

Oxidation of methylpentoses by sodium *N*-chlorobenzene sulphonamide in alkaline medium: A kinetic and mechanistic study

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Abstract. Kinetics and mechanism of oxidation of three methylpentoses, namely *D*-fucose, *L*-fucose and *L*-rhamnose with sodium *N*-chlorobenzene-sulphonamide (chloramine-B or CAB) in alkaline medium were studied at 313 K. The rate law, $\text{rate} = k [\text{CAB}] [\text{S}] [\text{HO}^-]$ was observed. Benzenesulphonamide and chloride ions, the reduced products of the oxidant had no effect on the reaction rate. The rate increased with increase in ionic strength of the medium and the dielectric effect was negative. Proton inventory studies were made in H₂O–D₂O mixtures. HPLC analysis of products indicated a mixture of aldonic acids in varying proportions. A mechanism involving the furanosidic ringform of methylpentoses which preferentially reacts with CAB in the rate limiting step is suggested.

Keywords. Kinetics; oxidation; chloramine-B; methylpentoses; NaOH medium.

1. Introduction

The chemistry of *N*-halogeno compounds has received considerable attention, because of their application in reactions where selective and/or limited oxidation of compounds are required. Compounds in which the *N*-halogen bond is attached to an aromatic moiety, generally known as organic *N*-haloamines, are stable and are suitable as mild oxidants for a variety of reductants. The prominent member of this group is chloramine-*T* (p-CH₃C₆H₄SO₂NCINa·3H₂O or CAT) which contains chlorine in the +1 state and is a byproduct in the manufacture of saccharin. The benzene analogue chloramine-B (C₆H₅SO₂NCINa·5H₂O or CAB) is easy to prepare and it has been employed in the oxidation of diverse substrates.

In our broad programme on the oxidation of monosaccharides by *N*-haloamines, we have studied the mechanistic of oxidation of simple monosaccharides^{1,2} uronic acids and aminosugars⁵. But a review of literature shows that there is little information on the oxidation of methylpentoses by positive halogen compounds from a kinetic point of view⁶. We report the kinetics of oxidation of *D*-fucose, *L*-fucose and *L*-rhamnose by CAB at 313 K in the present communication. HPLC analysis of the oxidation products indicated a mixture of aldonic acids. The results of this study suggest that the oxidation occurs through a cleavage of both C–C and C–H bonds in

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the sugar molecule. On the basis of these data, a novel pathway for the oxidation of methylpentoses by CAB is proposed.

2. Experimental

Chloramine-*B* was prepared⁷ by passing chlorine through a solution of benzenesulphonamide in 4.0 M NaOH for 1 h at 343 K. The product was collected, dried and recrystallized from water (m.p. 446 K with decomposition). Its purity was checked by iodometry for its active chlorine content and also by its ¹H and ¹³C NMR spectra. An aqueous solution of the compound was prepared, standardized and preserved in brown bottles to prevent its photochemical deterioration. *D*-fucose (Pfanstiehl Laboratories, Waukegan, IL, USA) *L*-fucose (Sigma) and *L*-rhamnose (Sigma) were used without further purification. All other reagents were of analytical reagent grade. Concentrated NaClO₄ solution was used throughout to maintain a constant high ionic strength of the medium. Solvent isotope studies were made with D₂O (99.4%) supplied by the Bhabha Atomic Research Centre, Trombay, India. Triply distilled water was used in the preparation of aqueous solutions.

2.1 Kinetic measurements

The reactions were carried out in glass-stoppered pyrex tubes coated black on the outside. Pseudo-first order conditions were maintained with respect to the oxidant concentrations. Aqueous solution of alkali, substrate and NaClO₄ (enough water for maintaining a constant total volume) were maintained in the pyrex tube at 313 K. The reaction was initiated by the rapid addition of CAB maintained separately at 313 K to this mixture. The progress of oxidation was monitored, for two half-lives, by iodometric determination of unconsumed CAB at various time intervals. Values of pseudo-first order rate constants (k_{obs}) were calculated from the plots of $\log [CAB]_0$ vs time plots and these were reproducible within $\pm 5\%$.

