Oxidation of some aldopentoses by chloramine-B in alkaline medium: a kinetic and mechanistic study

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ABSTRACT

The oxidation kinetics of D-xylose, D-ribose, and L-arabinose by chloramine-B (CAB) in alkaline medium at 35° obey the rate law, rate = [CAB][HO⁻][Pentose]. Based on the results, a mechanism is suggested involving the anion of the β anomer of the pentose. The addition of reaction products, benzenesul-phonamide and NaCl, had no effect on the rate of reaction whereas increase in the ionic strength and dielectric constant of the medium increased the rate. Proton-inventory studies were made in H₂O-D₂O mixtures. The rate of oxidation of pentoses follows the order[†]: D-xylose > D-ribose > L-arabinose. Kinetic and thermodynamic parameters for the reaction were computed from the Arrhenius plots. The isokinetic temperature $\beta = 416$ K, which is much above the experimental temperature, suggests enthalpy-controlled reactions.

INTRODUCTION

Chloramine-B, a source of positive chlorine, is used as an oxidant¹ in both acidic and alkaline media and undergoes a two-electron change per mole. We have recently reported² on the kinetics and mechanism of oxidation of several hexoses by chloramine-B (CAB), in alkaline medium. Here, we present the results of alkaline oxidation of three aldopentoses; L-arabinose, D-ribose, and D-xylose by CAB under similar experimental conditions for comparison with the kinetic results obtained for the hexoses.

EXPERIMENTAL

Materials. — Pure samples of L-arabinose (CRL, Bombay), D-ribose (Loba Chemie), D-xylose (Loba Chemie), and Analar grade chemicals were used. Fresh aqueous solutions of the pentoses were prepared using triply distilled water. CAB was prepared by the standard literature method². Its purity was checked by iodometry for its chlorine content and also by its ¹H- and ¹³C-n.m.r. spectra². Aqueous solution of CAB was standardized iodometrically and stored in brown bottles to arrest photochemical

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⁺ A referee queried whether sugars containing the same percent of β anomer react at the same rate, taking D-xylose, D-fructose, and D-glucose as the examples. We note that D-fructose has the highest rate because of the reactive carbonyl group (keto). As a group, the pentoses react faster than the hexoses¹⁶ as the latter are presumably stabilized by the -I effect of the CH₂OH group.

deterioration. Concentrated $NaClO_4$ solution was used throughout to maintain a constant high ionic strength of the medium.

Kinetic measurements. — The reactions were carried out in glass-stoppered pyrex boiling-tubes coated black on the outside. Pseudo-first-order conditions were maintained. The oxidant and the requisite amounts of pentose, alkali, NaClO₄ solutions, and H_2O (constant total volume), taken in separate boiling tubes, were thermostated for 30 min at 35°. The reaction was initiated by the rapid addition of CAB to the mixture and its progress was monitored by iodometric determination of unconsumed CAB in known aliquots of the mixture at regular intervals of time. The reaction was monitored for two half-lives. Rate constants, calculated from $log[CAB]_o vs$ time, were reproducible within $\pm 3\%$.

Regression analysis of experimental data to obtain regression coefficients "r" and "s", and standard deviations of the points from the regression line, was performed with an EC-72 statistical calculator.

Stoichiometry and product analysis. — The mixture containing pentose and alkali with an excess of CAB was kept for ~ 24 h at 35°. Unconsumed CAB was then determined iodometrically and indicated that one mol of oxidant was needed per mol of pentose to give the corresponding aldonic acid. The stoichiometric equation may be given as:

 $C_{5}H_{10}O_{5} + C_{6}H_{5}SO_{2}N \cdot NaCl + H_{2}O \rightarrow C_{5}H_{10}O_{6} + C_{6}H_{5}SO_{2}NH_{2} + Na^{+} + Cl^{-}$ (1)

To analyse the oxidation products, pentoses were oxidised under kinetic conditions. The reduced product (benzenesulphonamide, BSA) was detected by t.l.c. and the aldonic acid was identified by paper chromatography, as reported earlier².

