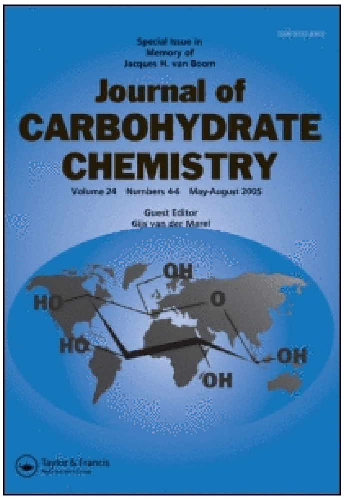

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

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To cite this Article Iyengar, T. A. and Mahadevappa, D. S.(1992) 'Oxidation of Pentoses by Sodium-N-bromo-P-toluene sulphonamide: A Kinetic and Mechanistic Study', Journal of Carbohydrate Chemistry, 11: 1, 37 — 58
To link to this Article: DOI: 10.1080/07328309208016140
URL: http://dx.doi.org/10.1080/07328309208016140

J. CARBOHYDRATE CHEMISTRY, 11(1), 37-58 (1992)

OXIDATION OF PENTOSES BY SODIUM-N-BROMO-P-TOLUENE SULPHONAMIDE: A KINETIC AND MECHANISTIC STUDY

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Received December 20, 1990 - Final form September 4, 1991

ABSTRACT

Kinetics of oxidation of D-xylose, D-ribose, D-lyxose and L-arabinose by bromamine-T (sodium *N*-bromo-*p*-toluene sulphonamide, BAT) was studied in alkaline medium at 30 °C. The rate was zero-order in $[BAT]_o$, but exhibited fractional order kinetics with respect to $[sugar]_o$ and $[HO^-]_o$. The rates levelled off at higher $[sugar]_o$ and $[HO^-]_o$. Stoichiometry experiments have shown that the sugar was oxidised to the respective aldonic acid. Variation of ionic strength of medium and addition of the reaction products, *p*-toluenesulphonamide and Cl^- ions have no effect on the rate. The rate increased with decrease in dielectric constant of the medium. Solvent isotope studies using D_2O have shown that $k_a(D_2O)/ k_a(H_2O) = 1.36$. The reaction has been studied at different temperatures and the overall activation parameters have been calculated. Activation parameters for the rate limiting step were determined from Michaelis-Menton type plots. A mechanism in which formation of the enediol anion of the sugar is the rate limiting step is proposed.

INTRODUCTION

Aldo- and ketohexoses and pentoses have been oxidized with several oxidants. Kinetics of oxidation of several sugars by halogens [1] and copper (II)[2] in alkaline medium are reported, but there is meagre information in the literature on the oxidation of sugars by *N*-metallo-halogen species, especially by the *N*-arylhalosulphonamides. We have recently studied the oxidation kinetics of hexoses[3] and pentoses[4] with chloramine-B (CAB) in NaOH medium. Mushran et al.[5] have reported the kinetics of oxidation of a few aldoses by chloramine-T in alkaline medium. However, the bromine analogues of *N*-arylhalosulphonamides have not been extensively used for oxidation studies of sugars. So, it was of interest to compare the oxidative behaviour of pentoses by bromamine-T (sodium *N*-bromo-*p*-toluenesulphonamide, BAT), with chlorine analogue. In this paper we present the kinetics of oxidation of four pentoses, viz., D-xylose, D-ribose, D-lyxose and L-arabinose with bromamine-T in alkaline medium at 30 °C.

RESULTS AND DISCUSSION

The kinetics of oxidation of the aldopentoses with BAT in NaOH medium were studied at several initial concentrations of reactants. With the pentose in large excess, plots of $[BAT]_o - [BAT]$ vs time are found to be linear ($r > 0.9965$) passing through the origin (Fig. 1) indicating zero-order dependence on $[oxidant]_o$. The standard zero-order rate constants, k_a were calculated from the equation, $k_a = k_o N/V$ where k_o is the slope of the plot, N and V are the normality of sodium thiosulphate used and the aliquot of the reaction mixture taken respectively. The zero-order dependence of the rate on $[BAT]_o$ is further confirmed by the constancy of the rate constants (Table 1)