Regression analysis of experimental data to obtain regression coefficient '*r*' and the standard deviation '*S*' of points from the regression line was performed with an EC-72 statistical calculator.

2.2 Stoichiometry and product analysis

Reaction mixtures containing substrate, alkali with an excess of CAB were kept for 24 h at 313 K. The unconsumed CAB was then determined iodometrically indicating that 3 moles of oxidant were consumed per mole of methylpentose to form the aldonic acids.

The oxidation products were analysed by Dionex HPLC with pulsed amperometric detection using a CarboPac PA1 high-*pH* anion exchange column (4 × 250 mm)⁸. An isocratic elution with 0.2 M NaOH was used. The products were identified by comparison of their HPLC retention times with retention times of the standard aldonic acids. Oxidation of both *D*-fucose and *L*-fucose yielded identical products, 5-deoxylyxonic acid, 5-deoxyxyliconic acid and 4-deoxythreonic acid while for *L*-rhamnose, the oxidation products were 5-deoxyarabinonic acid, 5-deoxyribonic acid, and 4-deoxyerythronic acids. Beside these products, small amounts of 2-hydroxypropanoic acid and 6-deoxyhexonic acids are formed (table 1, figure 1). The oxidation products of methylpentoses were also analyzed at 0.5, 1, 2, 4, 8, 16 and 24 h. The relative proportions of various aldonic acids formed (figure 1 and table 1) were similar at all

Table 1. HPLC analysis of the products formed by the oxidation of methylpentoses by CAB in alkaline medium.

Methylpentose	Products (mole percent)							
	5-Deoxy lyxonic acid	5-Deoxy xylonic acid	4-Deoxy threonic acid	4-Deoxy erythronic acid	5-Deoxy arabinonic acid	5-Deoxy ribonic acid	2-Deoxy propanoic acid	6-Deoxy hexonic acid
<i>L</i> -Rhamnose	—	—	—	50	25	10	5	10
<i>D</i> -Fucose	36	28	25	—	—	—	7	4
<i>L</i> -Fucose	30	35	26	—	—	—	6	3

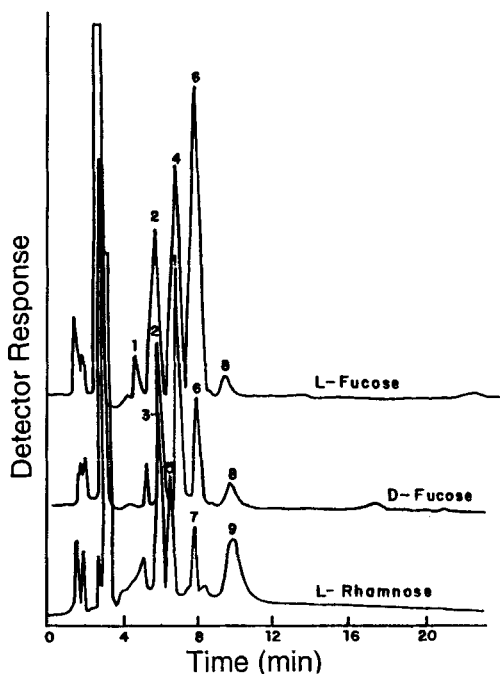


Figure 1. HPLC analysis of the products formed by the oxidation of methylpentoses by CAB in presence of NaOH at 313 K 1,2-hydroxypropanoic acid; 2,4-deoxythreonic acid; 3,4-deoxyerythronic acid; 4,5-deoxyxyliconic acid; 5,5-deoxyarabonic acid; 6, 5-deoxyxylonic acid; 7, 5-deoxyribonic acid; 8, 6-deoxygalactonic acid; 9,6-deoxymannonic acid. L-Fucose, D-Fucose and L-Rhamnose respectively represent reaction of CAT with L-fucose, D-fucose and L-rhamnose.

time points analyzed. However, the formation of six-carbon aldonic acids was observed only after 4 h, revealing that the lower-carbon aldonic acids were not derived from the initially formed six-carbon aldonic acids. Similar product profiles were observed even when the reactions were carried out under kinetic conditions.

