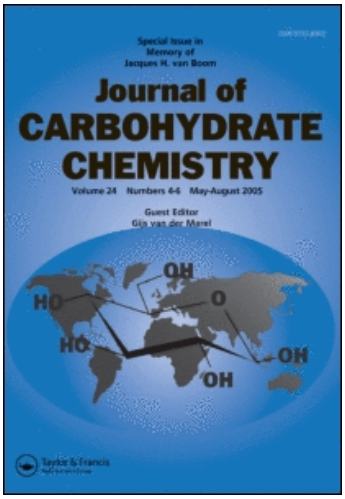

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V. Shashikala[a]; K. S. Rangappa[a]
[a] Department of Studies in Chemistry, University of Mysore, Mysore, India

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A NOVEL MECHANISM FOR THE OXIDATION OF *ERYTHRO*-SERIES PENTOSES AND HEXOSES BY *N*-ARYLBROMOSULPHONAMIDES IN ALKALINE MEDIUM

V. Shashikala and K. S. Rangappa*

Department of Studies in Chemistry, University of Mysore,
Manasagangotri, Mysore-570006, India

ABSTRACT

Kinetic studies of the oxidation of D-mannose, D-glucose, D-fructose, L-arabinose and D-ribose by bromamine-T (sodium *N*-bromo-*p*-toluenesulphonamide or BAT) and bromamine-B (sodium *N*-bromobenzenesulphonamide or BAB) in alkaline medium were investigated at 30°C. The rate of the reaction was first order both with respect to the oxidant and the sugar and second order with respect to $[HO^-]$. The addition of the reaction product, *p*-toluenesulphonamide (PTS) or benzenesulphonamide (BSA), and the variation of ionic strength of the medium have no effect on the rate. The rate decreases with decrease in dielectric constant of the medium and values of d_{AB}, the size of activated complex, were calculated. Proton inventory studies were made in H_2O-D_2O mixtures. The activation parameters of the reaction were computed from Arrhenius plots. HPLC and GLC-MS analysis of the products indicated that the sugars were oxidized to a mixture of aldonic acids consisting of arabi-

*Corresponding author. Fax: +91-821-518835, +91-821-421263; E-mail: rangappaks@yahoo.com

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nonic, ribonic, erythronic and glyceric acids. A general mechanism consistent with the observed results has been proposed.

Key Words: Erythrose series sugars; Oxidation; Bromamine-T; Bromamine-B; Kinetics; Mechanism

INTRODUCTION

Aldo and ketohexoses and pentoses have been oxidized with several oxidants. Kinetics of oxidation of sugars by halogens[1–3] and copper (II)[4,5] in alkaline medium are reported, but the information in the literature on the oxidation of sugars by *N*-arylhalosulphonamides is very scanty. In this laboratory, we have already studied the oxidation of hexoses, pentoses, amino sugars and uronic acids by both chloramine-T (CAT) and chloramine-B (CAB) in alkaline medium.[6–9] However, the bromine analogues of *N*-arylhalosulphonamides have not been extensively used for oxidation of sugars. It was, therefore, of interest to compare the oxidation of hexoses and pentoses by bromamine-T (BAT) and bromamine-B (BAB) with that of their chlorine analogues. In this paper, we have reported the kinetics of oxidation of three hexoses, namely, D-glucose, D-mannose and D-fructose, and two pentoses, namely, L-arabinose and D-ribose, with BAT and BAB in alkaline medium at 30°C and compared the results with those of their chlorine anologues (CAT and CAB).[6,7] Each sugar is oxidized to a mixture of several aldonic acids. Pentoses form mainly pentonic acids as major products, but hexoses also form pentonic acids. In the case of hexoses, oxidation occurs mainly with the cleavage of the C-1–C-2 and C-2–C-3 bonds, whereas pentoses oxidize mainly with cleavage of C-1–H and C-1–C-2 bonds. On the basis of the above results, a novel mechanism for the oxidation of *erythro*-series sugars by *N*-arylbromosulphonamides is proposed.