RESULTS

Reactant and alkali concentrations. — The kinetics of oxidation of pentoses by CAB was investigated at several initial concentrations of the reactants. With substrate in excess, at constant [HO⁻] and [Pentose]_o, plots of log[CAB]_o vs time were linear (r > 0.9903) with unit slopes, indicating a first-order dependence on [CAB], (Table I). This was further confirmed from the unit slopes of linear plots of $\log(-dc/dt)_{o}$ vs log[CAB], using the initial-velocity method. However, at higher [CAB], the pseudofirst-order constants, k_{obs} , decreased slightly, indicating possibly a side reaction³ involving the formation of NaClO₃ ($3NaOCl \rightarrow 2NaCl + NaClO_3$). The rate constant, k_{obs} , increased with increase in [Pentose], (Table I) and $\log k_{obs} - \log$ [Pentose], plots were linear (r > 0.9852), $s \le 0.06$) with unit slopes. The second-order rate constants $(k_{obs}/[Pentose]_o)$ were found to be constant, confirming the first-order dependence of rate on [Pentose]_o. Further, a plot of k_{obs} vs [Pentose]_o (Fig. 1), was linear (r>0.9914, $s \le 0.04$) and passed through the origin, showing the transient nature of the intermediate formed with the oxidant. The rate of reaction also shows a first-order dependence on [HO⁻], (Table II), as plots of log k_{obs} vs log[HO⁻] were linear (r>0.9929, s ≤ 0.03) with unit slopes.

TABLE

10 ³ [CAB] _o	10 ² [Pentose]	$10^4 k_{abs} s^{-1}$			
(M)	(M)	L-Arabinose	D-Ribose	D-Xylose	
1.0	2.0	4.68	5.98	8.71	
2.0	2.0	3.76	5.85	8.62	
2.5	2.0	3.72	5.76	8.77	
3.0	2.0	3.55	5.53	8.71	
3.5	2.0	3.52	5.18	8.23	
4.0	2.0	3.00		8.01	
3.0	1.0	1.65	2.65	4.04	
3.0	1.5	2.67	3.59	6.36	
3.0	2.5	4.76	6.81	10.77	
3.0	3.0	5.30	7.80	-	

Effect of reactant concentrations on the rate of oxidation of pentoses at 5.	Effect of reactant	concentrations"	on the rate	of oxidation of	of pentoses at 3	5
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"[HO⁻]= 0.05м, I = 0.5м.



Fig. 1. Plots of k_{obs} vs [Pentose]_o: A, L-arabinose; B, D-ribose; C, D-xylose; $[CAB]_o = 3 \times 10^{-3}$ M; $[HO^-] = 0.05$ M; I = 0.5M; temp. = 35°.

Effect of [BSA] and $[Cl^-]$. — The reaction rate was unaffected by the addition of reduced product (benzenesulphonamide, BSA), indicating that it was not involved in a pre-equilibrium with the oxidant. Similarly, the rate was unchanged by the addition of NaCl to the mixture, showing that free chlorine is not involved in the oxidation process.

Effect of ionic strength. — Increasing the ionic strength (I), of the medium from 0.1 to 1.0M (by adding NaClO₄ solution), increased the rate of reaction, and a plot of $\log k_{obs} vs(I)^{\frac{1}{2}}$ gave a straight line (r > 0.9868, $s \le 0.04$) having a slope ~ 0.6 (Fig. 2).

10²[NaOH]	$10^4 k_{abs} s^{-1}$					
(M)	L-Arabinose	D-Ribose	D-Xylose			
2.5	1.57	2.35	3.60			
4.0	2.78	4.18	6.92			
5.0	3.55	5.53	8.71			
6.0	4.29	7.29	10.89			
7.5	5.28	8.96	15.93			
10.0	7.30	11.98	18.37			

TABLE II

Effect of [NaOH] on the reaction^a at 35°

 a [CAB]₀ = 3.0 × 10⁻³M, [Pentose]₀ = 2 × 10⁻²M, I = 0.5M.