3. Results

The reactions were carried out under pseudo-first order conditions with $[\text{sugar}]_0 \gg [\text{oxidant}]_0$. Plots of $\log [\text{CAB}]$ vs time were linear ($r > 0.9988$ $s < 0.02$) indicating a first order dependence of reaction rate on $[\text{CAB}]_0$. The pseudo-first order rate constants (k_{obs}) obtained with different $[\text{CAB}]_0$ were constant (table 2). The values increased with increase in $[\text{S}]_0$ (table 2) and plots of $\log k_{obs}$ vs $\log [\text{S}]_0$ were linear ($r > 0.99765$ $s < 0.03$) with unit slopes. The second order rate constants, $k_2 = k_{obs}/[\text{S}]_0$ were constant within the experimental error, demonstrating a first-order dependence of rates on $[\text{S}]_0$.

At constant $[\text{CAB}]_0$ and $[\text{S}]_0$, values of k_{obs} increased with increase in $[\text{NaOH}]$ (table 3). Plots of $\log k_{obs}$ vs $\log [\text{HO}^-]$ ($r > 0.9934$ $s < 0.05$) were linear with unit slopes indicating a first order dependence on $[\text{HO}^-]$.

Addition of the reduced products benzenesulphonamide and chloride ions, the latter in the form of NaCl, did not affect the rate. It may thus be inferred that the sulphonamide is not involved in a pre-equilibrium step with the oxidant.

Table 2. Effect of reactant concentration on the rate $[\text{HO}] = 0.2 \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$, temperature = 313 K

$10^3[\text{CAB}]$ (mol dm^{-3})	$10^2[\text{S}]_0$ (mol dm^{-3})	$10^4 k_{\text{obs}} (\text{s}^{-1})$		
		<i>L</i> -Rhamnose	<i>D</i> -Fucose	<i>L</i> -Fucose
1.0	2.0	4.25	12.06	15.80
1.5	2.0	4.38	12.22	16.00
2.0	2.0	4.40	12.28	16.05
2.5	2.0	4.45	12.36	16.20
3.0	2.0	4.60	12.50	16.22
3.5	2.0	4.50	12.75	16.36
4.0	2.0	4.66	12.78	16.56
2.0	1.0	2.00	5.90	8.08
2.0	3.0	6.58	18.00	24.40
2.0	4.0	8.50	26.40	32.20
2.0	5.0	11.21	30.80	39.50
2.0	6.0	13.50	36.30	49.80

Table 3. Effect of $[\text{NaOH}]$ on the rate $[\text{CAB}]_0 = 0.002 \text{ mol dm}^{-3}$, $[\text{S}]_0 = 0.02 \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$, temperature = 313 K

$10^2[\text{NaOH}]$ (mol dm^{-3})	$10^4 k_{\text{obs}} (\text{s}^{-1})$		
	<i>L</i> -Rhamnose	<i>D</i> -Fucose	<i>L</i> -Fucose
10.0	2.20	5.96	7.79
20.0	4.40	12.28	16.05
30.0	6.05	19.20	24.20
40.0	8.20	23.50	31.60
50.0	10.86	31.83	38.30
60.0	12.50	37.30	47.60

Addition of NaClO_4 increased the rate of reaction. Plots of $\log k_{\text{obs}}$ vs $I^{1/2}$ where I is the ionic strength of medium were linear with fractional slopes around 0.5 (figure 2, $r > 0.9902$, $s < 0.06$).

The solvent composition of the medium was varied by adding methanol (0–40% v/v). Plots of $\log k_{\text{obs}}$ vs $1/D$ (D = dielectric constant of the medium) were linear with negative slopes (figure 3, $r > 0.9957$, $s < 0.04$).