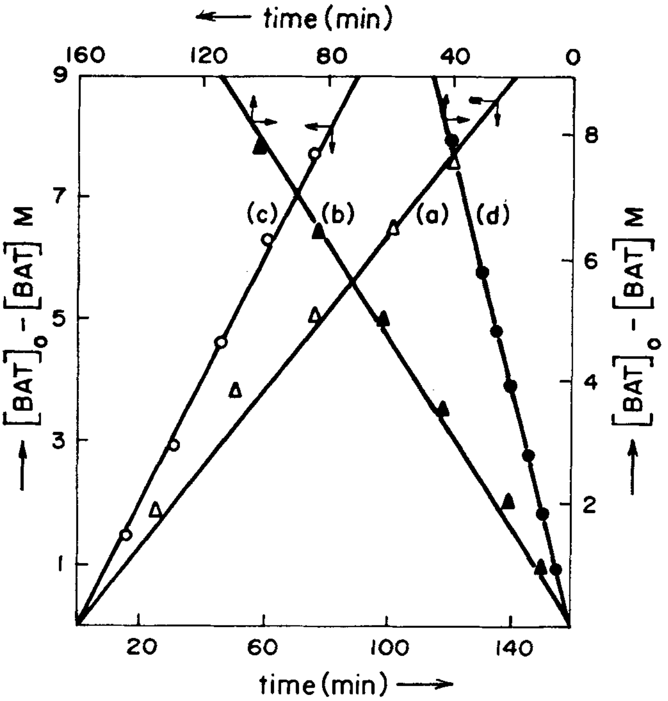


Fig. 1. Plot of $[BAT]_o$ - [BAT] vs time.
$[BAT]_o$ = 1.5 x 10^{-3}M; $[S]_o$ = 1.0 x 10^{-2}M,
$[HO^-]_o$ = 2 x 10^{-2}M, I = 0.5 M, temp = 30 °C,
a = D-xyl; b = D-rib; c = D-lyx; d = L-ara.

indicating that oxidation of pentoses terminated at the aldonic acid stage. The rate increases with $[Sugar]_o$ and log k_* vs log $[S]_o$ is linear (r > 0.9972, s ≤ 0.02) with a fractional slope, indicating fractional order in $[S]_o$. The rates tend to level off at higher $[S]_o$ (Table 1). At constant $[BAT]_o$ and $[S]_o$, the rate increases with increase in $[HO^-]_o$. A plot of log k_* vs log $[HO^-]_o$ is linear (r>0.9910, s ≤ 0.05) with a fractional slope, which proves the fractional order dependence on $[HO^-]_o$. At higher $[HO^-]_o$ the rate levels off (Table 2).

TABLE 1. Effect of Varying $[BAT]_0$ and $[Pentose]_0$ on the Rate of Oxidation of Pentose at 30 °C.

$[HO^-]_0 = 2.0 \times 10^{-2} M$; $I = 0.5 M$.

$[BAT]_0$ x 10^3M	$[Pentose]_0$ x 10^2M	k_0 x 10^5 M min^{-1} D-xyl	D-rib	D-lyx	L-ara
1.0	1.0	5.87	3.04	2.05	1.96
1.5	1.0	5.84	3.04	2.12	1.91
2.0	1.0	5.72	3.00	2.10	1.85
2.5	1.0	6.11	3.02	2.00	1.82
3.0	1.0	6.29	2.75	2.01	1.85
4.0	1.0	5.98	2.81	1.92	1.87
1.5	0.5	3.52	1.68	1.21	1.14
1.5	1.5	7.72	4.36	3.87	2.63
1.5	2.0	9.97	5.51	-	3.13
1.5	2.5	10.64	-	-	3.89
1.5	3.0	10.58	7.73	5.63	4.50
1.5	4.0	11.11	9.94	7.56	5.11
1.5(a)	1.0	5.70	2.80	1.92	1.75
1.5(a')	1.0	5.77	3.24	1.78	1.88
1.5(b)	1.0	5.54	3.00	1.89	1.90
1.5(b')	1.0	5.12	2.64	2.00	1.85
1.5(c)	1.0	5.80	2.95	2.10	1.90
1.5(c')	1.0	5.85	3.02	2.15	1.93

(a) $I = 0.02M$, (a') $I = 1.0M$; (b) $[PTS] = 1.5 \times 10^{-3}M$, (b') $[PTS] = 6 \times 10^{-3}M$; (C) $[Cl^-] = 1.0 \times 10^{-2}M$; (c') $[Br^-] = 1.0 \times 10^{-2}M$.

TABLE 2. Effect of varying $[HO^-]_0$ on the Reaction Rate at 30 °C. $[BAT]_0 = 1.5 \times 10^{-3}M$; $[S]_0 = 1.0 \times 10^{-2}M$; $I = 0.5M$.

$[HO^-]_0$ x 10^2M	10^5 k_0 M min^{-1} D-xyl	D-rib	D-lyx	L-ara
1.0	2.99	1.71	1.10	1.14
1.5	4.20	2.58	-	1.52
2.0	5.84	3.04	2.12	1.91
2.5	6.58	3.70	2.54	2.28
3.0	7.62	4.02	2.88	2.53
4.0	9.20	5.10	-	3.13

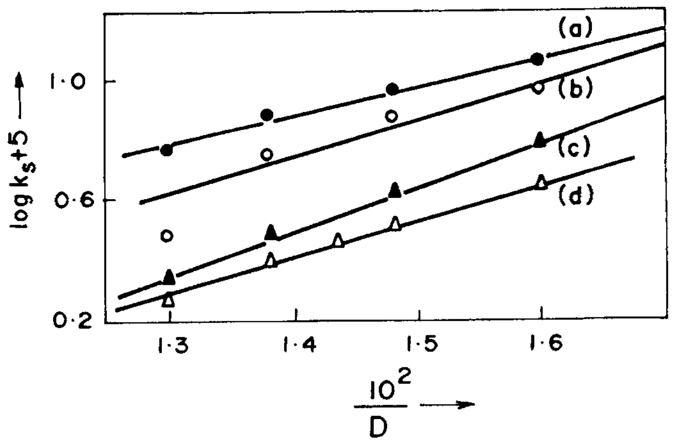


FIG. 2. Plot of log k_s vs 1/D. Conditions are as in Fig. 1.

