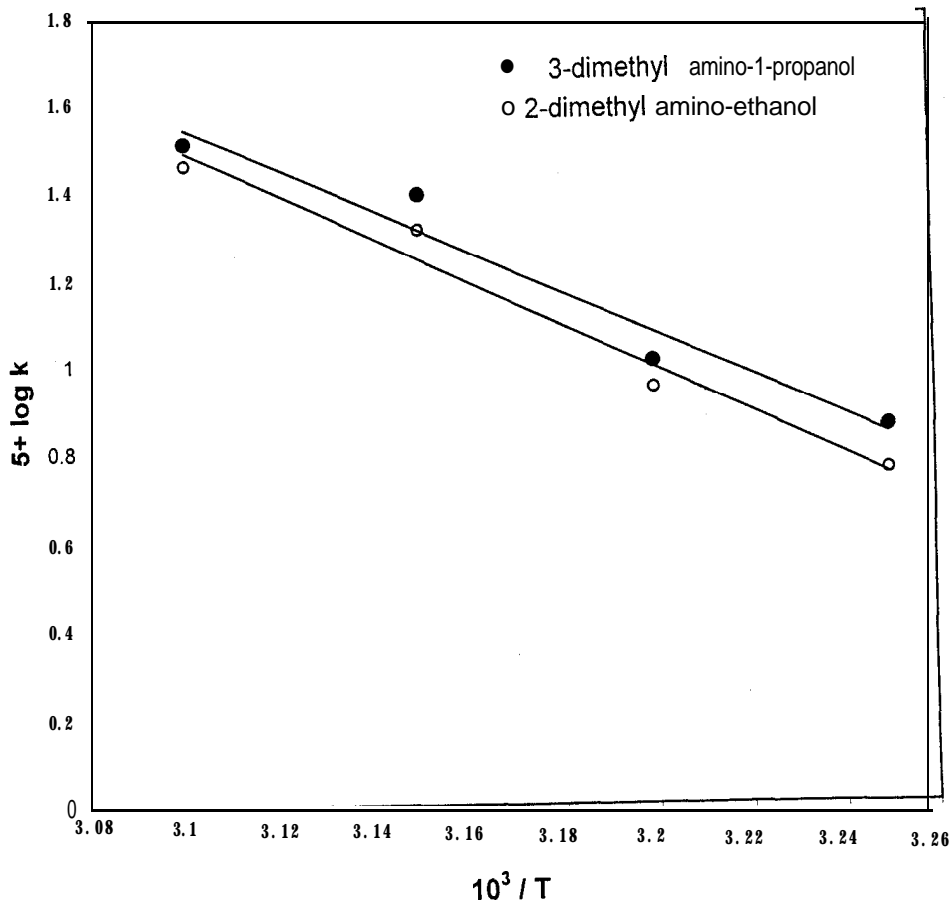


Fig. 4.8

DISCUSSION

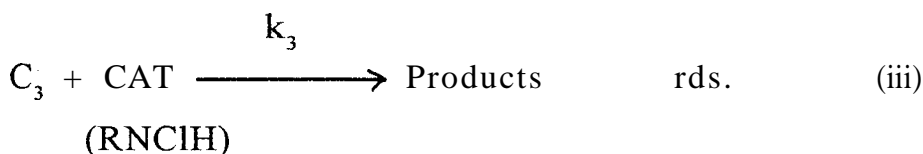
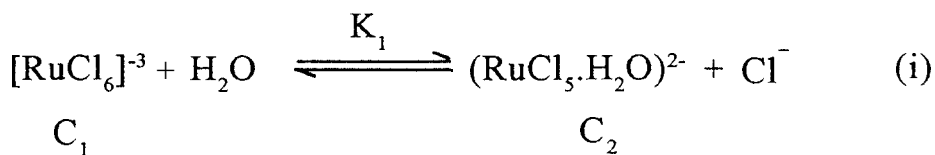
In aqueous solution, the sodium salt of aryl-N-halosulphonamide ionizes into several species in a pH dependent manner. In acidic solution the oxidising species of CAT are RNClH , RNCl_2 and HOCl , while in alkaline solution RNCl^- is the predominant oxidant species. The oxidation potential for CAT is 1.14v at pH 0.65 and 0.5v at pH 12.

Electronic spectral studies of Cady and Connick²⁷⁴, Connick and Fine²⁷⁵ reveal that species such as $[\text{RuCl}_5(\text{H}_2\text{O})]^{-2}$, $[\text{RuCl}_4(\text{H}_2\text{O})_2]^-$, $[\text{RuCl}_3(\text{H}_2\text{O})_3]$, $[\text{RuCl}_2(\text{H}_2\text{O})_4]^+$ and $[\text{RuCl}(\text{H}_2\text{O})_5]^{2+}$ do not exist in the aqueous solution of RuCl_3 . A study on oxidation states of ruthenium has shown that Ru (III) exists in the following equilibrium²⁷⁶⁻²⁷⁸ in acid medium :



Singh et al^{268,279} employed the above equilibrium in Ru (III) catalysed bromamine-T oxidation of some primary alcohols in acid medium and in the Ru (III) chloride catalysed oxidation of ethylene glycols by N-bromoacetamide (NBA) in HClO_4 medium. In the present case, addition of Cl^- ion in the form of NaCl at fixed $[\text{H}^+]$ retards the rate of reaction indicating that $[\text{Ru (III)Cl}_5(\text{H}_2\text{O})]^{-2}$ is the likely catalysing species.

In view of the first order dependence of rate on $[\text{CAT}]$ and $[\text{RuCl}_3]$, fractional order in $[\text{DMAE}]$ and inverse fractional order in $[\text{Cl}]$, the following mechanism is proposed for explaining the observed kinetics:



Scheme 4.1

Assuming steady state conditions for the intermediates, the rate law can be derived in the following manner for the oxidation of λ -dimethylamino ethanol by CAT :

$$\begin{aligned}
 [\text{Ru}]_t &= [C_1] + [C_2] + [C_3] \\
 &= \frac{[C_2][\text{Cl}^-]}{K_1[\text{H}_2\text{O}]} + \frac{[C_3]}{K_2[\text{S}]} + [C_3] \\
 &= \frac{[C_3][\text{Cl}^-]}{K_1[\text{H}_2\text{O}]K_2[\text{S}]} + \frac{[C_3]}{K_2[\text{S}]} + [C_3] \\
 &= [C_3] \left\{ \frac{[\text{Cl}^-]}{K'_1 K_2 [\text{S}]} + \frac{1}{K_2 [\text{S}]} + 1 \right\} \quad \text{where } K'_1 = K_1 [\text{H}_2\text{O}]
 \end{aligned}$$

$$= [C_3] \left\{ \frac{[Cl^-] + K'_1 + K'_1 K_2 [S]}{K'_1 K_2 [S]} \right\}$$

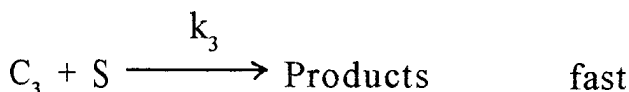
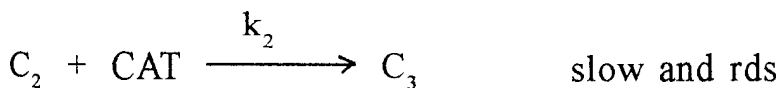
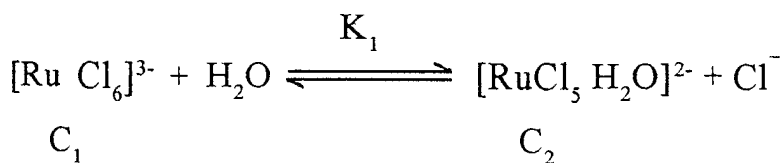
$$[C_3] = \frac{K'_1 K_2 [S] [Ru]_t}{[Cl^-] + K'_1 + K'_1 K_2 [S]}$$

$$\text{Rate} = k_3 [C_3] [CAT]$$

$$\frac{d [CAT]}{dt} = \frac{k_3 K'_1 K_2 [S] [Ru]_t [CAT]}{([Cl^-] + K'_1) + K'_1 k_2 [S]} \quad \dots 4.3$$

The above rate law is in agreement with the observed experimental results for DMAE.