The reaction was studied at different temperatures (308–323 K). Arrhenius plots of $\log k_{\text{obs}}$ vs $1/T$ were linear (table 4, $r > 0.9969$, $s < 0.03$) and the activation energy E_a was calculated from the slope. Values of other activation parameters, ΔH^\ddagger , ΔS^\ddagger , and ΔG^\ddagger were computed⁹ from the measured E_a values (table 4).

Solvent isotope studies were conducted in pure D_2O (99.6% D). The rate values, k_{obs} were almost doubled in D_2O medium for each substrate, leading to a solvent isotope effect, $k_{\text{obs}}(\text{H}_2\text{O})/k_{\text{obs}}(\text{D}_2\text{O}) = 0.52 - 0.62$. Proton inventory studies with the same substrates were made in H_2O – D_2O mixtures (table 5).

Absence of free radicals in the reaction mixture was indicated by the negative test with the olefinic manomer, acrylamido.

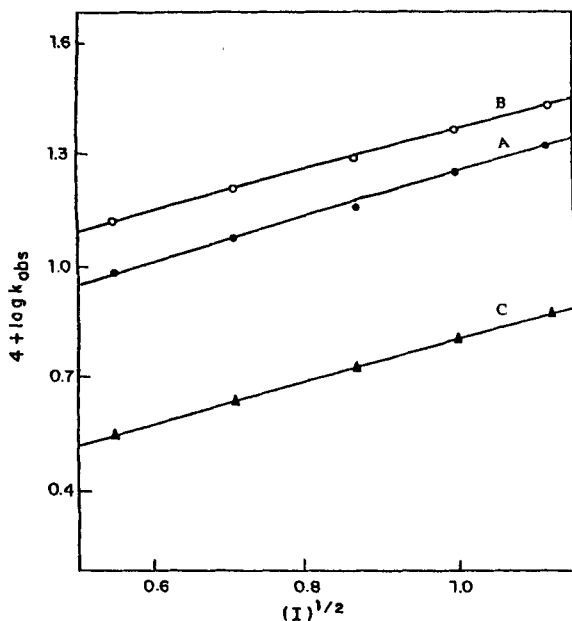


Figure 2. Plots of $\log k_{obs}$ vs $I^{1/2}$. A, *D*-Fucose; B, *L*-Fucose; C, *L*-Rhamnose. $[CAB]_0 = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[S]_0 = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[HO^-] = 0.2 \text{ mol dm}^{-3}$; temperature = 313 K.

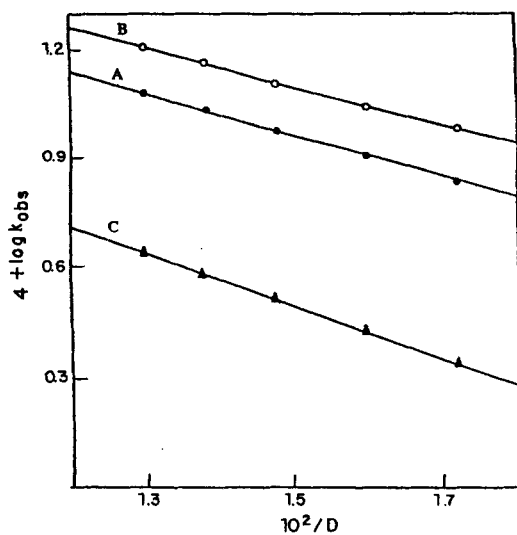


Figure 3. Plots of $\log k_{obs}$ vs $1/D$. A, *D*-Fucose; B, *L*-Fucose; C, *L*-Rhamnose. $[CAB]_0 = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[S]_0 = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[HO^-] = 0.2 \text{ mol dm}^{-3}$; $I = 0.5 \text{ mol dm}^{-3}$; temperature = 313 K.

Table 4. Kinetic data for the oxidation of methylpentoses by CAB in alkaline medium. $[\text{CAB}]_0 = 0.002 \text{ mol dm}^{-3}$, $[\text{S}]_0 = 0.02 \text{ mol dm}^{-3}$, $[\text{HO}^-] = 0.2 \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$.