The rate of oxidation of aldopentoses was unaltered when the ionic strength (I) of the medium was changed using $NaClO_4$ solution (Table 1). Addition of the reaction products, *p*-toluenesulphonamide and Br^- ion and Cl^- ion had negligible influence on the rate of the reaction (Table 1). The solvent composition was varied by adding methanol (0-30% v/v). The reaction rate increased with methanol content of the medium. A plot of log k_s vs 1/D where D is the dielectric constant of the medium gives a straight line ($r > 0.94$, $s \leq 0.09$) with a positive slope (Fig. 2).

The rate of oxidation of sugars was studied at different temperatures in the range 298-313 °K. The Arrhenius plot of log k_s vs 1/T was linear ($r > 0.9965$, $S \leq 0.03$) and activation parameters Ea, ΔH^*, ΔS^*, ΔG^* and log A were calculated for the composite reaction (Table 3).

TABLE 3. Kinetic and Thermodynamic Parameters for the Oxidation of Pentoses with BAT at 30 °C.

	D-xyl	D-rib	D-lyx	L-ara
Ea kJ/M	100.0 (90.1)	98.97 (80.9)	112.8 (85.1)	104.3 (93.7)
ΔH^* kJ/M	97.5±0.1 (87.6±0.1	96.4±0.1 (78.3±0.1	110.3±0.1 (82.6±0.1)	101.8±0.1 (91.1±0.1)
ΔS^* $JK^{-1}M^{-1}$	-39.1±0.5 (-27.6±0.2)	-47.3±0.1 (-59.7±0.4)	-4.5±0.4 (-46.9±0.5)	-34.4±0.6 (-21.9±0.7)
ΔG^* kJ/M	109.4±0.2 (96.0±0.1)	110.9±0.3 (96.9±0.4)	111.6±0.1 (96.9±0.3)	112.3±0.3 (97.8±0.2)
Log A	10.8±0.0 (11.4±0.0)	10.3±0.0 (9.7±0.0)	12.6±0.0 (10.4±0.0)	11.0±0.0 (11.7±0.0)

Parenthesis values refer to the activation parameters for the rate limiting step obtained from the plot of log k_2 vs 1/T.

Solvent-isotope studies were made in D_2O with D-xylose as the substrate. The values are $k_o(D_2O)$ = 7.95 x 10^{-5}M min^{-1} while $k_o(H_2O)$ = 5.84 x 10^{-5} M min^{-1}, with other conditions as in Table 1. This led to an inverse solvent isotope effect, $k_o(D_2O)/k_o(H_2O)$ = 1.36. Proton-inventory studies were made in H_2O - D_2O mixtures, with D-xylose as the substrate. The results are shown in Table 4. The corresponding proton inventory plot for the rate constant k_o^n in a solvent mixture of deuterium atom fraction 'n' is given in Fig. 3.

The work of Bishop and Jennings,[6] Morris et al.[7] and Hardy and Johnston[8] has shown that identical equilibria

TABLE 4. Proton Inventory Studies for Oxidation of D-xylose by BAT in H_2O - D_2O mixtures at 30 °C.

Atom fraction of D (n)	$10^5 k_s^n$ M min^{-1}
0.00	5.84
0.248	6.42
0.397	6.60
0.595	7.21
0.724	7.40
0.898	7.92

$[BAT]_o = 1.5 \times 10^{-3}$ M; $[Xylose]_o = 1 \times 10^{-2}$ M;
$[HO^-]_o = 2.0 \times 10^{-2}$ M; I = 0.5 M.