A zero order in [S] is observed in respect of 3-dimethyl amino-1-propanol, which can be explained by scheme 4.2



Scheme 4.2

Assuming steady state conditions for the intermediates, rate law can be derived in the following manner.

$$[\text{Ru}]_t = [\text{C}_1] + [\text{C}_2] = \frac{[\text{C}_2] [\text{Cl}^-]}{K'_1} + \text{C}_2 = \text{C}_2 \left\{ \frac{[\text{Cl}^-] + K'_1}{K'_1} \right\}$$

$$[\text{C}_2] = \frac{K'_1 [\text{Ru}]_t}{[\text{Cl}^-] + K'_1}$$

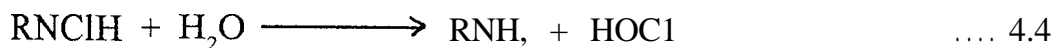
$$\text{rate} = k_2 [\text{C}_2] [\text{CAT}]$$

$$= \frac{k_2 K'_1 [\text{Ru}]_t [\text{CAT}]}{[\text{Cl}^-] + K'_1}$$

$$\frac{-d[\text{CAT}]}{dt} = \frac{k_2 K'_1 [\text{Ru}]_t [\text{CAT}]}{[\text{Cl}^-] + K'_1}$$

The above rate law is agreement with the experimental results.

It is noted that the rate of reaction decreases slightly with the added *p*-toluenesulphonamide which is one of the reaction products. It is likely that a small part of the reaction proceeds through an alternate mechanism involving HOCl as the oxidant species formed in the reaction



the proposed oxidant species in scheme 4.1 is predominately RNCIH.

The rate of reaction decreases with the decrease in the dielectric constant of the media. And a plot of $\log k_{\text{obs}}$ vs $1/D$ is linear (Table 4.8, Fig4.6, where D is the dielectric constant of the medium) with a negative slope. Suggesting an ion-dipole reaction (scheme - 4.1).

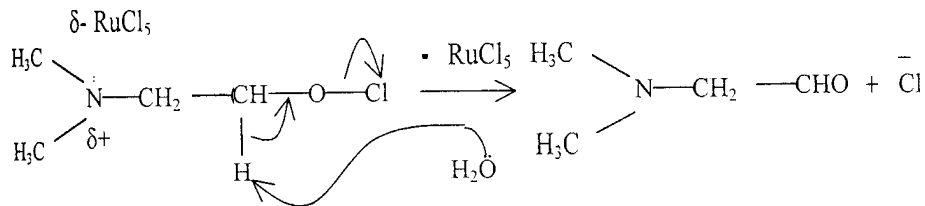
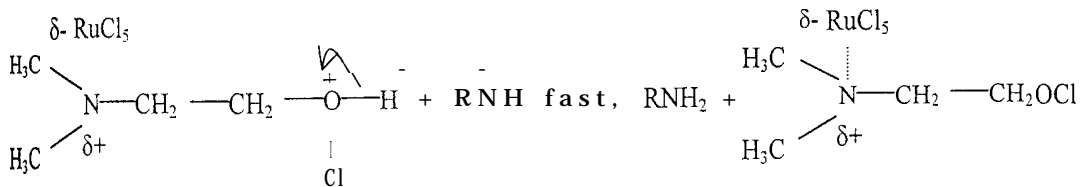
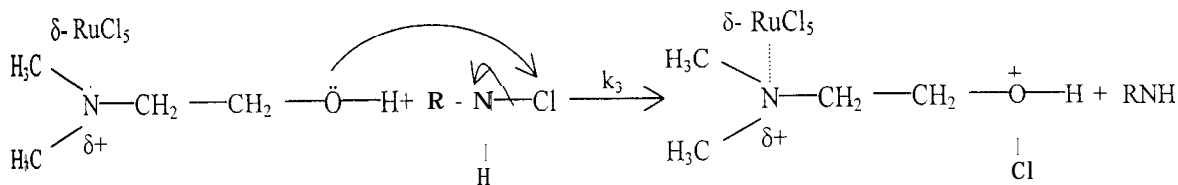
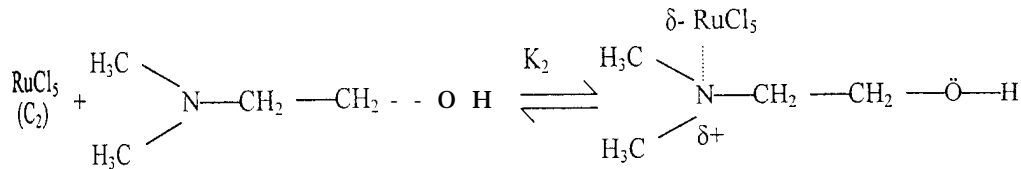
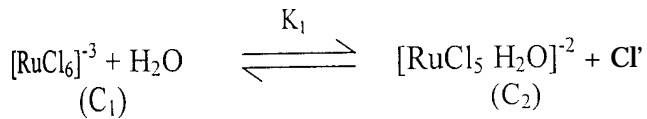
Variation of ionic strength of the medium had no effect on the rate, indicating that neutral molecules are involved in the rds.

The values of energy of activation are moderate and supports the rates observed for both the alcohols. The entropy of activation (ΔS^\ddagger) is negative indicating fairly ordered transition state.