Fig. 2. Plots of log k_{obs} vs (1)¹: [CAB]_o = 3 × 10⁻³ M; [Pentose]_o = 2 × 10⁻² M; [HO⁻] = 0.05 M; temp. = 35°.

Effect of solvent composition. — The solvent composition of the medium was varied by adding methanol (0-40%). The rate decreased with increase in methanol content, and plots of $\log k_{obs} vs 1/D$, where D is the dielectric constant of the medium⁴, were linear (r > 0.9917, $s \le 0.04$) with a negative slope (Fig. 3).

Activation parameters. — To compute the activation parameters, the reaction was studied over a range of temperatures (305–317 K) and the Arrhenius plot, $\log k_{obs} vs 1/T$ was found to be linear (r > 0.9896). The activation energy, E_a , was calculated from the slope of this plot, and the other parameters, ΔH^* , ΔS^* , and ΔG^* (Table III) were calculated as reported earlier².

Solvent isotope-studies. — Solvent isotope-studies were conducted in pure D_2O for D-xylose, and the value of $(k_{obs})D_2O$ was found to be $14.24 \times 10^{-4}s^{-1}$ as compared to $(k_{obs})H_2O = 8.71 \times 10^{-4}s^{-1}$, leading to the solvent isotope-effect, $(k_{obs})H_2O/(k_{obs})D_2O$ of 0.61. Proton-inventory studies with D-xylose as probe were made in H_2O-D_2O mixtures (Table IV). The corresponding proton-inventory plot, relating the rate constant k_0^n with n (the deuterium atom fraction in the solvent mixture), is given in Fig. 4.



Fig. 3. Plots of log $k_{obs} vs 1/D$: $[CAB]_o = 3 \times 10^{-3} \text{m}$; $[Pentose]_o = 2 \times 10^{-2} \text{m}$; $[HO^-] = 0.05 \text{m}$; I = 0.5 m, temp. = 35°.

TABLE III

Kinetic and thermodynamic parameters for the oxidation of pentoses by CAB in presence of NaOH

Pentose	E _a kJmol ⁻¹	$\Delta^{\ddagger} k Jmol^{-1}$	$\Delta G^{\ddagger} k Jmol^{-1}$	$\Delta S^{\ddagger}JK^{-1}mol^{-1}$	Log A
L-Arabinose D-Ribose D-Xylose	96.4 92.8 88.6	93.8 ± 0.04 90.2 ± 0.04 86.0 ± 0.04	96.0 \pm 0.18 94.9 \pm 0.15 93.6 \pm 0.06	$\begin{array}{r} - 7.0 \pm 0.60 \\ - 15.0 \pm 0.50 \\ - 24.50 \pm 0.04 \end{array}$	$\begin{array}{r} 15.9 \pm 0.03 \\ 15.6 \pm 0.05 \\ 15.1 \pm 0.03 \end{array}$



Fig. 4. Proton-inventory plot for the oxidation of D-xylose by CAB in H_2O-D_2O mixtures at 308K. Experimental conditions as given in Table IV.

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Atom fraction of deuterium (n)	$10^4 k_{obs} s^{-1}$	<u></u>
0.00	8.71	
0.248	9.65	
0.496	11.15	
0.744	12.93	
0.860	14.24	

TABLE IV

Proton inventory plot for the oxidation" of D-xylose by CAB in H₂O-D₂O mixtures at 35°

 $^{"}$ [CAB]_o = 3 × 10⁻³M, [Pentose]_o = 2 × 10⁻²M, [HO⁻] = 0.05M, I = 0.5M.

Free-radical test. — To test for free-radical species in the reaction mixture, it was added to acrylamide. Polymerization did not occur, confirming the absence of free-radical species in the mixture.