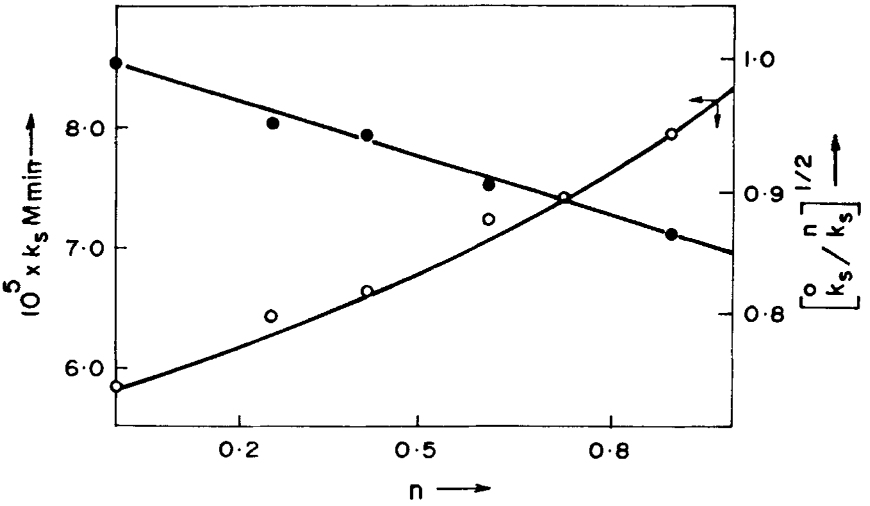


Fig. 3. Proton Inventory Plots for the Oxidation of D-xylose by BAT in H_2O-D_2O at 303 °K. Experimental conditions are as in Table 4.

exist in aqueous solutions of *N*-metallo-*N*-haloarylsulphonamides of the general formula RNXNa (R = $C_6H_5SO_2$ - or *p*-$CH_3C_6H_4SO_2$- and X = Cl or Br). Bromamine-T behaves like a strong electrolyte in aqueous solution. The anion is protonated in acidic solutions (eq.1) :

$$TsNBr^- + H^+ \rightleftharpoons TsNBrH \quad \ldots\ldots (1)$$

$(Ts = p\text{-}CH_3C_6H_4SO_2-)$

The free acid formed can undergo hydrolysis and/or disproportionation (eq.2 and 3):

$$TsNBrH + H_2O \rightleftharpoons TsNH_2 + HOBr \quad \ldots\ldots (2)$$

$$2\ TsNBrH \rightleftharpoons TsNH_2 + TsNBr_2 \quad \ldots\ldots (3)$$

Thus in acid solutions of BAT, the probable oxidising species are the free acid TsNBrH, dibromamine-T($TsNBr_2$) and HOBr.

In aqueous alkaline medium, BAT may exist in the following equilibria :

$$TsNBr^- + H_2O \rightleftharpoons TsNBrH + HO^- \quad \ldots\ldots (4)$$

$$TsNBrH + HO^- \rightleftharpoons TsNH_2 + BrO^- \quad \ldots\ldots (5)$$

In the present investigations, the rate of oxidation of sugars indicates a zero-order dependence on $[BAT]_o$, showing that the oxidant is involved in a fast step of the reaction sequence. Under these conditions, identification of the reactive oxidant species would become kinetically unimportant. However, equation (4) involves a base retarding step which is not observed experimentally. Hence the anion $TsNBr^-$, which is in higher concentrations in alkaline solutions[6] could be the likely oxidising species for the pentoses. Further confirmation of the zero-order in $[BAT]_o$ is obtained, as the reaction product, *p*-toluenesulphonamide ($TsNH_2$) has no effect on the rate indicating that it is not involved in a pre-equilibrium.

Since the rate of reaction is dependent on $[S]_o$ and $[HO^-]_o$, the first step of the mechanism involves an

$$S + HO^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Y \qquad \ldots\ldots \text{(i)}$$

$$Y \xrightarrow{k_2} \bar{E} + H_2O \qquad \ldots\ldots \text{(ii)}$$

rate limiting step

$$\bar{E} + TsNBr^- \xrightarrow{k_3} \text{Products} \qquad \ldots\ldots \text{(iii)}$$

fast

SCHEME 1

Assuming Michaelis-Menten type kinetics with interaction between the reducing sugar molecule (S) and HO^- ion forming an enediol anion ($\bar{E}$) which is subsequently oxidized by BAT in a fast step. Since the aldopentoses have exhibited similar kinetics, the following mechanism (Scheme 1) is proposed in the present study :

$[S] = [S]_0 - [Y]$ and $[HO^-] = [HO^-]_0 - [Y]$ and steady state conditions for the intermediate Y, rate law (6) can be derived for the disappearance of BAT, after neglecting[7] the higher order term in [Y] :

$$\frac{-d[S]}{dt} = \frac{-d[BAT]}{dt} = k' = \frac{k_1k_2[S]_0\,[HO^-]_0}{(k_{-1} + k_2) + k_1[S]_0 + k_1[HO^-]_0} \qquad \ldots\ldots (6)$$

Rate law (6) is in agreement with the experimental findings. The rate is linear at lower concentrations of S and HO^- and becomes independent at higher concentrations of these species. Equation (6) can be transformed into equation (7):

$$\frac{1}{k'} = \frac{(k_{-1} + k_2)}{k_1k_2\,[S]_0\,[HO^-]_0} + \frac{1}{k_2\,[HO^-]_0} + \frac{1}{k_2\,[S]_0} \qquad \ldots (7)$$