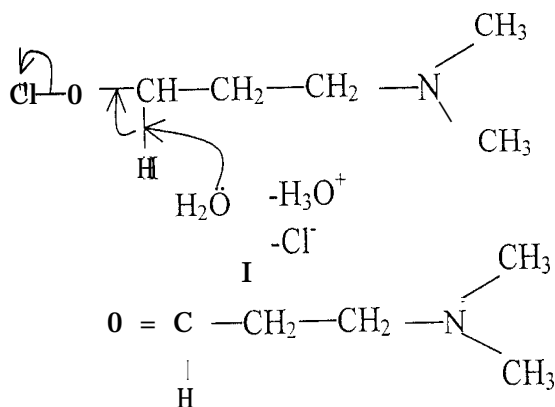
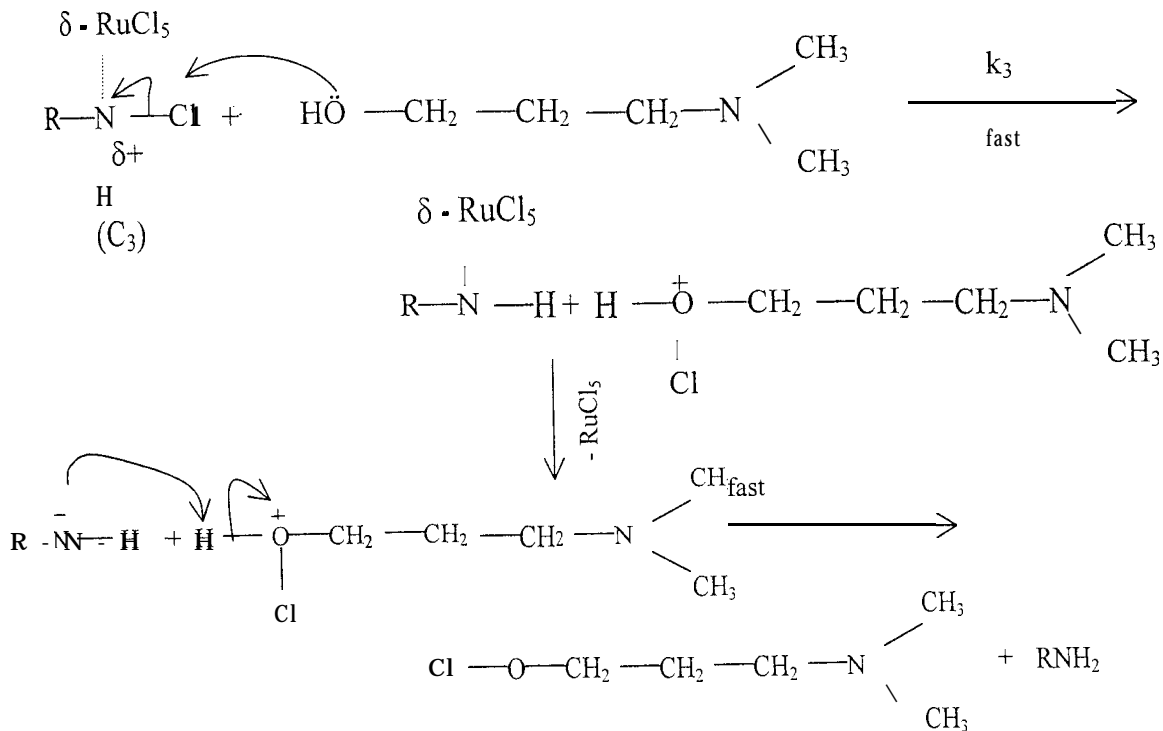
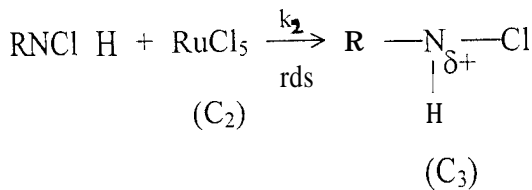
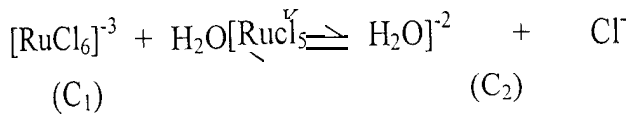
In case of DMAE it is observed that the lone pair of nitrogen on the substrate, undergoes complexation with (C_2) forming a species (C_3) . The rds involves the reaction of C_3 with $RNClH$ forming O -chlorination of species C_3 . Next the intermediate exchanges proton with RNH^- giving rise to hypohalite, which further decomposes to the product eliminating Cl^- .

In the case of DMAP it was observed that the $RuCl_5$ formed from $[RuCl_6]^{3-}$ first complexes with $RNClH$ forming a species C_3 in a rate limiting step. These species undergo reaction with DMAP in a fast step.

A detailed mechanistic picture of the oxidation of the two alcohols is given in schemes 4.3 and 4.4 respectively for DMAE and DMAP.



Scheme 4.3



Scheme 4.4

SUMMARY

The aromatic sulphonyl haloamines are organic haloamines with a positive halogen attached to nitrogen. They have diverse properties and behave both as oxidizing and halogenating agents. They are also used as analytical reagents in estimating a variety of reductants in solution. The prominent member of the aromatic sulphonyl haloamine series is the sodium salt of N-chloro-p-toluene sulphonamide, chloramine-T ($\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCINa} \cdot 3\text{H}_2\text{O}$) abbreviated as CAT. Chloramine-T is a by product of saccharin manufacture and its chemistry has been extensively reviewed.

In the present studies, the oxidative behaviour of CAT towards neutral a-amino acids ; D-glycine, DL-valine, L-alanine and L-phenylalanine, threose series sugars ; D-galactose (hexose), L-sorbose (keto-hexose), D-xylose and D-lyxose (pentoses), tertiary amino alcohols : 3-dimethylamino-1-propanol and 2-dimethylaminoethanol, have been studied extensively from a kinetic and mechanistic point of view.

Chapter I briefly sketches the chemistry of the aromatic sulphonyl haloamines, introduction to reaction kinetics, isotope effects and a literature survey of chloramine-T kinetics.

The kinetics and mechanism of oxidation of some neutral a-amino acids by CAT in perchloric acid medium at 30°C. Section 2.1 gives a brief introduction to a-amino acids, while section 2.2 reviews the available kinetic data on the oxidation of a-amino acids. Section 2.3 reports the kinetics and mechanism of oxidation of neutral a-amino acids by CAT in perchloric acid medium at 30°. In the present study, four neutral

u-amino acids namely, D-glycine, DL-Valine, L-alanine and L-phenylalanine have been studied.

It is observed that, first order dependence of rate on $[CAT]_0$ and $[SH^+]$ and inverse first order on $[H^+]$. Bearing these facts in mind, the general scheme involving the direct interaction of the amino acid $[S]$ formed from the protonated amino acid $[SH^+]$, with $RNCl^-$ in the rate determining step is proposed.

In stoichiometry experiments with $[CAT]_0 > [Amino\ acid]_0$, iodometric determination of the unconsumed CAT showed that one mole of the oxidant was consumed per mole of the amino acid to form the corresponding aldehyde. The aldehydes were characterized by their DNP derivatives and by their spectral data in comparison with the authentic aldehyde samples. The reduction product of CAT, p-toluene sulphonamide among the reaction products was detected by TLC using dichloromethane and petroleum ether (7:3 v/v) as the solvent system and iodine as the detecting agent ($R_f = 0.34$).

The variation of ionic strength and the addition of p-toluenesulphonamide and chloride ion had no effect on the rate. The rate of reaction decreases with increase in methanol content. The ratio $k_{obs}(D_2O)/k_{obs}(H_2O)$ was found to be ≈ 0.5 for all four amino acids. Tests for the applicability of Taft equation as well as single parameter correlations for the amino acids were also made. The near constancy of ΔG^\ddagger values indicates that a similar mechanism is operative in the oxidation of all the four amino acids. The rate of oxidation of amino acids increase in the order Ala > phe > val > Gly. It was found that ΔH^\ddagger and ΔS^\ddagger of the reaction were linearly related from which isokinetic

temperature ' β ' was found to be 323K. The relationships was found to be genuine by the exner criterion from which ' β ' was calculated as 333 K. It is seen that the value of ' β ' is higher than the experimental temperature (303 K) indicating enthalpy control of the reactions.

The kinetic and mechanistic investigations of threose series sugars by CAT in alkaline medium at 35° is described. A kinetic and mechanism of oxidation of threose series sugars, viz, D-galactose and L-sorbose (hexoses), D-lyxose & D-xylose (pentoses) have been studied. The oxidation reaction obeys the rate law.

$$\text{Rate} = k_{\text{obs}} [\text{S}] [\text{OH}^-]^2 [\text{CAT}]$$

In alkaline medium, the sugar undergoes the familiar Lobry de Bruyn Alberda van Ekenstein transformation and the enediol anion formed reacts with oxidant to form intermediate, which undergoes cleavage to form products.

From the stoichiometry experiments the amount of the oxidant consumed per mole of sugar was calculated iodometrically. The oxidation products were analyzed by HPLC, indicating that lyxonic, xylonic, threonic and glyceric acids are the products of oxidation for all threose series hexoses and pentoses. Besides these products, small quantities of corresponding aldonic acids were also detected. The identities of all the oxidation products were confirmed from their mass fragmentation patterns.

The addition of halide ions and reduced product p-toluensulphonamide did not affect the rate of reaction while change in ionic strength (I) increased the rate slightly and a plot of $\log k_{\text{obs}}$ vs $(I)^{1/2}$ was linear with a slope of 0.60 - 0.85. The rate decreased with decrease in dielectric constant (D) of medium. A plot of $\log k_{\text{obs}}$ vs $1/D$

was a straight line from which the size of activated complex " d_{AB} " could be calculated. The proposed mechanism is supported by the solvent isotope studies as the rate is almost doubled in D_2O medium suggesting a fast pre-equilibrium hydroxyl ion transfer. The solvent-isotope effect, $k_{obs}(H_2O) / k_{obs}(D_2O)$, was about 0.5 for all sugars. The constancy of ΔG^\ddagger values suggests that a common mechanism is operating in the kinetics of oxidation of threose series sugars by CAT in NaOH medium. The fractionation factor ϕ_j for the oxidation of sugars by CAT is about 0.6. This value resembles the fractionation factor of OH⁻ ion.