RESULTS AND DISCUSSION

The reactions were carried out with varying concentrations of the oxidant (BAT or BAB) at constant $[HO^-]$ and $[S]_o$ with substrate (S) in large excess. Plots of log [OX] vs time, where OX is oxidant, were linear indicating a first order dependence of the reaction rate on $[BAT]_o$ or $[BAB]_o$. The pseudo first order rate constants k_{obs} obtained with different $[OX]_o$ were similar, confirming the first order dependence of the rate on $[OX]_o$ (Table 1). The k_{obs} values increased with increase in $[S]_o$ (Table 1). The plots of log k_{obs} vs. log $[S]_o$ were linear with unit slopes. The second order rate constants ($k_2 = k_{obs}/[S]_o$) were constant within the experimental errors demonstrating a first order dependence of the rate on $[S]_o$. Furthermore, the plots of k_{obs} vs. $[S]_o$ gave straight lines (Figure 1) passing through the origin indicating that the intermediates formed are of transient existence. At constant $[OX]_o$, $[S]_o$ and temperature, values of k_{obs} increased with an increase in [NaOH] (Table 2). The plots of log k_{obs} vs. log $[HO^-]$ were linear with slopes of 2, indicating a second order dependence of the rate on $[HO^-]$. Addition of the reaction products, *p*-toluenesulphonamide (PTS) or benzenesulphonamide (BSA) (0.008 M), and Br^- and Cl^- ions had negligible influence on

Table 1. Effect of Varying Reactant Concentrations on the Rate of Oxidation of Sugars by BAT and BAB at 30°C

10^3 $[BAT]_oM$ or 10^3 $[BAB]_oM$	10^2 $[S]_0M$	10^4 k_{obs} (s^{-1})									
		D-Mannose		D-Glucose		D-Fructose		L-Arabinose		D-Ribose	
		BAT	BAB	BAT	BAB	BAT	BAB	BAT	BAB	BAT	BAB
1.50	3.00	1.32	1.75	3.76	4.39	17.1	20.3	2.50	2.75	5.89	6.21
2.00	3.00	1.32	1.73	3.58	4.38	16.8	20.2	2.51	2.74	5.80	6.24
2.50	3.00	1.32	1.79	3.61	4.39	16.8	19.9	2.51	2.79	5.80	6.24
3.00	3.00	1.34	1.72	3.57	4.38	16.9	20.2	2.49	2.74	5.79	6.31
3.50	3.00	1.32	1.78	3.56	4.37	16.8	19.9	2.48	2.70	5.79	6.24
4.00	3.00	1.36	1.70	3.52	4.30	16.6	20.2	2.40	2.70	5.80	6.14
2.00	1.00	0.440	0.580	1.21	1.45	5.61	6.73	0.840	0.910	1.93	2.08
2.00	2.00	0.880	1.16	2.39	2.92	11.3	13.4	1.68	1.83	3.87	4.16
2.00	4.00	1.75	2.31	4.78	5.83	22.1	26.8	3.35	3.65	7.74	8.32
2.00	5.00	2.19	2.89	5.98	7.30	28.1	33.6	4.18	4.57	9.66	10.4
2.00	6.00	2.64	3.46	7.16	8.82	33.6	40.4	5.10	5.50	11.6	12.5

$[HO^-] = 2.00 \times 10^{-2}$ M; I = 0.100 M.

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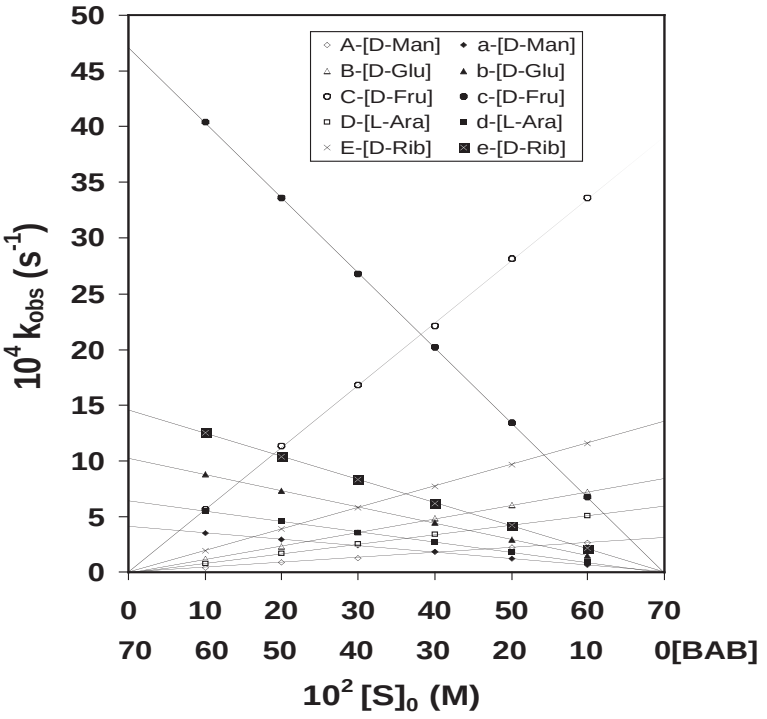