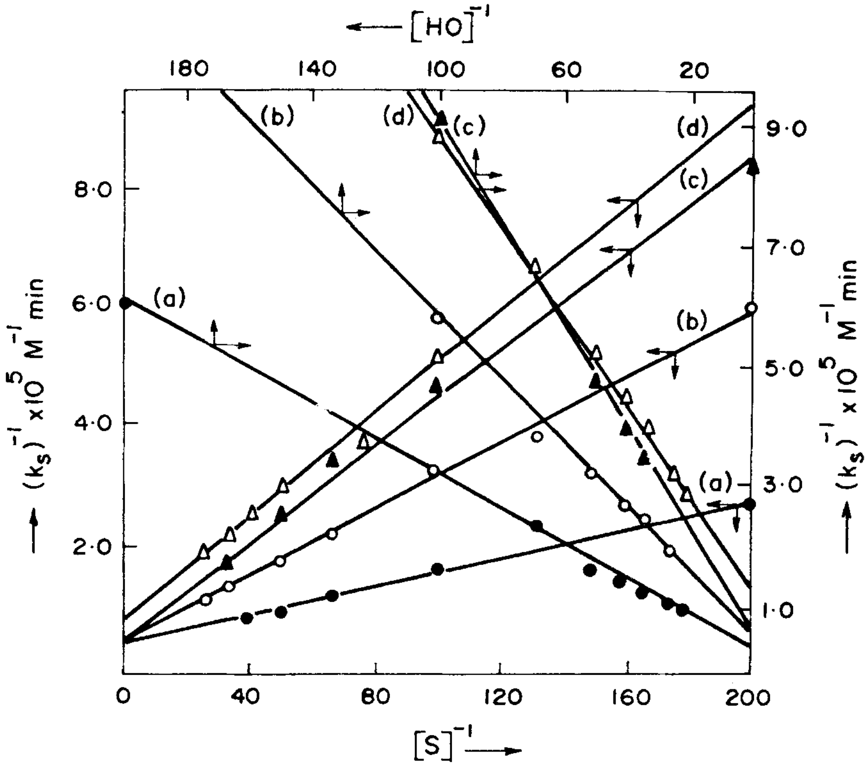


Fig 4. Plots of $1/k_s$ vs $1/[S]$ and plots of $1/k_s$ $1/[HO^-]_o$. Conditions are as in Fig. 1.

Double reciprocal plots, $1/k_s$ vs $1/[S]_o$ and $1/k_s$ vs $1/[HO^-]_o$ were constructed (Fig. 4). The plots are linear with intercepts ($r > 0.9958$) and values of k_2 could be calculated.

Activation Parameters for the Rate Limiting Step

Evidence for the enediol anion formation was obtained by the UV spectrum (obtained on a Jasco UV spectrophotometer) . UV spectrum of basified reaction mixture was taken immediately after mixing, when a band at 310 nm was

TABLE 5. Enediol Anion Formation Constants k_E at different temperatures.

Substrate Temp °K	$k_E \times 10^3$ min^{-1}			
	D-xyl	D-rib	D-lyx	L-ara
298	5.88	5.55	4.17	2.70
303	10.98	9.09	8.33	5.55
308	19.23	15.62	14.29	10.98
313	35.71	25.0	22.22	16.67

noticed. The intensity of the enediol band[10] decreased with time, presumably due to its reaction with the oxidant. Since k_E represents the rate constant for enediol formation it could be employed for determining the activation parameters for the rate limiting step (Scheme 1). The HO^- and oxidant concentrations were kept constant and $[S]_o$ was varied at several temperatures in the range of 298-313 °K. The value of k_E was calculated from the double reciprocal plots at each temperature (Table 5) and Arrhenius plot of log k_E vs 1/T was made (Fig. 5). This was linear ($r > 0.9948$, $s \leq 0.04$) and from the slope, the energy of activation Ea was obtained. The other activation parameters ΔH^*, ΔG^*, ΔS^* and log A were calculated (Table 3) using the following equations:

$$\Delta H^* = Ea - RT \quad \ldots . \quad (8)$$

$$\Delta S^{*} = \frac{\Delta H^{*}}{T} - 4.576 \log T/k_{2} - 47.22 \quad .... \quad (9)$$

where k_2 is in sec^{-1}

$$\Delta G^{*} = \Delta H^{*} - T\Delta S^{*} \quad .... \quad (10)$$

$$\log A = \log \frac{RT}{Nh} + \frac{\Delta S^{*}}{2.303\ R} \quad .... \quad (11)$$

A probable mechanistic picture of oxidation of pentoses by BAT is shown in Scheme 2.

At low alkali concentrations, the sugar molecule is converted into an enediol (Lobry de Bruyn-Alberda Van Ekenstein reaction). The enediol anion formed in the rate limiting step is subjected to an electrophilic attack by the positive halogen species $TsNBr^{-}$. Elimination of benzenesulphonamide anion followed by HBr produces a ketene which on hydrolysis forms the aldonic acid.