The kinetics and mechanism of oxidation of tertiary amino alcohols by CAT in hydrochloric acid medium at 45° using $RuCl_3$ as catalyst is described.

In the case of DAME, the reaction rate follows the first order dependence with respect to oxidant, $[RuCl_3]$ and fractional order dependence with respect to $[S]_0$, $[HCl]$, $[Cl^-]$ and $[PTS]$.

In the case of DMAP, the reaction rate follows the first order dependence with respect to oxidant, $[RuCl_3]$ and fractional order dependence with respect to $[HCl]$, $[Cl^-]$ and $[PTS]$. The reaction rate follows zero order with respect to substrate.

The effect of PTS, ionic strength and dielectric constant of the medium and temperature effect were studied to support the conclusion regarding the proposed reaction mechanism. Kinetic and thermodynamic parameters have been computed.

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APPENDIX

Regression analysis of the experimental data

Regression coefficient 'r' is given by the formula*,

$$r = \frac{\overline{XY} - \bar{X} \cdot \bar{Y}}{S_x \cdot S_y}$$

$$\text{Where } S_x = \sqrt{\frac{\sum X^2}{n} - \left(\frac{\sum X}{n}\right)^2}$$

$$\text{and } S_y = \sqrt{\frac{\sum Y^2}{n} - \left(\frac{\sum Y}{n}\right)^2}$$

where n = Number of trials

Using the above equations for a given set of X and Y values, S_x and S_y can be calculated and 'r' the regression coefficient can be obtained.

Standard deviation 'S' of the points from the regression line can be calculated by the formula,

$$S = \sqrt{\frac{nS_y^2 - \frac{n(\overline{XY} - \bar{X} \cdot \bar{Y})^2}{S_x^2}}{n - 2}}$$

Also, 'r' can be calculated by the formula, $r = m \frac{\sigma_y}{\sigma_x}$

where the standard deviation in X, namely, $\sigma_x = \sqrt{\frac{\sum X^2}{n} - (\bar{X})^2}$,

the standard deviation in Y, namely, $\sigma_y = \sqrt{\frac{\sum Y^2}{n} - (\bar{Y})^2}$,

and 'm' is the slope for a given straight line for a set of X and Y values.

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Oxidation of threose-series pentoses and hexoses by sodium *N*-chloro-*p*-toluenesulfonamide

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Received 17 November 1997; accepted 25 January 1998

Abstract

The kinetics and mechanism of oxidation of threose-series hexoses and pentoses by chloramine-T in alkaline medium was investigated. Kinetic studies with D-galactose, D-sorbose, D-xylose, and D-lyxose showed that the rate of the reaction was first order with respect to sugar and chloramine-T, and second order with respect to hydroxide ion. *p*-Toluenesulfonamide and chloride ions, the reduced products of chloramine-T, have no effect on the reaction rate. The rate increases with increase in ionic strength of the medium, and the dielectric effect is negative. Proton inventory studies in H₂O-D₂O mixtures suggested a single transition state. Product analysis for D-gulose, D-idose, L-sorbose, D-galactose, D-talose, D-tagatose, D-xylose, and D-lyxose revealed that all lyxose-series hexoses gave mainly mixtures of lyxonic and threonic acids with minor proportions of hexonic, xylonic and glyceric acids, whereas all xylose-series hexoses gave mixtures of lyxonic, threonic and glyceric acids with minor amounts of xylonic and hexonic acids. Xylose and lyxose gave mixtures consisting mainly of lyxonic, threonic, and glyceric acids with minor proportions of xylonic acid. From the results of kinetic studies, reaction stoichiometry, and product analysis, a possible mechanism for the oxidation of threose-series sugars with chloramine-T is suggested.

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Keywords: Threose-series sugars; Oxidation with chloramine-T; Kinetics and mechanism

1. Introduction

Recently, we reported on the kinetics and mechanism of oxidation of erythrose-series sugars,

D-glucose, D-mannose, D-fructose, D-arabinose and D-ribose, with chloramine-T (CAT) in alkaline medium at 35 °C [1]. The observed reaction stoichiometry, 2-3 moles of CAT per mole of sugar, was significantly different from the previously reported sugar to oxidant stoichiometry of 1:1 for aldoses and 1:2 for fructose [2-4]. We have also shown by HPLC and GLC-MS analyses that the products of oxidation for erythrose-series sugars (both pentoses and hexoses) were mixtures of aldonic acids consisting of arabinonic, ribonic, erythronic, and glyceric acids [1]. These product

Abbreviations: CAT, RNCINa or chloramine-T, sodium salt of *N*-chloro-*p*-toluenesulfonamide; S, sugar, D, dielectric, T, absolute temperature; E_a, activation energy; n, atom fraction of deuterium, TS, transition state; RS, reactant site; I, ionic strength; d_{AB}, size of the activated complex; k, Boltzmann constant; HPLC, high-performance liquid chromatography; GLC-MS, gas-liquid chromatography-mass spectrometry.

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profiles were also different from those reported previously, the corresponding aldonic acids for aldoses and arabinonic acid for fructose [2-4].

Our recent study on the oxidation of erythrose-series sugars with CAT gave two interesting results [1]. First, the sugars that can exist in the furanose ring form in appreciable proportions reacted with CAT much faster than those which exist almost exclusively in the pyranose form. Thus, for hexoses, rate of oxidation of fructose was higher than glucose and mannose. Similarly, ribose was oxidized faster than arabinose. Second, surprisingly the products formed from both pentoses and hexoses, including keto-hexoses, were strikingly similar for all erythrose-series sugars studied. Based on these results, we proposed a novel pathway for the oxidation of erythrose-series sugars by CAT [1]. In the present study, the mechanism of oxidation of threose-series sugars by CAT was investigated by kinetic studies and product analysis. The results demonstrate that the kinetic and thermodynamic properties, and mechanism of oxidation of threose-series sugars are generally similar to those observed for the erythrose-series sugars.

2. Experimental

Materials.—Chloramine-T (E. Merck) was purified from dichloro contaminants by washing with CCl_4 . D-galactose, D-xylose, D-lyxose, D-idose, D-talose, D-tagatose, D-gulose, D-gluconic acid, D-galactono-1,4-lactone, and D-ribo-1,4-lactone, were purchased from Sigma Chemical Co. (St. Louis, MO). L-sorbose, D-mannono-1,4-lactone, D-xylo-1,4-lactone, and D-arabino-1,4-lactone, were from Pfanstiehl (Waukegan, IL). D_2O (99.4%) was from Bhabha Atomic Research Center (Bombay, India).

Kinetic measurements.—The reactions were carried out in glass stoppered pyrex boiling tubes coated black on the outside [1]. Pseudo-first order conditions ($[\text{sugar}]_0 \gg [\text{CAT}]_0$) were maintained for all kinetic studies. Stock solutions of alkali, CAT, sugars, and NaClO_4 were maintained at 35 °C. From these stock solutions, the requisite mixtures of sugars, alkali, and NaClO_4 were prepared. The reaction was initiated by the addition of CAT and monitored by iodometric determination of unconsumed CAT at various time-intervals. Sodium perchlorate was used to "swamp" the

reaction. The solvent isotopic studies were performed with D_2O .

Pseudo-first order rate constants (k_{obs}) were calculated from the plots of $\log[\text{CAT}]_0$ versus time, and these were within $\pm 3\%$. Regression coefficient r and the standard deviation s , were determined by regression analysis of the experimental data using an EC-72 statistical calculator.