DISCUSSION

Chloramine-B, like chloramine-T, is a moderately strong electrolyte in aqueous solutions⁵:

$$PhSO_2NCI Na \rightleftharpoons PhSO_2NCI^- + Na^+$$
⁽²⁾

The probable oxidising species of CAB in acid medium are PhSO₂NHCl, PhSO₂NCl₂, and HOCl. In alkaline solutions, the following equilibria are reported: PhSO₂NCl⁻ + H₂O \rightleftharpoons PhSO₂NH₂ + OCl⁻ (3) PhSO₂NCl⁻ + H₂O \rightleftharpoons PhSO₂NHCl + HO⁻ (4) PhSO₂NHCl + H₂O \rightleftharpoons PhSO₂NH₂ + HOCl (5) PhSO₂NHCl + HO⁻ \rightleftharpoons PhSO₂NH₂ + OCl⁻ (6)

Equations 3, 5, and 6 suggest rate retardation with the addition of benzenesulphonamide, while Eq. 4 predicts a decrease in rate by HO⁻ ions. As these predictions are contrary to our experimental observations, the likely reacting species in the present investigations is the anion PhSO₂NCl⁻. Hence, the following tentative kinetic scheme is suggested for the oxidation reaction:

$$S + PhSO_2NCl^- + HO^- \frac{k_1}{k_{-1}}X$$
⁽⁷⁾

$$X = \frac{\kappa_2}{\text{slow \& rds}} X' + PhSO_2N^{2-} + HO^{-}$$
(8)

$$X' \xrightarrow{k_3} \text{products} \tag{9}$$

This mechanism satisfactorily fits into the experimental rate-law, rate = k [CAB][S][HO⁻] where S = pentose, which reacts mostly as the β anomer. It also explains the first-order dependence on [CAB]_o, [Pentose]_o, and [HO⁻] and the lack of effect of the reaction product, benzenesulphonamide. Assuming steady-state conditions for the intermediate X, rate law 10 may be derived for the disappearance of oxidant:

Rate =
$$\frac{-d[CAB]}{dt} = \frac{k_2 k_{-1}[S][HO^-][CAB]}{k_{-1} + k_2}$$
 (10)

A possible mode of oxidation of the pentoses to the aldonic acids by CAB is shown in Scheme 1.



Scheme 1. A possible oxidation mechanism for D-xylose, D-ribose, and L-arabinose by CAB in alkaline medium.

(i) The proposed mechanism is supported by the increased rate of reaction in D_2O medium, which implies⁶ a fast pre-equilibrium hydroxyl-ion transfer (Eq. 7). The proton-inventory studies throw light on the nature of the transition state. Assuming the formation of a single transition state involving the HO⁻ ion, the dependence of the rate constant, k_{obs}^n on *n*, the atom fraction of deuterium, in a solvent mixture of H₂O and D₂O is given^{7,8} by Eq. 11:

$$(k_{obs}^{o}/k_{obs}^{n})^{\frac{1}{2}} = [1 + n(\emptyset_{j} - 1)]$$
(11)

where Φ_j is the isotopic fractionation factor for HO⁻ ion. The plot of $(k_o^o/k_o^n)^{\frac{1}{2}} vs n$ (Fig. 4) is linear $(r > 0.9976, s \le 0.02)$ with a slope $(\Phi_j - 1) = (-0.25)$. The fractionation factor is thus 0.75, a value in good agreement with values reported by earlier workers^{9,10}.

(*ii*) The increase in rate of reaction with ionic strength (*I*), suggests a primary salt-effect and supports the involvement of two negative ions in the reaction sequence. A plot of $\log k_{obs} vs I^{i}$ (Fig. 2), was linear with a slope of ~0.6, although the concentrations employed are above the formal Debye-Hückel range.