The fact that ionic strength has no effect on rate supports the involvement of neutral species in the rate sequence. The increase in rate, in solvents of lower dielectric constant compared to water, formed by the addition of methanol to the reaction mixture can be explained if the transition state is expected to be less polar than the initial state, because although it may have the same charge it is spread over a larger volume. Such transition states are destabilised relative to the initial state by highly polar solvents, while it is anticipated that the rate constant will be greater in non-polar than in polar solvents.[11]

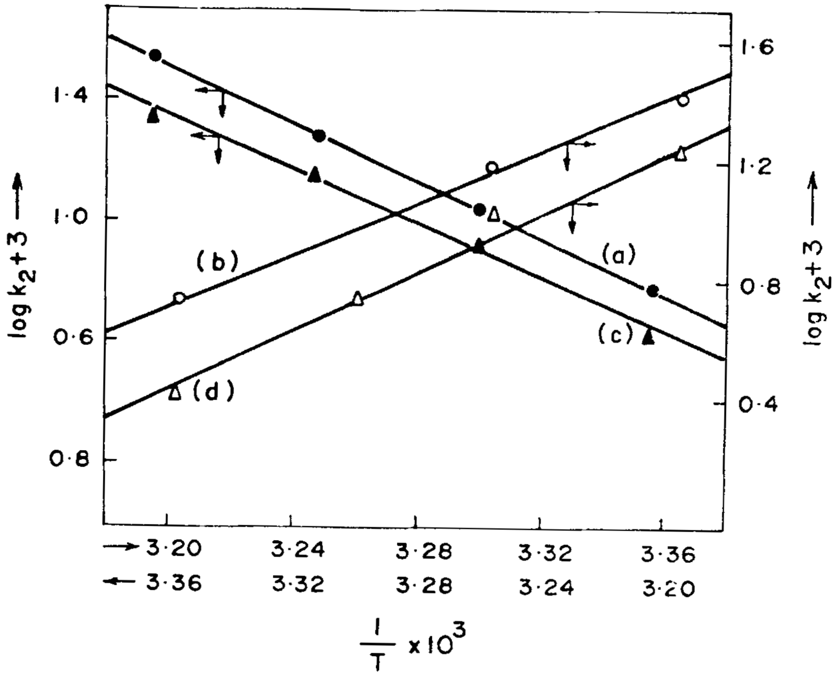
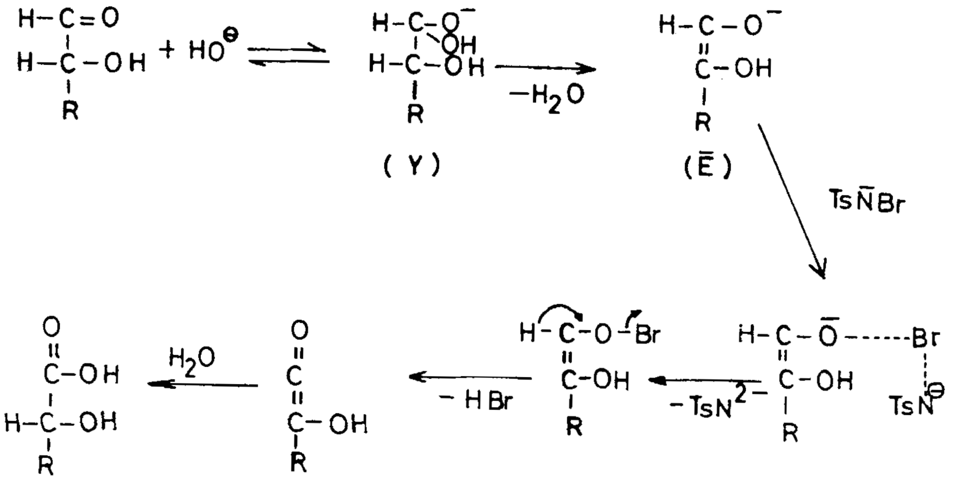


Fig. 5. Plots of log k_2 vs 1/T.
(a) D-xyl; (b) D-rib; (c) D-lyx; (d) L-ara.



SCHEME 2

Solvent isotope studies in D_2O have shown that the inverse solvent isotope effect, $k_s(D_2O)/k_s(H_2O) = 1.36$. For a fast pre-equilibrium proton transfer, it is generally expected from a knowledge of electrophilicities of H_3O^+ and D_3O^+ ions and nucleophilicities of OH^- and OD^-, that $k(D_2O)/k(H_2O) = 2-3$, since D_3O^+ and OD^- are stronger acid and stronger base than H_3O^+ and OH^- ions.[12] Hamill and Lamer[13] and Maron and Lamer[14] observed a slight decrease in rate in D_2O medium for the mutarotation of glucose and isomerization of nitromethane, respectively, although a proton transfer is indicated in these reactions. A similar observation has been made by us[15] during the oxidation of dimethylsulphoxide by chloramine-T in acid medium. It is concluded that the ratio of dissociation constants of the proto and deutero acids depends only on the ratio of their dissociation constants and is completely independent of their rates of association. Further, a rapid exchange of sulphoxide hydrogens with D_2O to form DMSO-d_6 is also invoked[15] to explain the rate decrease in D_2O medium. In the present investigations, a rapid O-H/O-D exchange cannot be ruled out[16] and formation of the enediol anion from the deuterated sugar molecule involves a substantial primary isotope effect, $k_H/k_D > 1$ because of the cleavage of O-H bonds in H_2O and O-D bonds in D_2O. The latter can compensate for the expected increase in inverse solvent isotope effect, with the net result that $k_s(D_2O)/k_s(H_2O)$ is considerably less than the usual value of 2-3.