Figure 1. Plots of k_{obs} vs. $[S]_o$; $[BAT]_o = 2.00 \times 10^{-3}$ M, $[HO^-] = 2.00 \times 10^{-2}$ M, temp = 30°C. A, B, C, D and E refer to BAT and a, b, c, d and e refer to BAB.

the rate of reaction. The rate of oxidation of sugars was unaltered when ionic strength (I) of the medium was changed using sodium perchlorate. When the solvent composition of the medium was varied by adding methanol (0 to 40% v/v), the reaction rate decreased with increasing methanol content of the medium. Plots of log k_{obs} vs. $1/\varepsilon$ (ε-dielectric constant of the medium) were linear with negative slopes (Figure 2). The reactions were studied at different temperatures (298 to 318 K) and the Arrhenius plots of log k_{obs} vs 1/T were found to be linear. The activation parameters for the composite reaction were calculated (Table 3). The solvent isotope studies were made in D_2O and the ratios, $k_{obs}(H_2O)/k_{obs}(D_2O)$ were 0.5 to 0.56 (Figure 3).

Proton inventory studies were made in H_2O-D_2O mixtures (Table 4). Addition of an aqueous solution of acrylamide to the reaction mixture did not cause polymerization, showing the absence of free radical species during oxidation. A comparison of HPLC and GLC-MS retention times of the reaction products with those of the standards, indicated that arabinonic, ribonic, erythronic and glyceric acids are the major oxidation products for all the *erythro*-series sugars. In addition to these acids, small proportions of hexonic acids were formed from hexoses (Figure 4, Table 5). Incubation of sugars with alkali alone under the reaction conditions did not degrade the sugars.

The oxidation products of sugars were also analyzed at 0.5, 1, 2, 4, 8, 16 and 24 h. The formation of various six-carbon aldonic acids was observed only after 4 h,

Table 2. Effect of Varying $[OH^-]_o$ on the Rate of Oxidation of Sugars by BAT and BAB at 30°C

10^3 [NaOH] M	10^4 k_{obs} (s^{-1})									
	D-Mannose		D-Glucose		D-Fructose		L-Arabinose		D-Ribose	
	BAT	BAB	BAT	BAB	BAT	BAB	BAT	BAB	BAT	BAB
3.00	0.0290	0.0400	0.0850	0.097	0.380	0.450	0.0570	0.0610	0.130	0.140
5.00	0.0800	0.110	0.240	0.270	1.06	1.26	0.160	0.170	0.360	0.390
10.0	0.320	0.430	0.900	1.090	4.21	5.04	0.630	0.690	1.45	1.56
15.0	0.710	0.970	2.01	2.46	9.46	11.4	1.41	1.54	3.26	3.52
20.0	1.32	1.73	3.58	4.38	16.8	20.2	2.51	2.74	5.80	6.24
25.0	1.97	2.69	5.60	6.84	26.3	31.5	3.92	4.28	9.06	9.25
30.0	2.96	3.89	8.06	9.84	37.7	45.5	5.65	6.17	13.1	14.0
35.0	4.12	5.20	10.6	13.2	51.2	60.9	7.68	8.39	17.8	19.1

$[BAT]_o = [BAB]_o = 2.00 \times 10^{-3}$ M; $[S]_o = 3.00 \times 10^{-2}$ M; I = 0.100 M.