Stoichiometry and product analysis.—The reaction mixtures containing sugar (0.01 M), alkali (0.1 M), and CAT (0.05 M) were kept for 24 h at 35 °C. The unconsumed CAT was determined iodometrically. From these data, the amount of the oxidant consumed per mole of sugar was calculated.

The oxidation products were analyzed by a Dionex HPLC system with pulsed amperometric detection using a CarboPac PA1 high-pH anion-exchange column (4x250 mm) as reported previously [1,5]. Isocratic elution with 0.2 M NaOH was used. The products were identified by comparison of the retention times with retention times of the standard aldonic acids, as reported previously [1].

3. Results

The kinetics of oxidation of threose-series sugars with CAT were generally similar to those observed previously for the erythrose-series sugars [1]. When sugars were used in excess, the plots of $\log[\text{CAT}]$ versus time were linear ($r > 0.9980$, $s \leq 0.02$), indicating a first-order dependence of reaction rate on $[\text{CAT}]_0$. The pseudo-first-order rate constants (k_{obs}) calculated from these plots are shown in Table 1. The rate increased with increase in $[\text{S}]_0$ (where S = sugar) and the plots of $\log k_{\text{obs}}$ versus $\log[\text{S}]_0$ were linear ($r > 0.9998$, $s \leq 0.01$) with unit slopes, indicating a first-order dependence with respect to sugars. Furthermore, the plots of k_{obs} versus $[\text{S}]_0$ passed through the origin ($r > 0.9855$, $s \leq 0.04$), suggesting that the sugar-oxidant complexes have only transient existence.

The rate of oxidation also increased with an increase in alkali concentration (Table 2). The plots of $\log k_{\text{obs}}$ versus $\log[\text{HO}^-]$ ($r > 0.9990$, $s \leq 0.01$) indicated that the reactions follow second-order dependence on $[\text{HO}^-]$.

Addition of p-toluenesulfonamide (0 to 0.008 M) did not affect the reaction rate, suggesting that the reduced product of CAT, p-toluenesulfonamide, is

Table 1
Effect of reactant concentrations on the rate of oxidation of sugars by CAT at 35 °C

[CAT] ₀ (m)	10 ² [S] ₀ (m)	10 ⁴ k _{obs} (s ⁻¹)			
		D-galactose	L-sorbose	D-xylose	D-lyxose
0.5	2.0	3.2	13.3	14.0	5.8
1.0	2.0	3.0	12.9	13.4	5.5
1.5	2.0	3.1	12.9	13.4	5.6
2.0	2.0	3.2	13.0	13.9	5.6
2.5	2.0	3.2	13.0	14.1	5.5
3.0	2.0	3.3	13.0	14.4	5.6
4.0	0.6	0.9	3.8	4.9	1.6
5.0	0.8	1.2	5.0	6.0	2.1
6.0	1.0	1.5	6.3	7.8	2.7
8.0	3.0	4.9	19.8	23.8	8.4
10.0	4.0	6.6	26.3	33.3	11.3
15.0	6.0	10.2	41.9	64.0	15.4

[HO⁻] = 0.1 M, and [I] = 0.4 M.

not involved in pre-equilibrium with the oxidant. Addition of NaCl (0 to 0.02 M) to the reaction mixtures had no effect on the rates, suggesting that the free chloride ion was not formed before the rate-limiting step.

Addition of NaClO₄ (0 to 0.8 M) increased the rate of reaction. The plots of log k_{obs} versus I^{1/2} (I = the ionic strength of medium) were linear with fractional slopes of 0.60–0.85 (not shown).

The rate decreased with an increase in methanol content. The plots of log k_{obs} versus 1/D (r > 0.9970, s ≤ 0.04; D = dielectric constant of the medium) were linear with negative slopes (Fig. 1).

The Arrhenius plots of log k_{obs} versus 1/T (T = absolute temperature), for reactions studied over a range of temperatures (303 to 318 K), were found to be linear (r > 0.9991, s ≤ 0.01) (not shown). The activation energies (E_a, Table 3) were calculated from the slopes of the plots. From the values of E_a and the thermodynamic parameters ΔH[#], ΔS[#], and ΔG[#] (Table 3) were computed. Sor-

Table 2
Effect of [NaOH] on the rate of oxidation of sugars by CAT at 35 °C

10 ² [NaOH] (m)	10 ⁴ k _{obs} (s ⁻¹)			
	D-galactose	L-sorbose	D-xylose	D-lyxose
2.0	0.2	0.5	1.1	0.3
4.0	0.6	2.1	3.4	1.0
6.0	1.5	5.0	7.1	2.4
8.0	2.2	8.0	11.3	4.1
10.0	3.0	12.9	13.4	5.5
15.0	6.8	36.2	38.4	17.8

[CAT]₀ = 0.002 M, [S]₀ = 0.02 M, and [I] = 0.4 M.

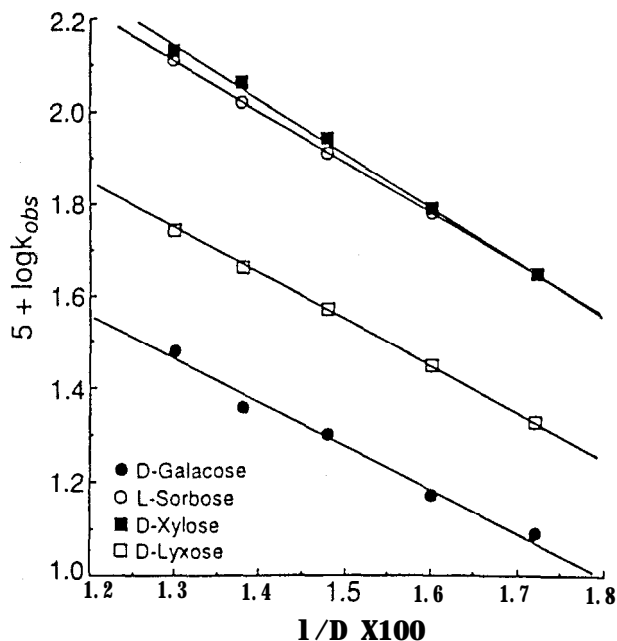


Fig. 1. Plots of log k_{obs} versus 1/D. [CAT]₀ = 0.002 M, [S]₀ = 0.002 M, [OH⁻] = 0.1 M, [I] = 0.4 M; temperature = 35 °C.

bose and xylose have lower E_a and ΔS[#] values as compared with other sugars studied. A low enthalpy change for sorbose and a negative enthalpy change for xylose suggest that the structures of sorbose and xylose are favorably disposed for oxidation by CAT. Thus, a keto-enolic anion appears to be the readily reacting structure for hexoses and an aldo-enolic one for pentoses. Previously, it was observed, for erythrose-series sugars, that a fructose-enolic anion is the readily reacting structure for the hexoses and an aldo-enolic form is that reacting for the pentoses [1].

The oxidation of sugars by CAT was studied in H₂O–D₂O mixtures containing varying deuterium atom fractions n. As in the case of erythrose-series sugars [1], the oxidation was faster in D₂O for the threose-series sugars (Table 4). The solvent-isotope effects, k_{obs}(H₂O)/k_{obs}(D₂O), were between 0.5 and

Table 3
Thermodynamic parameters for the oxidation of sugars by CAT at 35 °C

Sugars	E _a (kJ mol ⁻¹)	ΔH [#] (kJ mol ⁻¹)	ΔG [#] (kJ mol ⁻¹)	ΔS [#] (JK ⁻¹ mol ⁻¹)	Log A
D-galactose	121	119	96	72	21
L-sorbose	98	96	93	9	17
D-xylose	91	89	93	-12	16
D-lyxose	111	109	95	44	19

[CAT]₀ = 0.002 M, [HO⁻] = 0.1 M, [S]₀ = 0.05 M, and [I] = 0.4 M.