In the present studies, the increase of rate in D_2O supports the fast pre-equilibrium hydroxyl ion transfer[12] (Scheme 1). The dependence of rate constant (K_s^n) on n, the atom fraction of deuterium in a solvent mixture of H_2O and D_2O, is given [17,18] by equation (12),

$$(k_s^{o})/(k_s^{n}) = \frac{\prod^{TS} (1-n + n\phi_i)}{\prod^{RS} (1-n + n\phi_j)} \qquad (12)$$

where ϕ_i and ϕ_j are the isotopic fractionation factors for isotopically exchangeable hydrogen sites in the transition and reactant states respectively. If it is assumed that the reaction proceeds through a single transition state, equation (12) can be transformed into equation (13),

$$[k_s^{o}/k_s^{n}]^{1/2} = [1 + n(\phi_j - 1)] \qquad (13)$$

From the linear relation of $(k_s^{o}/k_s^{n})^{1/2}$ vs n ($r = 0.9939$, Fig. 3), the slope $(\phi_j - 1) = -0.15$ from which $\phi_j = 0.85$. Kresge and Allred[19] obtained a value of 0.8 by NMR technique for the isotopic fractionation factor of HO^- which was confirmed by Gold and Grist.[20] A similar value was noted in the oxidation of aliphatic ketones by *N*-bromamines.[21] Hence the formation of a single transition state with the active participation of HO^- ion is indicated here also.

Isokinetic Relationship

A constancy of ΔG^* values (Table 3) indicates the operation of a common mechanism for the oxidation of pentoses by BAT. From plots of ΔH^* vs ΔS^* (Table 3, Fi . 6, $r = 0.9921$) the isokinetic temperatures β was 319.3 °K. The relation was found to be genuine by the Exner[22] criterion where $\log k_{s(308\ °K)}$ vs $\log k_{s(298\ °K)}$ was linear

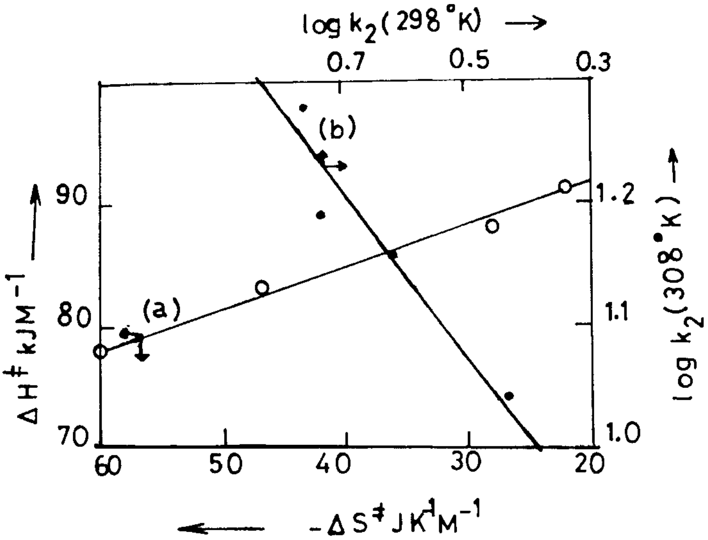


Fig. 6. Plot of, (a) ΔH* vs ΔS*,
(b) Plot of log k_2(308 °K) vs log k_2(298 °K).

(r = 0.9520; Fig. 6). The isokinetic temperature was calculated from the relation β = T_1T_2 (1-f)/ (T_1-T_2f), where f is the slope of the Exner plot, and β was 326 °K. Since the value of β is above the experimental temperature (303 °K) it can be concluded that enthalpy is a controlling factor of the reaction.

CONCLUSIONS

Since a common mechanism is operative, a relative comparison of the rates of oxidation of pentoses by BAT is desirable. If the values of standard zero order rate constants are taken into consideration, then D-xylose has the highest and L-arabinose has the lowest rate:

	D-xyl >	D-rib >	D-lyx >	L-ara
$k_a \times 10^5$ M min^{-1}	5.84	3.04	2.12	1.91
$k_2 \times 10^3$ min^{-1}	10.98	9.09	8.33	5.55