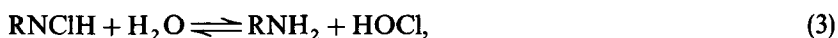
Methylpentose	Temp 10^4 (K)	k_{obs} (S^{-1})	E_a (kJ mol^{-1})	ΔH^\ddagger (kJ mol^{-1})	ΔG^\ddagger (kJ mol^{-1})	ΔS^\ddagger (kJ mol^{-1})
<i>L</i> -Rhamnose	308	2.00	129.7	127.1	97.3	96.5
	313	4.40				
	318	8.60				
	323	20.88				
<i>D</i> -Fucose	308	6.30	89.2	86.6	94.3	-24.4
	313	12.28				
	318	21.60				
	323	46.50				
<i>L</i> -Fucose	308	8.90	80.0	77.4	93.6	-51.9
	313	16.05				
	318	28.40				
	323	53.74				

Table 5. Proton inventory studies for the oxidation of methylpentoses by CAB in $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixtures at 40°C . $[\text{CAB}]_0 = 0.002 \text{ mol dm}^{-3}$, $[\text{S}]_0 = 0.02 \text{ mol dm}^{-3}$, $[\text{HO}^-] = 0.2 \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$, temperature = 313 K

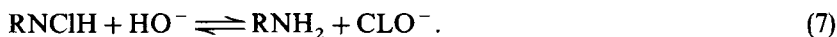
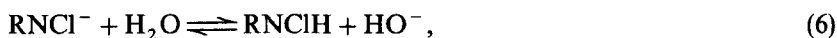
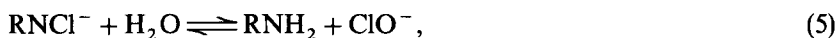
Atom fraction of deuterium (n)	$10^4 k_{obs} (\text{s}^{-1})$		
	<i>L</i> -Rhamnose	<i>D</i> -Fucose	<i>L</i> -Fucose
0.000	4.40	12.28	16.05
0.250	5.16	13.80	17.80
0.500	5.95	15.80	19.80
0.750	7.10	18.30	22.75
0.917	8.45	21.50	25.98

4. Discussion

The identical orders observed with respect to CAB, substrate and alkali concentrations suggest a common mechanism for the oxidation of methylpentoses by CAB. The organic haloamines behave as strong electrolytes in aqueous solutions and the several equilibria present are predominantly pH dependent¹⁰⁻¹³. The equilibria for chloramine-B solutions RNCINa where $R = \text{PhSO}_2^-$ involve disassociation of salt protonation of the anion and the hydrolysis and disproportion of the free acid formed (1-4) are shown below,



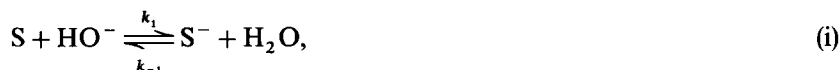
In alkaline solutions, the following equilibria are reported



Equations 3, 5, and 7 suggest a retardation of rate by the added benzenesulphonamide, while (6) predicts a rate retardation by alkali. Since neither of these were observed in our present work, the likely reacting species for the oxidation of methylpentoses is the anion RNCl^- ¹⁴.

Methylpentoses generally exist in the furanosidic ring form. In alkaline solutions, methylpentoses undergo enolization to form the enediol anion (S^-). In the absence of other reactants, the anion undergoes epimerization and isomerization through the Lobry de Bruyn-Alberda van Ekenstein transformation¹⁵ to form a mixture of aldoses and ketoses¹⁶. However, in the presence of CAB, the enediol anion (S^-) reacts with RNCl^- ion to form an intermediate, which in turn undergoes cleavage to form the products (table 1, figure 1).

In view of the observed first order dependence each with respect to $[\text{CAB}]_0$, $[\text{S}]_0$ and $[\text{HO}^-]$, the following reaction sequence (scheme 1) is proposed for the oxidation of methylpentoses by CAB in alkaline solutions.



Scheme 1.