(*iii*) The effect of solvent composition on the reaction rate involving two negative ions is given by Eq. 12, derived on the basis of a double-sphere model¹¹:

$$\log k = \log k_{o} - \frac{Z_{A} Z_{B} e^{2}}{D k T d_{AB}}$$
(12)

where k_o is the rate constant in a medium of infinite dielectric constant, $Z_A e$ and $Z_B e$ are the charges, d_{AB} is the size of the activated complex, and k and T are the Boltzmann constant and absolute temperature, respectively. The size of the activated complex, d_{AB} , was calculated from the slope $= -Z_A Z_B e^2 / kT d_{AB}$ of the linear plot of $\log k_{obs} vs 1/D$ (Fig. 3), and was found to be between 3 and 7 Å: D-xylose (3.65 Å), D-ribose (4.62 Å), and L-arabinose (6.5 Å). The values are found to be reasonable in comparison with those of other reactions of similar nature¹¹.

(*iv*) The plot of $\Delta H^* vs \Delta S^*$ is linear(r > 0.9923, $s \le 0.03$) suggesting an isokinetic relationship (Fig. 5) and the operation of a common mechanism in the oxidation of pentoses by CAB. From the slope, the isokinetic temperature is determined to be β 416K, which is much higher than the experimental temperature (308K). The enthalpy– entropy relation was proved to be genuine through the Exner-criterion¹² by plotting $\log(k_{obs})_{317K} vs \log(k_{obs})_{305K}$ (r > 0.9899, $s \le 0.04$) (Fig. 5), from which $\beta = 405$ K. The value, being higher than the experimental temperature, indicates that the reaction is enthalpy controlled. This conclusion is further supported by the values of E_a (Table III) from which may be seen that the slowest reaction has the highest activation energy and vice versa.



Fig. 5. Isokinetic plots of (a) $\Delta H^* vs \Delta S^*$ and (b) log $(k_{obs})_{317K} vs \log (k_{obs})_{305K}$.

There are similarities in the oxidation of aldopentoses and aldohexoses by CAB in alkaline medium. Both follow identical kinetics and are enthalpy-controlled reactions. A common oxidation mechanism thus seems to be operating. It is reported¹³ that, in general, the rate of reaction of aldopentoses is higher than that of aldohexoses. Comparing their second-order rate constants($10^2k''Lm^{-1}s^{-1}$), the order followed is: D-fructose, 5.31 > D-xylose, 4.20 > D-ribose, 2.9 > L-arabinose, 1.7 > D-galactose, 1.61 > D-glucose, 1.52 > D-mannose 0.63.

The aldoses exist mainly in the pyranoid and furanoid forms; the former are the

more stable, and adopt chair conformations. The conformation having the anomeric hydroxyl group equatorially disposed (β anomer) is more stable and reacts faster because of the ready availability of HO-1 to the oxidant than the conformer having HO-1 axially oriented (*a* anomer). This is supported by the interaction energies of the chair conformers reported in the literature¹³. In the case of D-glucose, D-galactose, D-ribose, and D-xylose, the preponderant β anomer reacts faster. With L-arabinose, the *a* anomer is more stable than the β form and has *a*HO-1 oriented equatorially. For D-mannose, the *a* anomer is preponderant and as its axial HO-1 group is less exposed and thus less accessible to the oxidant, it is the β anomer which reacts more rapidly, although its percentage in the anomeric equilibrium is small².

From the present studies, we observe that the rate of oxidation of aldopentoses is higher than that of aldohexoses, and the ketohexose, fructose has the highest rate, giving the sequence: D-fructose > aldopentose > aldohexose. The higher rate of oxidation of D-fructose may be attributed to tautomeric contribution from the (minor, but reactive) furanoid form. The 5-hydroxymethyl group¹⁴ in the aldohexoses exhibits a greater -I effect and stabilizes the ring as compared to the hydrogen atom at C-5 in the aldopentoses. This difference could account for the lower rate of oxidation observed with the aldohexoses. The estimated interaction energies of chair conformers for the aldoses also support this observation¹³. The ΔS^* values for aldohexoses are positive and higher than those of aldopentoses (Table V), in accord with the observation that ΔS^* is related to the rigidity of the organic molecule¹⁵. The slight differences in rates of oxidation of aldoses having the same substituents at C-5 (either H or CH₂OH) may be attributed to the configurational differences and orientations of hydroxyl substituents at C-2, C-3, and C-4.