A similar behaviour is noted if the enolization rate coefficients (k_2) are compared. Isbell and coworkers[23] in their tritium exchange experiments have observed the rate sequence: rib > lyx > xyl > ara. DeWit et al.[10] have studied the behaviour of monosaccharides in aqueous alkaline solution through UV absorption spectroscopy, by monitoring the 310 nm band. The rates of enediol formation are xyl > ara > rib. Gleason and Barker[24] noted that the rate of oxidation of pentoses by oxygen in presence of alkali is dependent on the medium. In dilute KOH solution the relative rate was, xyl > rib > ara > lyx, while in the presence of 0.5 M sodium carbonate, the sequence was rib > lyx > xyl > ara. However, using the published pk_a values of the pentoses, relative rates for the oxidation in carbonate system were calculated as xyl > rib > lyx > ara. This is also the order found in the present investigations. The differences found between this work and the rate sequences reported by other workers could possibly be due to the formation of 1,2-enediols either in the *E* or *Z* forms. Isbell and co-workers[23] propose that aldoses and ketoses generally yield mixtures of *Z*- and *E*-enediols, the proportions of which differ from sugar to sugar. In the present work, a perusal of ΔS^* values for the rate limiting step (Table 3) could indicate the probability of formation of *E*-or *Z*-enediol. Values of ΔS^* obtained are negative and are in the order:

	rib >	lyx >	xyl >	ara
ΔS^{*}, JK^{-1} mol^{-1}	-59.7	-46.9	-27.6	-21.9

We believe that the trend also reflects the probability of *E*- enediol formation, which is more stable than the *Z*-isomer. The probability is greatest with D-ribose while L-arabinose has the least tendency to form the trans isomer.

Oxidation of pentoses by chloramine-B (CAB) in alkaline medium[4] indicates a rate law of the type rate = $k[CAB]\ [S]_0\ [HO^-]_0$ which amounts to the involvement of oxidant in a rate limiting step. Substantial primary salt, solvent isotope and dielectric effects were noticed. But in the present oxidation studies it is seen that enolization is rate limiting and the sugar molecule is oxidised by BAT in a fast step. It has been observed that oxidations are generally faster with the bromine analogue[25,26] which has been rationalised in terms of the differences in electrophilicity of halonium cations, cl^+ and Br^+ which are generally the reactive species in these reactions[27] and is also partly due to the moderate differences in the Van der Waal's radii of bromine and chlorine.

EXPERIMENTAL

Materials and Method

Bromamine-T (P-$CH_3C_6H_4SO_2N$, BrNa, $3H_2O$): This reagent (BAT) was prepared according to the method of Nair et al.[28] The solid BAT when heated to ~ 800 °C left stoichiometric residue of NaBr. It's UV, IR and NMR spectra were in accord with published results.

An aqueous solution of BAT (~ 0.1N) was prepared, standardized iodometrically and preserved in brown bottles to arrest its photochemical deterioration.

Aqueous solutions of sugars, D-xylose, D-ribose, (Loba Chemie), D-lyxose (Sigma) and L-arabinose (BDH) were freshly prepared whenever required. All other reagents used were of analytical grade. The reaction medium was maintained at a constant ionic strength of 0.5 M using concentrated $NaClO_4$ solution.

Stoichiometry

The stoichiometry run of the oxidation reaction with excess BAT solution over that of $[sugar]_o$ indicated that one mol of the oxidant was consumed per mol of the sugar to form the corresponding aldonic acid. The stoichiometric equation can be expressed by equation (14):

$$C_5H_{10}O_5 + TsN.NaBr + H_2O \dashrightarrow C_5H_{10}O_6 + TsNH_2 + Na^+ + Br^- \quad ....(14)$$

where Ts = p-$CH_3C_6H_4SO_2$-.

The reduction product, *p*-toluene sulphonamide (PTS) was detected by paper chromatography. Benzyl alcohol, saturated with water, was used as the solvent with 0.5% vanillin in 1% HCl in ethanol as spray reagent (R_f = 0.905).

From an aliquot of the reaction mixture, *p*-toluene sulphonamide was extracted into the ether and the residual solution was then successively passed through Amberlite IR-120 (H^+) column and Dowex-2 (HO^-) column for the removal of Na^+ and Br^- ions. The final eluate was then concentrated to 30% and analysed by paper chromatography (1-butanol -

acetic acid - water, 4:1:5) and the aldonic acid was detected with *p*-anisidine hydrochloride.

Attempts to detect the presence of free radicals in the reaction mixture using acrylonitrile solution gave negative results as no polymerization was induced even after 24 hrs.

Kinetic Measurement

The mixture of oxidant, alkali, $NaClO_4$ and water (for constant total volume) was taken in a boiling tube coated black on the outside surface and thermostated at 30 °C for about 20 min. Freshly prepared aldopentose solution, taken separately in a tube was also equilibrated at the same temperature. The reaction was initiated by adding the requisite amount of sugar solution to the first boiling tube. The progress of reaction was monitored through the iodometric determination of unconsumed BAT in aliquots of reaction mixture taken out at regular intervals of time. The reaction was followed for two half-lives. The rate constants calculated were reproducible to ± 3%.

Regression analysis of experimental data was carried out on a EC-72 Statistical Calculator to obtain the regréssion coefficient "r" and standard deviation "s", of the points from the regression line.

ACKNOWLEDGEMENT

One of the authors (TAI) gratefully acknowledges the award of a Senior Research Fellowship to her by the University Grants Commission, New Delhi.

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