Table 4
Proton-inventory studies for the oxidation of sugars by CAT in
D₂O mixtures at 35 °C

Form fraction deuterium (<i>n</i>)	10 ⁴ <i>k</i> _{obs} (s ⁻¹)			
	D-galactose	L-sorbose	D-xylose	D-lyxose
0	3.2	12.9	13.4	5.5
0.5	3.4	15.4	16.1	6.4
1.0	4.0	18.3	18.6	7.6
1.5	5.0	22.0	22.3	8.9
2.0	5.8	25.5	25.3	10.4

[CAT]₀ = 0.002 M, [HO⁻] = 0.1 M, [S]₀ = 0.02 M, and [I] = 0.001 M.

for all sugars (Table 4). Proton-inventory plots (not shown), *k*_{obs}(H₂O)/*k*_{obs}(D₂O) versus *n*, were linear and similar to those obtained previously for erythrose-series sugars (1).

The oxidant to sugar stoichiometry of nearly 3 was observed for all sugars except for lyxose (Table 5).

Although kinetic studies could not be carried out for gulose, idose, talose and tagatose due to the limited availability of the sugars, the oxidation products were analyzed for all threose-series hexoses (Fig. 2). HPLC analysis indicated that lyxonic, xylo-lyxonic, threonic, and glyceric acids are the products of oxidation for all threose-series hexoses and pentoses (Fig. 2a-c, and Table 5). Xylose and lyxose gave major proportions of lyxonic, threonic and glyceric acids and minor proportions of xylo-lyxonic acid (Fig. 2c). The xylose-series hexoses (gulose, idose, and sorbose) gave predominantly threonic and glyceric acids with minor proportions of xylo-lyxonic and lyxonic acids (Fig. 2b). On the other hand, all lyxose-series hexoses (galactose, talose,

and tagatose) gave threonic and lyxonic acids as predominant products with small amounts of glyceric and xylo-lyxonic acids (Fig. 2a). All hexoses except sorbose gave minor amounts of hexonic acids (Fig. 2a and b). Furthermore, all threose-series sugars except lyxose and galactose were oxidized almost quantitatively by CAT; after 24 h incubation with CAT at 35 °C, 20-25% of lyxose and 5% of galactose remained unoxidized (Fig. 2a-c).

The oxidation products were analyzed at 0.5, 1, 2, 4, 8, 20, and 24 h for all the sugars. The relative proportions of various aldonic acids formed were similar at all time-points analyzed. Approximately 95% of sorbose and idose were oxidized by CAT in 4 h at 35 °C, whereas 90% oxidation of gulose required about 8 h. When gulose and idose were treated with alkali in the absence of CAT, a gradual build up of sorbose was observed for both sugars; for example, about 30% of gulose was isomerized to sorbose in 2 h. However, when gulose and idose were treated with both CAT and alkali, only a minor proportion of sorbose was detected from each reaction mixture at all time-points analyzed, suggesting that sorbose formed by the alkali-catalyzed isomerization readily reacts with CAT. Sorbose treated with alkali alone was not isomerized to gulose and idose to detectable levels. These data indicate that the keto-isomer is the reactive species.

About 95% of tagatose was oxidized by CAT in 2 h at 35 °C, whereas oxidation of similar amounts of galactose and talose required >20 h. When galactose and talose were treated with alkali alone, significant amounts of tagatose formed by the isomerization of these sugars could be detected. For example, 17% of talose and 23% of galactose were

Table 5
HPLC analysis of the products formed by the oxidation of sugars by CAT in alkaline medium

Sugar	Mol of CAT consumed per mol of sugar	Products (approximate percentage) ^a				
		Glyceric acid	Threonic acid	erythroic acid ^b	Xylo-lyxonic acid	Lyxonic acid
D-galactose	2.8	9	44	3	32	12
D-talose	n.d.	9	45	2	32	11
D-tagatose	n.d.	12	47	2	27	12
D-gulose	2.9	38	38	12	5	7
D-idose	n.d.	40	40	8	5	7
D-sorbose	n.d.	44	44	9	3	—
D-xylose	2.8	20	37	7	36	—
D-lyxose	1.9	25	32	6	37	—

^a based on the peak areas.

^b Peak 2 in Fig. 4 represents 95-96% threonic acid and 4-5% threonic acid, which can be separated by using a low flow rate.

n.d., Not determined.

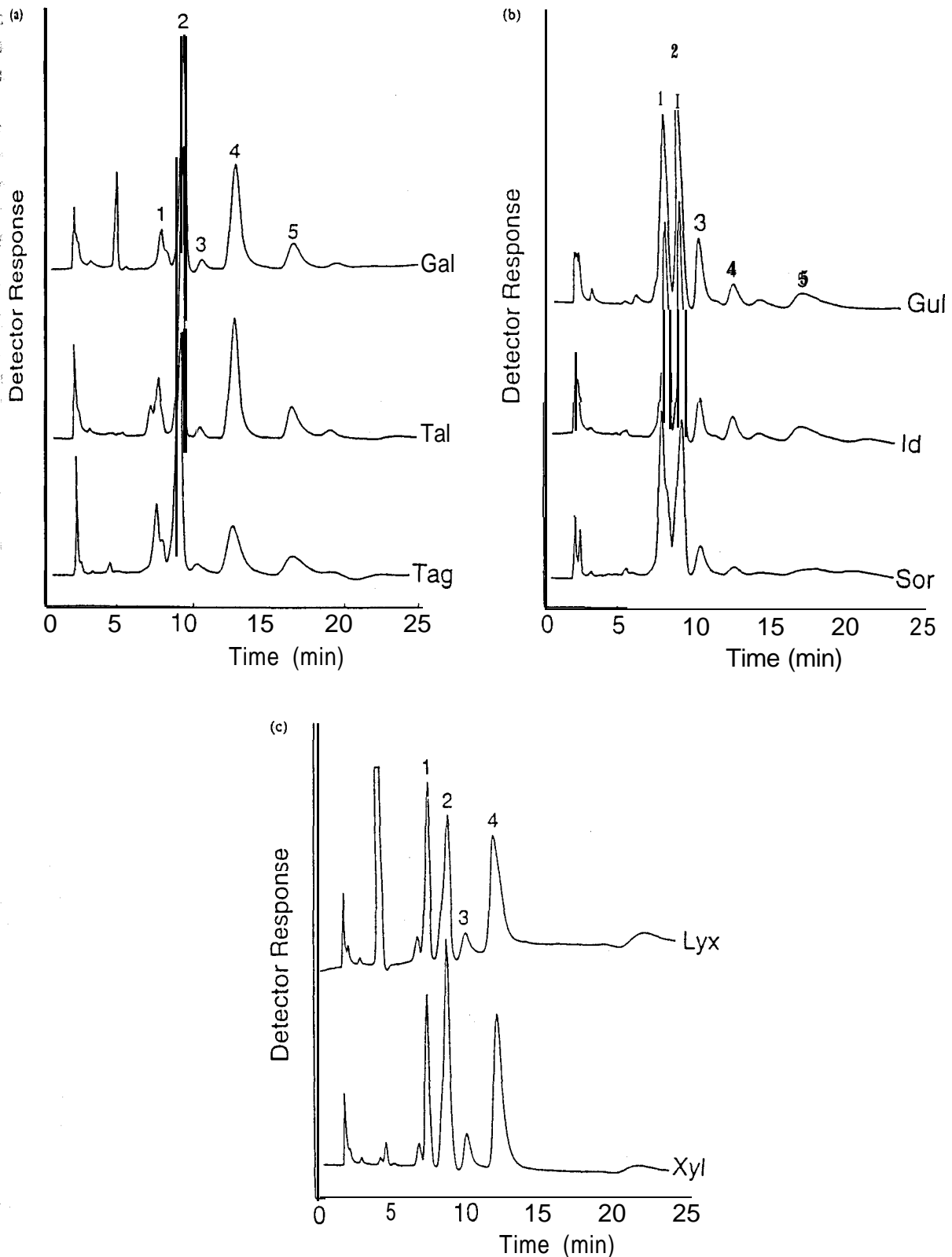


Fig. 2. HPLC analysis of the products formed by the oxidation of sugars (0.01 M) by CAT (0.05 M) in the presence of alkali (0.1 M) at 35 °C. 1, glyceric acid; 2, threonic acid (~95%) plus erythronic acid (-5%); 3, xylonic acid; 4, lyxonic acid; 5, hexonic acid. Gal, Tal, Tag, Gul, Ido, Sor, Xyl and Lyx, respectively represent HPLC chromatograms of the reaction of CAT with D-galactose, D-talose, D-tagatose, D-gulonic acid, D-idonic acid, L-sorbitol, D-xylose, and D-lyxose. Peak 2 in (a)-(c) represents 95-96% threonic acid and 4-5% threonic acid which can be separated by using a low flow rate. Note: about 20-25% of lyxose (retention time 4.6 min in (c)) and -5% galactose (retention time 5.0 min in (a)), and 1-2% of xylose (retention time 5.0 min in (c)) were not oxidized by CAT; all other sugars were almost quantitatively oxidized.