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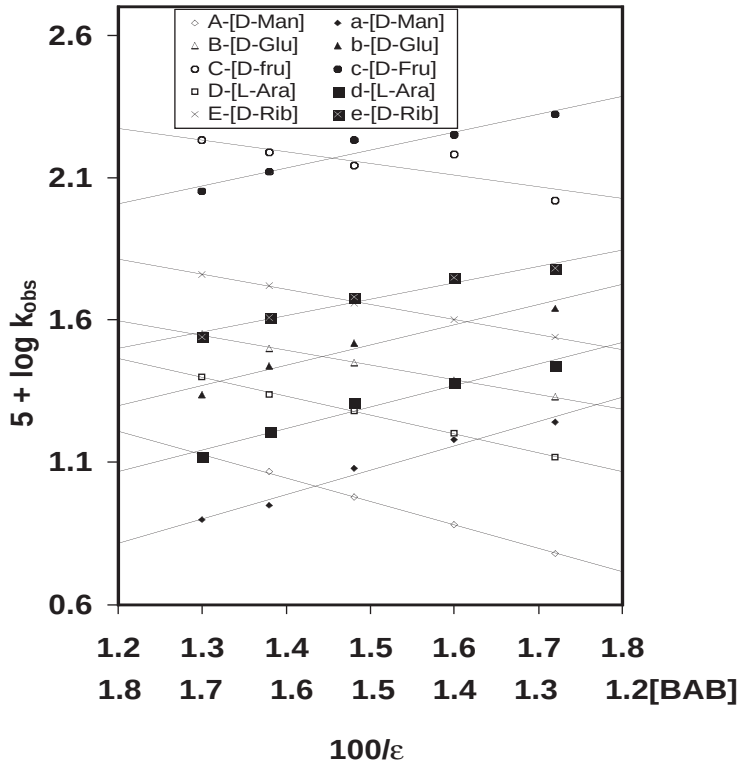


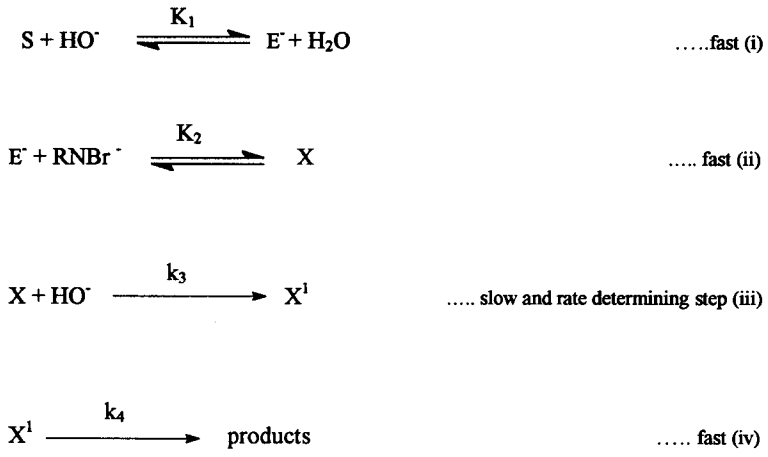
Figure 2. Plots of log k_{obs} vs. 1/D; $[BAT]_o = [BAB]_o = 2.00 \times 10^{-3}$ M, $[S]_o = 3.00 \times 10^{-2}$ M, $[HO^-] = 2.00 \times 10^{-2}$ temp = 30°C. A, B, C, D and E refer to BAT and a, b, c, d and e refer to BAB.

revealing that the lower carbon aldonic acids were not derived from the initially formed six-carbon aldonic acids.

Similar products were observed even when the reactions were carried out under kinetic conditions mentioned in Tables 1 and 2.

The identical orders observed with respect to both oxidant (BAT or BAB) and all sugars suggest a common mechanism for the oxidation process. The organic haloamines behave as strong electrolytes in aqueous solutions and the several equilibria present are predominantly pH dependent.[10,11] Although the oxidizing species in acidic solutions of BAT or BAB are RNBrH and $RNBr_2$ and hypobromous acid, it has been established that in alkaline medium $RNBr^-$ is the active oxidant[12–14] (R = *p*-$CH_3C_6H_4SO_2$ for BAT and R = $C_6H_5SO_2$ for BAB).