Applying steady state conditions to $[\text{S}^-]$, the rate of disappearance of oxidant is given by (8)

$$\text{Rate} = -\frac{d[\text{CAB}]}{dt} = \frac{k_1 k_2 [\text{CAB}][\text{S}][\text{HO}^-]}{k_{-1}[\text{H}_2\text{O}] + k_2[\text{CAB}]}. \quad (8)$$

Since k_{-1} is fairly large and k_2 is small, being the rate constant for the rate limiting step, the approximation $k_{-1}[\text{H}_2\text{O}] \gg k_2[\text{CAB}]$ is valid and rate law (8) is reduced to (9) which is in agreement with experimental results

$$\begin{aligned} \text{Rate} &= -\frac{d[\text{CAB}]}{dt} = \frac{k_1 k_2 [\text{CAB}][\text{S}][\text{HO}^-]}{k_{-1}[\text{H}_2\text{O}]} \\ &= k^1 [\text{CAB}][\text{S}][\text{HO}^-]. \end{aligned} \quad (9)$$

The proposed mechanism is supported by the increase of rate in D_2O medium. Since DO^- is a stronger base than HO^- is a stronger base than HO^- by a factor of 2, we expect a doubling of rate in heavy water medium¹⁷. The value of the inverse solvent isotope effect, $k(\text{D}_2\text{O})/k(\text{H}_2\text{O}) \approx 2.0$ (table 5) thus justifying our expectations and also substantiating a pre-equilibrium hydroxyl ion transfer¹⁷. Proton inventory plots could throw some light on the nature of the transition state^{18,19}. The dependence of rate

constant (k_{obs}^n) on 'n', the atom fraction of deuterium, in a solvent mixture containing H_2O and D_2O is given by the Gross-Butler equation²⁰ (10).

$$k_{obs}^o/k_{obs}^n = \frac{\prod_{TS} (1 - n + n\phi_i)}{\prod_{RS} (1 - n + n\phi_j)}, \quad (10)$$

where ϕ_i and ϕ_j are the isotopic fractionation factors for isotopically exchangeable hydrogen sites in the transition state (TS) and reactant states (RS), respectively. A qualitative examination of the proton inventory plots by comparing their curvature with standard curves available in literature, shows that there is a single transition state and one HO^- ion is involved in its formation.

A primary salt effect is observed as the rate increases with increase in ionic strength of medium and this is indicative of involvement of two negative ions in the reaction sequence. The plot of $\log k_{obs}$ vs $(I)^{1/2}$ is linear with a slope of 0.5 (figure 2). The expected slope of unity has not been realised²¹ possibly due to the fact that the ionic strength is well above the formal Debye-Hückel range and there could be Bjerrum ion pair formation²¹. It is also probable that there is charge delocalization in the sugar and oxidant molecules participating in the rate limiting step (scheme 1).

The rate decreased with decrease in the dielectric constant (D) of the medium. The effect of composition of the solvent on rate for a reaction involving two negative ions of charges $Z_A e$ and $Z_B e$ is given by the Scatchard equation (11)

$$\log k = \log k_0 - Z_A Z_B e^2 / DkT d_{AB}, \quad (11)$$

where k_0 is the rate constant in a medium of infinite dielectric constant, d_{AB} refers to the size of activated complex and k and T are the Boltzmann constant and absolute temperature, respectively. From the slope of $\log k_{obs}$ vs $1/D$ plot (figure 3), d_{AB} is computed as 3.86 Å, 4.10 Å and 3.23 Å for *D*-fucose, *L*-fucose and for *L*-rhamnose respectively. The values are found to be reasonable in comparison with those of other reactions of similar nature²².