omerized to tagatose in 4 h. However, when xylulose was treated with both CAT and alkali, 98% of oxidized xylulose was accounted by 1% tagatose, 1% galactose, and 98% talose. Similarly, when fructose was treated with both CAT and alkali, tagatose was barely detectable. Upon treatment with alkali at 35 °C, only 1–2% of tagatose was isomerized into galactose and talose. Together, these data indicated that for lyxose-series hexoses, in the case of the xylo-series hexoses, the keto-enolomer (tagatose) is the reactive species.

All of the aldohexoses studied here were oxidized mainly to pentonic and tetronic acids rather than to hexonic acids. This finding is in agreement with the foregoing conclusion that hexoses are oxidized by CAT in the keto-enolic form. Moreover, we have previously shown, based on the ease of aldose–ketose isomerization, and relative rates of oxidation and product profiles, that glucose and mannose undergo oxidation by CAT predominantly in the fructose-enolic form [1].

For all the hexoses studied here, threonic and pentonic acids were formed within 30 min; hexonic acids were detectable in minor proportions only after significant amounts of the former products were formed. This demonstrates that the lower-carbon aldonic acids were not derived from the initially formed six-carbon aldonic acids. We have previously shown that D-gluconic, D-mannonic, D-galactonic, D-ribonic, and D-arabinonic acids were not oxidized by CAT [1].

Formation of high proportions of pentonic acids from xylulose and lyxose suggest that pentoses react with CAT predominantly in the aldo-enolic form. The formation of glyceric acid also in high proportion suggest that appreciable amounts of xylose and lyxose react in the keto-enolic form to give glyceric and threonic acids.

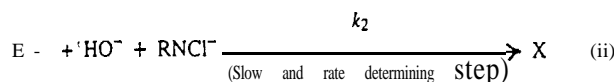
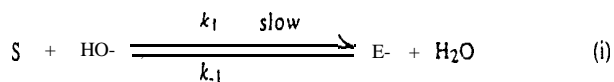
4. Discussion

In aqueous solutions, sodium salts of aryl-*N*-halosulfonamides ionize into several species in a pH dependent manner [6–8]. In acidic solutions, the oxidizing species of CAT are RNCIH, RNCI₂, and HOCl, while in alkaline solution RNCI⁻ is the active oxidant [6–10].

In alkaline solutions, sugars undergo isomerization to an equilibrium mixture of aldoses and ketoses which exist as enediol anions (E⁻) [11]. The enediol-anions (E⁻, keto-enolic anions of hexoses

and aldo-enolic anions of pentoses) react with RNCI⁻ to form an intermediate (X), which undergoes cleavage to form products (Fig. 3). From the results of the kinetic study, the oxidation of sugars is predicted to proceed through the reaction sequences shown in Scheme 1.

Under steady state conditions for E⁻, the rate of



Scheme 1.

disappearance of CAT is given by

$$\text{Rate} = -\frac{d[\text{CAT}]}{dt} = \frac{k_2 k_1 [S][HO^-]^2 [\text{CAT}]}{k_{-1} [H_2O] + k_2 [HO^-] [\text{CAT}]} \quad (1)$$

Since $k_{-1} [H_2O] > k_2 [HO^-] [\text{CAT}]$, rate law (1) is reduced to

$$\text{Rate} = -\frac{d[\text{CAT}]}{dt} = \frac{k_2 k_1 [S][HO^-]^2 [\text{CAT}]}{k_{-1} [H_2O]} \quad (2)$$

which agrees with the observed rate = $k_{\text{obs}} [S][OH^-]^2 [\text{CAT}]$.

The observed first-order dependence of rate on [CAT], and [S]₀ and second-order dependence on [HO⁻] agree with eq (2).

Since DO⁻ is a stronger base than HO⁻ by a factor of 2, the reaction rate is expected to be doubled in D₂O for reactions involving a fast pre-equilibrium H⁺ or HO⁻ ion transfer [12]. In agreement with this, the observed values of the inverse solvent isotope effect $k_{\text{obs}}(\text{D}_2\text{O})/k_{\text{obs}}(\text{H}_2\text{O})$ were approximately 2 for the sugars (Table 4). The results of proton inventory plots (not shown) are also in accordance with Scheme 1. The dependence of rate constant (k_{obs}^n) on n (n = the atom fraction of deuterium in a solvent mixture of H₂O and D₂O) [13,14] is given by the Gross-Butler eq (3).

$$k_{\text{obs}}^n/k_{\text{obs}}^o = \frac{\prod^{\text{TS}}(1 - n + n\phi_i)}{\prod^{\text{RS}}(1 - n + n\phi_j)} \quad (3)$$

where ϕ_i and ϕ_j are isotopic fractionation factors for the isotopically exchangeable hydrogen sites in the transition state (TS) and reactant site (RS), respectively. If the reaction proceeds through a single transition state, then eq (3) becomes eq (4):

$$(k_{\text{obs}}^n/k_{\text{obs}}^o) = 1 + n(\phi_j - 1) \quad (4)$$

A comparison of the plots of k_{obs} versus n (not shown) with the standard curves [15], suggested a single proton exchange in the transition state. Furthermore, the plots of $k_{\text{obs}}^n/k_{\text{obs}}^o$ versus n (Fig. 1) were linear with slopes ($\phi_j - 1$). The ϕ_j for the oxidation of sugars by CAT is about 0.6. This value resembles the fractionation factor of HO⁻ ion.

Since the rate-determining step in Scheme 1 involves three negative ions, the reaction rate is expected to increase with an increase in the ionic strength (I) of reaction medium. The plots of $\log k_{\text{obs}}$ versus $I^{1/2}$ were linear with slopes between 0.50 and 0.85, even though the ionic strengths employed were beyond the Debye-Hückel range. The theoretical slope of unity has not been realized, possibly due to the formation of Bjerrum ion pairs in concentrated solutions [16].

The rate decreased with decrease in the dielectric constant (D) of the reaction medium. The plots of $\log k_{\text{obs}}$ versus $1/D$ (D = dielectric constant) were linear with negative slopes (Fig. 1). The effect of solvent composition on the rate of a reaction involving two negative ions is given by eq (5) [16]:

$$\log k = \log k_o - Z_A Z_B e^2 / DkT d_{AB} \quad (5)$$

where k_o is the rate constant in a medium of infinite dielectric constant, $Z_A e$, and $Z_B e$ are the charges on ions, d_{AB} is the size of the activated complex, k is the Boltzmann constant, and T is the absolute temperature. From the slopes of the straight lines in Fig. 1 (slope = $-Z_A Z_B e^2 / kT d_{AB}$), d_{AB} was calculated. The derived d_{AB} values for D-galactose, L-sorbose, D-xylose, and D-lyxose are 2.70, 2.20, 2.02, and 2.40 Å, respectively. These values are comparable with those obtained for similar reactions [16].