In alkaline solution, sugars undergo enolization to form enediolate anions in the absence of other reactants. These anions undergo epimerizaton and isomerization (Lobry de Bruyn–Alberda Van Ekenstein transformation) to form a mixture of isomeric aldoses and ketoses. However, in the presence of BAT or BAB the enediolate anions (E^-) react with $RNBr^-$ to form intermediate (X), which in turn undergoes a cleavage to form products (Table 5).



Scheme 1. Kinetic scheme.

In view of the observed first order dependence of the rate on oxidant and $[S]_o$ and second order dependence on $[HO^-]_o$, the following reaction sequence (Scheme 1) is proposed for the oxidation of sugars by BAT or BAB in alkaline medium.

$$\text{Rate} = k_3[X][HO^-] \tag{1}$$

or

$$\text{Rate} = \frac{K_1K_2k_3[S][OX]_t[HO^-]^2}{[H_2O][1 + K_2[E^-]]} \tag{2}$$

where $[OX]_t = [BAT]_t$ or $[BAB]_t$, K_1 and K_2 represent the equilibrium constants for steps (i) and (ii) respectively, and k_3 represents the specific reaction rate for the rate

Table 3. Activation Parameters for the Oxidation of Sugars by BAT and BAB at 30°C

Activation	D-Mannose		D-Glucose		D-Fructose		L-Arabinose		D-Ribose	
Parameter	BAT	BAB	BAT	BAB	BAT	BAB	BAT	BAB	BAT	BAB
E_a kJ mol^{-1}	126	124	117	115	84.7	83.8	124	122	111	110
$\Delta H^{\neq}$ kJ mol^{-1}	123	121	115	112	82.1	81.2	121	119	108	108
$\Delta G^{\neq}$ kJ mol^{-1}	96.2	95.7	94.1	93.7	90.5	90.0	94.8	94.5	93.3	92.9
$\Delta S^{\neq}$ JK^{-1} mol^{-1}	88.1	83.2	66.2	60.8	−27.1	−32.7	84.9	79.4	48.2	47.8
Log A	22.8	22.5	21.7	21.4	16.8	16.7	22.6	22.3	20.7	20.6

$[BAT]_o = [BAB]_o = 2.00 \times 10^{-3}$ M; $[HO^-] = 2.00 \times 10^{-2}$ M; $[S]_0 = 3.00 \times 10^{-2}$ M; I = 0.100 M.

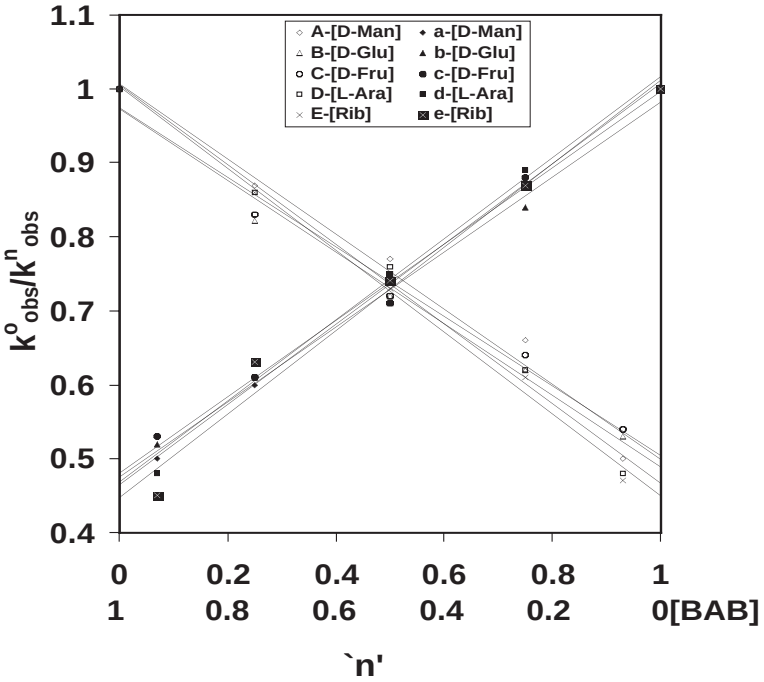


Figure 3. Plots of k^{o}_{obs}/k^{n}_{obs} vs. 'n' in H_2O-D_2O mixtures; $[S]_o = 3.00 \times 10^{-2}$ M, $[BAT]_o = [BAB]_o = 2.00 \times 10^{-3}$ M, $[HO^-] = 2.00 \times 10^{-2}$ M, temp = 30°C. A, B, C, D and E refer to BAT and a, b, c, d and e refer to BAB.