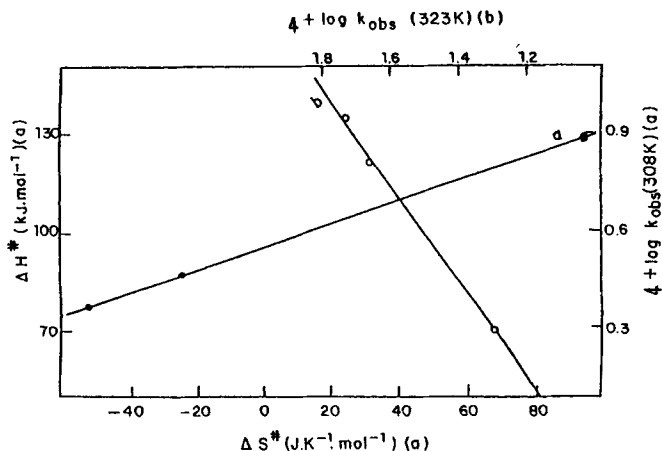
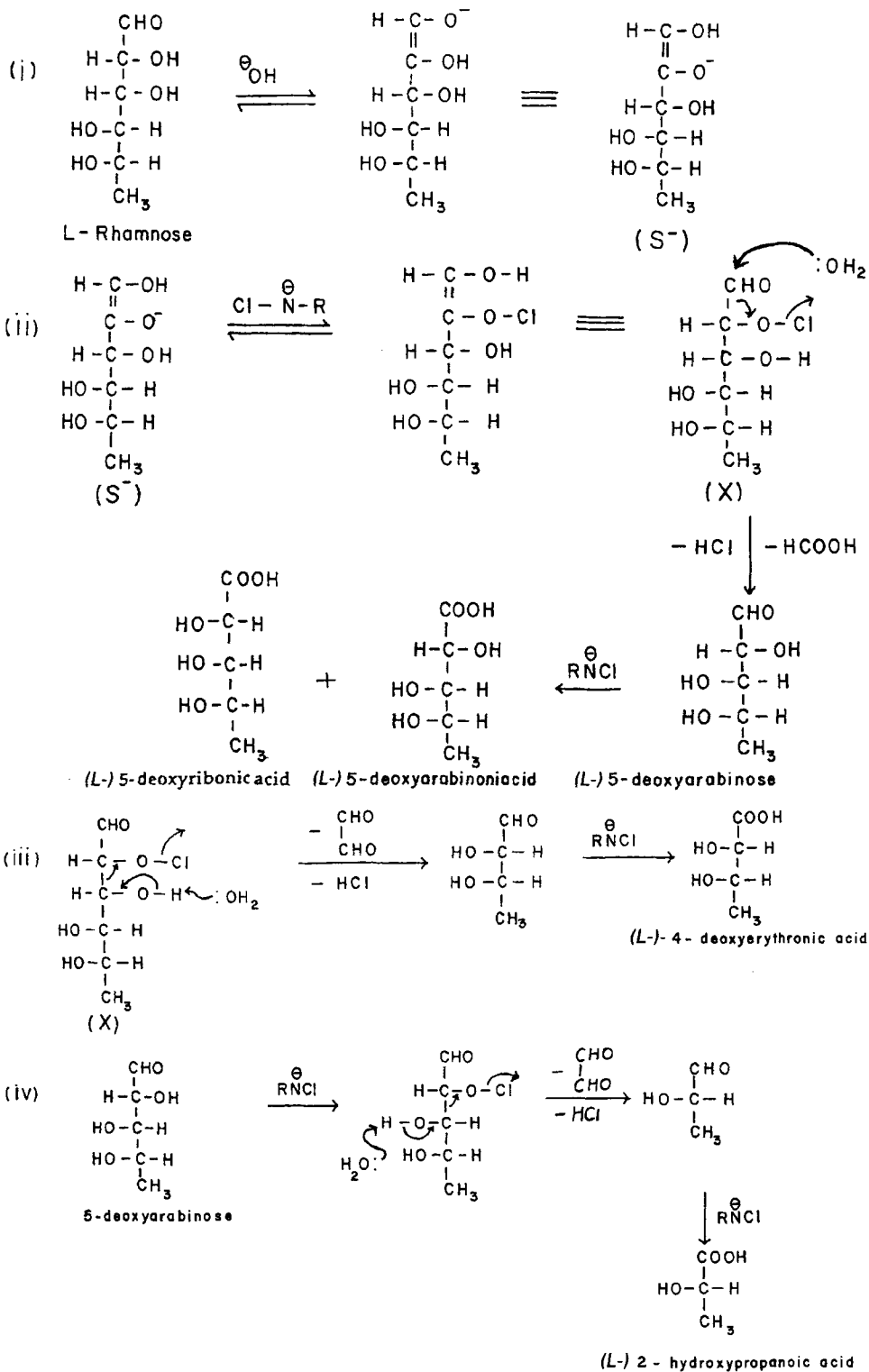