Sugar	$\mathbf{E}_{a}kJmol^{-1}$	$\Delta H^* k Jmol^{-1}$	$\Delta G^* k Jmol^{-1}$	$\Delta S*JK^{-1}mol^{-1}$	Log A
L-Arabinose	96.4	93.8 ±0.04	96.0 ±0.2	-7.0 ± 0.6	15.9 ±0.03
D-Ribose	92.8	90.2 ± 0.04	94.9 ± 0.2	-15.0 ± 0.50	15.6 ± 0.1
D-Xylose	88.6	86.0 ± 0.04	93.6 ± 0.1	-24.5 ± 0.4	15.1 ±0.03
D-Mannose	113.7	111.1 ± 0.1	98.7 ± 0.5	$+39.5 \pm 1.0$	17.9 ±0.1
D-Glucose	101.2	98.6 ± 0.1	96.0 ± 0.2	$+ 8.2 \pm 0.5$	16.3 ± 0.1
D-Galactose	99.5	96.8 ± 0.1	96.1 ± 0.2	$+ 2.5 \pm 0.5$	16.0 ± 0.1
D-Fructose	69.0	66.4 ± 0.1	93.8 ± 0.7	-87.5 ± 0.8	11.2 ± 0.0

TABLE V

Comparison of the thermodynamic parameters of hexoses and pentoses

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REFERENCES

- 1 K. K. Banerji, B. Jayaram, and D. S. Mahadevappa, J. Sci. Ind. Res., 46 (1987) 65-76.
- 2 T. A. Iyengar, Puttaswamy, and D. S. Mahadevappa, Carbohydr. Res., 197 (1990) 119-130.
- 3 M. C. Agarwal and S. P. Mushran, J. Chem. Soc., Perkin Trans II, (1973) 762-765.
- 4 G. Akerloff, J. Am. Chem. Soc., 54 (1932) 4125–4139; M. Balakrishnan, G.Venkoba Rao and N. Venkatasubramanian, Proc. Indian Acad. Sci., 80A (1974) 50–56.
- 5 E. Bishop and V. J. Jennings, Talanta., 1 (1958) 197-212.
- 6 C. J. Collins and N. S. Bowman, Isotope Effects in Chemical Reactions, Van-Nostrand-Reinhold, New York, 1970, p. 267.
- 7 W. J. Albery and M. H. Davies, J. Chem. Soc., Faraday Trans, 68 (1972) 167-181.
- 8 G. Gopalakrishnan and J. L. Hogg, J. Org. Chem. 50 (1985) 1206-1212.
- 9 A. J. Kresge and A. L. Allred, J. Am. Chem. Soc., 85 (1963) 1541.
- 10 V. Gold and S. Grist, J. Chem. Soc., Perkin Trans II, (1972) 89-95.
- 11 K. J. Laidler, Chemical Kinetics, 2nd edn, Tata McGraw-Hill, Bombay, 1965, p. 214.
- 12 O. Exner, Collect. Czech. Chem. Commun., 29 (1964) 1094-1100.
- 13 B. Capon, Chem. Rev. 69 (1969) 407-498.
- 14 J. Shorter, Correlation Analysis In Organic Chemistry: An Introduction to Linear Free Energy Relations, Clarendon Press, Oxford, 1973, p. 35.
- 15 F. P. Price Jr. and L. P. Hammett, J. Am. Chem. Soc., 63 (1941) 2387-2393.
- 16 H. S. Isbell and W. W. Pigman, J. Res. Nat. Bur. Stand., 18 (1937) 141-194.