According to Scheme 1, the rate-determining step should involve interactions between similarly

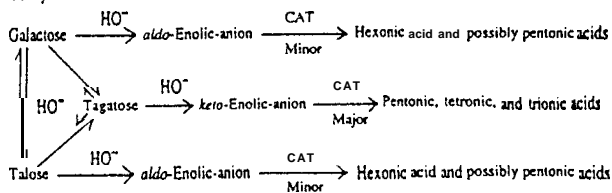
charged ions (eq (ii) requiring a very high activation energy. The observed high activation energies (Table 3) agree with this prediction. Nearly constant ΔG^\ddagger values (Table 3) suggest that a common mechanism is operative for the oxidation of sugars.

In a previous study on erythrose-series hexoses [1], it was observed that each of the sugars studied was oxidized by CAT predominantly to pentonic and threonic acids. However, for the threose-series hexoses studied here, the product profiles can be grouped into three categories, profiles consisting of: (a) predominant proportions of lyxonic and threonic acid formed from lyxose-series sugars (Fig. 2a), (b) threonic and glyceric acids as major products formed from xylose-series hexoses (Fig. 2b), and (c) high proportions of pentonic, threonic, and glyceric acids formed from xylose and lyxose (Fig. 2c). Based on these results and on the observed isomerization of sugars in alkaline solutions, the following reaction pathway (Scheme 2) can be suggested:

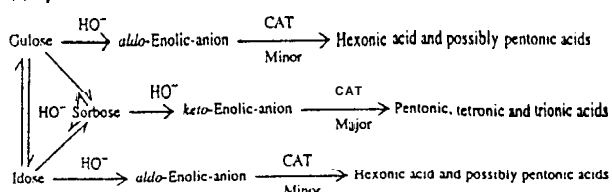
The observed reaction stoichiometry (Table 5) agrees with the formation of mixtures of pentonic, tetric and trionic acids.

For lyxose-series hexoses, the major products are formed by the loss of one or two carbon atoms with the cleavage of C-1-C-2 and C-2-C-3 bonds, respectively from the keto-enolic anion intermediates. The predominance of lyxonic acid and

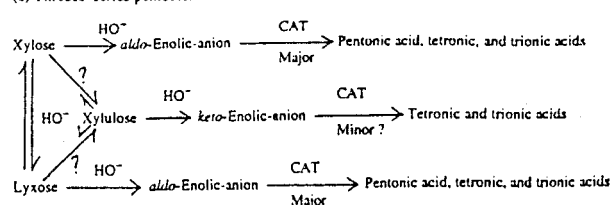
(a) Lyxose-series hexoses:



(b) Xylose-series hexoses:



(c) Threose-series pentoses:



Scheme 2.

minor amounts of xylonic acid from all lyxose-series sugars suggest that, for these sugars, the cleavage of the C-1-C-2 bond occurs without appreciable epimerization at C-3 (Fig. 2a). The formation of significant amounts of hexonic acid from these sugars, suggest that appreciable proportions of the sugars react with CAT in the aldo-enolic forms, which upon cleavage of the C-1-H bond form hexonic acids. Minor amounts of pentonic acids are formed by the cleavage of the C-1-C-2 bond from the aldo-enolic anions of hexoses. The formation of hexonic acid from tagatose is presumably due to isomerization to the aldo-enolic form.

The xylose-series hexoses, gulose, idose and sorbose, gave mainly threonic and glyceric acids and minor proportions of pentonic acids (xylonic and negligible amounts of lyxonic acid) (Fig. 2b). The predominance of threonic and glyceric acids indicate the preferential cleavage of C-2-C-3 and C-3-C-4 bonds compared with C-1-C-2 bonds. Since xylonic acid was formed in higher proportion compared with lyxonic acid, the cleavage of the C-1-C-2 bond in xylose-series hexoses must occur without appreciable epimerization at C-3, as in the case of lyxose-series hexoses (cf. Fig. 2b with Fig. 2a). Formation of small amounts of hexonic acids from gulose and idose was presumably due to slow oxidation of the aldo-enolic form. Formation of only a trace amount of hexonic acid from sorbose is due to negligible isomerization of sorbose to gulose and idose.

In contrast to hexoses, xylose and lyxose gave high proportions of pentonic acids (Fig. 2c). Clearly, these major products are formed by the cleavage of the C-1-H bond. Both xylose and lyxose also gave high proportions of threonic and glyceric acids, which are formed by cleavage of the C-1-C-2 and C-2-C-3 bonds, respectively. Since the latter type of bond-cleavage is facilitated through the involvement of the keto-enolic form, it is possible that portions of pentoses react in the keto-enolic form. However, lyxose and xylose were not isomerized to xylulose to a significant level. Together, these data suggest that pentoses undergo oxidation by CAT mainly through aldo-enolic intermediates, and only minor proportions may be oxidized via the keto-enolic form. In accordance with the observed three-times faster reaction rate of xylose compared with lyxose, a large amount of lyxose was not oxidized by CAT, even after 24 h at 35 °C (Fig. 2c). Under similar conditions, xylose was almost completely oxidized.

In view of the foregoing considerations, a plausible mechanism for the oxidation of sugars by CAT is proposed in Scheme 3. This mechanism accounts for the observed kinetics, reaction stoichiometry, and products formed.

In the proposed mechanism (Scheme 3), the anions (E^-) of sugars react with CAT to form intermediates X1-X3. For threose-series hexoses, the anions (E^\pm) intermediates are predominantly the keto-enolic forms and minor proportions of aldo-enolic forms. However, for pentoses, the major reacting species are the aldo-enolic anions; probably minor proportions of keto-isomer may also be involved. In the case of anions (E^-) from hexoses, the loss of hydrogen can occur at either C-1 or C-3 to form C-1-C-2 or C-2-C-3 enediols containing a hypochlorite group at C-2. Since epimerization at C-3 was limited, as evidenced by the formation of only very minor proportions of epimeric pentonic acids from hexoses, it can be concluded that cleavage of the C-1-H bond occurs preferentially as compared with cleavage of the C-3-H bond to form C-1-C-2 enediols. The ene-diols thus formed contain polarized double bonds to which hydroxide ion can add at C-2 to form intermediates X1 (major) and X2 (minor). X1 and X2 then can undergo cleavage of C-C bonds between C-1 and C-2, the former giving lyxonic acid and the latter forming a mixture of lyxonic and xylonic acids.

In the case of aldo-enolic anions from pentoses, hydrogen can be removed only from C-2 to form the C-1-C-2 enediol-anion, which in the presence of CAT and alkali forms intermediate X3 with epimerization at C-2. The cleavage of C-1-H bonds from X3 gives a mixture of lyxonic and xylonic acids. The cleavage of C-C bonds between C-2 and C-3 in X1 and X2, and the breaking of C-C bonds between C-1 and C-2 in X3 yield aldo-tetrose without epimerization at C-4 (hexoses) or at C-3 (pentoses). The aldo-tetrose further oxidizes to yield threonic acid and a minor proportion of erythronic acid (Table 5). The reaction can proceed further, with the cleavage of C-C bonds between C-3 and C-4 of hexoses and the breaking of C-C bonds between C-2 and C-3 of pentoses, to form glyceric acid. Minor proportions of threonic and glyceric acids could also be formed by the cleavage of C-1-C-2 and C-2-C-3 bonds, respectively, from the keto-enolic form of pentoses through the reactions sequences similar to those outlined for keto-hexoses in Scheme 3.

Acknowledgements

The proposed mechanism for the reaction is based on suggestions given by Professor Derek Horton for the oxidation of erythrose-series sugars by CAT [1], and we thank Professor Horton for his help. H.M and M.P.R. are grateful to the University of Mysore for the University Grants Commission, India, research fellowships. K.S.R. thanks the CSIR, India, for the financial support.

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