Figure 4. Isokinetic plots of (a) ΔH^\ddagger vs ΔS^\ddagger and (b) $\log k_{obs}$ (308 K) vs $\log k_{obs}$ (323 K).



The rate determining step involves an interaction between similarly charged ions and hence would require a high energy of activation which is found to be the case. Also, the data in table 4 shows that the energy of activation is highest for the slowest reaction, indicating that the reaction is enthalpy controlled. Further, values of ΔH^\ddagger and ΔS^\ddagger can be correlated linearly (figure 4, $r = 0.9994$, $s = 0.01$) resulting in an isokinetic relation. It suggests that a common mechanism operates in the oxidation of methylpentoses by CAB, as also suggested by the near constancy of ΔG^\ddagger values (table 4). From the slope of ΔH^\ddagger vs ΔS^\ddagger plot (figure 4) the value of the isokinetic temperature β is 346 K, which is much higher than the experimental temperature (313 K). This reaction proved to be genuine through Exner criterion²³ by plotting $\log k_{obs}$ (308 K) vs $\log k_{obs}$ (323 K) (figure 4, $r > 0.9986$, $s < 0.02$). The value of β calculated from the relation $\beta = T_1(1 - q)/(T_1/T_2) - q$, where 'q' is the slope of the Exner plot, was found to be 356 K in agreement with the isokinetic temperature calculated from the enthalpy-entropy relation. A comparison of rates of oxidation of the three methylpentoses is desirable (table 2). It is seen that the rates are in order, *L*-fucose > *D*-fucose > *L*-rhamnose. The β -anomer (equatorial-OH) in general is oxidised more rapidly than the corresponding α -anomer (axial-OH). *L*-fucose has the highest oxidation rate because of the presence of equatorial-OH group while *D*-fucose has axial-OH group²⁴ in C-1 conformation. Between *L*-fucose and *L*-rhamnose, *L*-fucose has $\Delta 2$ instability condition¹⁵. (The -OH on C-2 is axial while the -OH on C-1 is equatorial), while *L*-rhamnose has a more stable C1 configuration. In *D*-fucose C-1 OH is axial but there is more of β -isomer than that in *L*-rhamnose, which accounts for the higher rate of oxidation of the former.

A probable mechanistic picture of oxidation of *L*-rhamnose is shown in scheme 2. In alkaline solutions, the enediol anion (S^-) of the sugar reacts with the oxidant in the rate determining step to form an intermediate 'X'. Here, the cleavage of C-C bonds between C_1 and C_2 with epimerization at C_3 forms mixtures of 5-deoxypentonic acids. *L*-Rhamnose gives a mixture of (*L*-)5-deoxyarabinonic and (*L*-)5-deoxyribonic acid. The cleavage of C-C bonds between C_2 and C_3 in X, of methylpentose yield (*L*-)4-deoxy tetronic acid with no significant epimerization at C_4 of methylpentose. This explains the formation of (*L*-)4-deoxyerythronic acid. The reaction can proceed further with the cleavage of C-C bond between C_2 and C_3 of (*L*-)5-deoxyarabinose to form (*L*-)2-hydroxy-propanoic acid.

A similar scheme can be drawn for the oxidation of *L*-fucose into a mixture of (*L*-)5-deoxylyxonic acid, (*L*-)4-deoxyxylonic acid, (*L*-)4-deoxythreonic acid and (*L*-)2-hydroxy propanoic acid in alkaline medium.

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