limiting step. It is assumed that $[H_2O] > 1 + K_2\,[E^-]$ and the rate law Eq. 2 is reduced to Eq. 3.

$$\text{Rate} = \frac{K_1 K_2 k_3 [S][OX]_t [HO^-]^2}{[H_2O]} \tag{3}$$

which agrees with the observed rate law, rate = k_{obs} [S] $[HO^-]^2$ [OX].

Table 4. Proton Inventory Studies for the Oxidation of Sugars by BAT and BAB in H_2O-D_2O Mixtures at 30°C

Atom Fraction of Deuterium (n)	$10^4\ k_{obs}\ (s^{-1})$									
	D-Mannose		D-Glucose		D-Fructose		L-Arabinose		D-Ribose	
	BAT	BAB	BAT	BAB	BAT	BAB	BAT	BAB	BAT	BAB
0.000	1.32	1.73	3.58	4.37	16.8	20.2	2.51	2.74	5.80	6.24
0.250	1.51	1.96	4.36	5.21	20.0	24.2	3.91	3.08	6.74	7.14
0.500	1.72	2.34	4.97	6.12	23.5	28.5	3.31	3.64	7.92	8.44
0.750	2.01	2.86	5.80	7.20	26.2	33.3	4.02	4.38	9.48	9.98
0.930	2.44	3.46	6.82	8.40	31.3	38.4	5.27	5.71	12.4	13.7

$[BAT]_o = [BAB]_o = 2.00 \times 10^{-3}$ M; $[S]_o = 3.00 \times 10^{-2}$ M; $[HO^-] = 2.00 \times 10^{-2}$ M; I = 0.100 M.

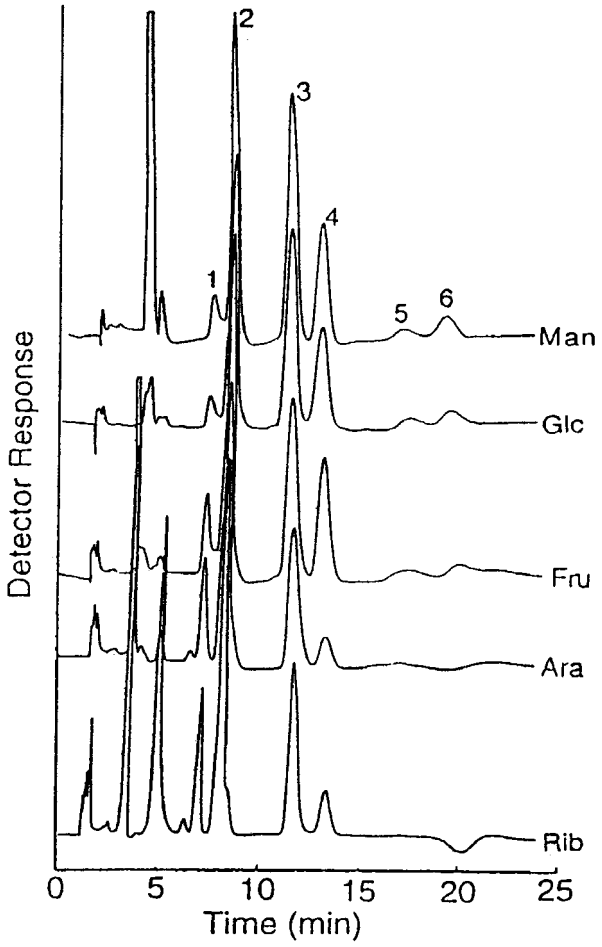


Figure 4. HPLC analysis of the products formed by the oxidation of sugars by bromamines in presence of NaOH at 30°C. 1. Glyceric acid; 2. erythronic acid; 3. Arabinonic acid; 4. ribonic acid; 5 and 6. hexonic acids. Man, Glc, Fru, Ara and Rib, respectively, represent the reaction of BAT or BAB with D-mannose, D-glucose, D-fructose, L-arabinose and D-ribose. The skewed shoulder on the tailing edge of the peak 2 represent a small amount (2–4%) of threonic acid.

The following results support the above conclusion:

(i) For reaction involving a fast pre-equilibrium of H^+ or HO^- ion transfer, the rate increases in deuterium oxide medium, because D_3O^+ is a stronger acid than H_3O^+ and DO^- is a stronger base than HO^-. Therefore, the observed increase of oxidation rate in deuterium oxide agrees with the fast pre-equilibrium transfer of H^+ to HO^- ion[15] (step i). The dependence of rate constant (k^n_{obs}) on 'n' (n = the atom fraction of deuterium oxide in a solvent mixture of water and deuterium oxide) is given by the Gross–Butler[16,17] Eq. 4,

$$k^o_{obs}/k^n_{obs} = \frac{\pi_{TS}(1 - n + n\Phi_j)}{\pi_{RS}(1 - n + n\Phi_j)} \quad (4)$$

Table 5. HPLC Analysis of the Products Formed by the Oxidation of Sugars by BAT and BAB in Alkaline Medium

		Products (Approximate Mole %)[a]				
Sugar	Mole of BAT or BAB Consumed per Mole of Sugar	Arabon Acid	Ribonic Acid	Erythronic and Threonic Acid	Glyceric Acid	Hexonic Acid
D-Mannose	2.50	36.0	19.0	35.0	4.00	6.00
D-Glucose	2.80	35.0	21.0	36.0	3.00	5.00
D-Fructose	2.90	30.0	20.0	40.0	8.00	4.00
L-Arabinose	2.20	28.0	8.00	49.0	14.0	–
D-Ribose	1.70	30.0	8.00	48.0	14.0	–

[a]Based on the areas normalized using response factors obtained by analyzing standard aldonic acid solutions.

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. 4 becomes Eq. 5.

$$k^o_{obs}/k^n_{obs} = [1 + n(\Phi_j - 1)] \tag{5}$$

A comparison of the plots of k^n_{obs} vs. 'n' (not shown) with the standard curves[18] suggested a single proton exchange in the transition state. Furthermore, the plots of (k^o_{obs}/k^n_{obs}) vs. 'n' (Figure 3) were linear with slopes $(\Phi_j - 1)$ from which Φ_j the fractionation factor of HO^- ion can be calculated. The Φ_j for the oxidation of *erythro*-series sugars by BAT or BAB is about 0.5. Hence the formation of a single transition state with the active participation of HO^- ion are indicated in the present studies.

(ii) Addition of methanol to the reaction mixture decreased the rate. The plots of log k_{obs} vs. $1/\varepsilon$ were linear with negative slopes (Figure 2). Assuming a double sphere model[17] for the reaction, the effects of solvent composition on the rate of a reaction involving two negative ions are given by Eq. 6,

$$\log k = \log k_o - Z_A Z_B e^2/DKTd_{AB} \tag{6}$$

where k_o is the rate constant in a medium of infinite dielectric constant, Z_Ae and Z_Be are the charges on the ions, d_{AB} is the size of the activated complex, K is Boltzmann constant and T is absolute temperature. From the slopes of the straight lines, in Figure 2 (slope = $-Z_AZ_Be^2/KTd_{AB}$), d_{AB} values are calculated. The values are 3.3 Å, 4.5 Å, 4.8 Å, 3.6 Å and 4.6 Å in the case of BAT and 2.8 Å, 3.6 Å, 4.1 Å, 3.01 Å and 3.7 Å in the case of BAB for D-mannose, D-glucose, D-fructose, L-arabinose, and D-ribose, respectively. These values are comparable with those obtained for similar reactions.[19]

(iii) Scheme 1 shows that the rate determining step, Eq. iii, involves interaction between two negatively charged ions which requires a very high activation energy. The observed high activation energies agree with this prediction (Table 3). Positive values of

$\Delta S^{\neq}$ and relatively high values of $\Delta H^{\neq}$ indicate more disorders in the transition state, and near constancy of $\Delta G^{\neq}$ values supports the proposed similar mechanism for the oxidation of sugars.

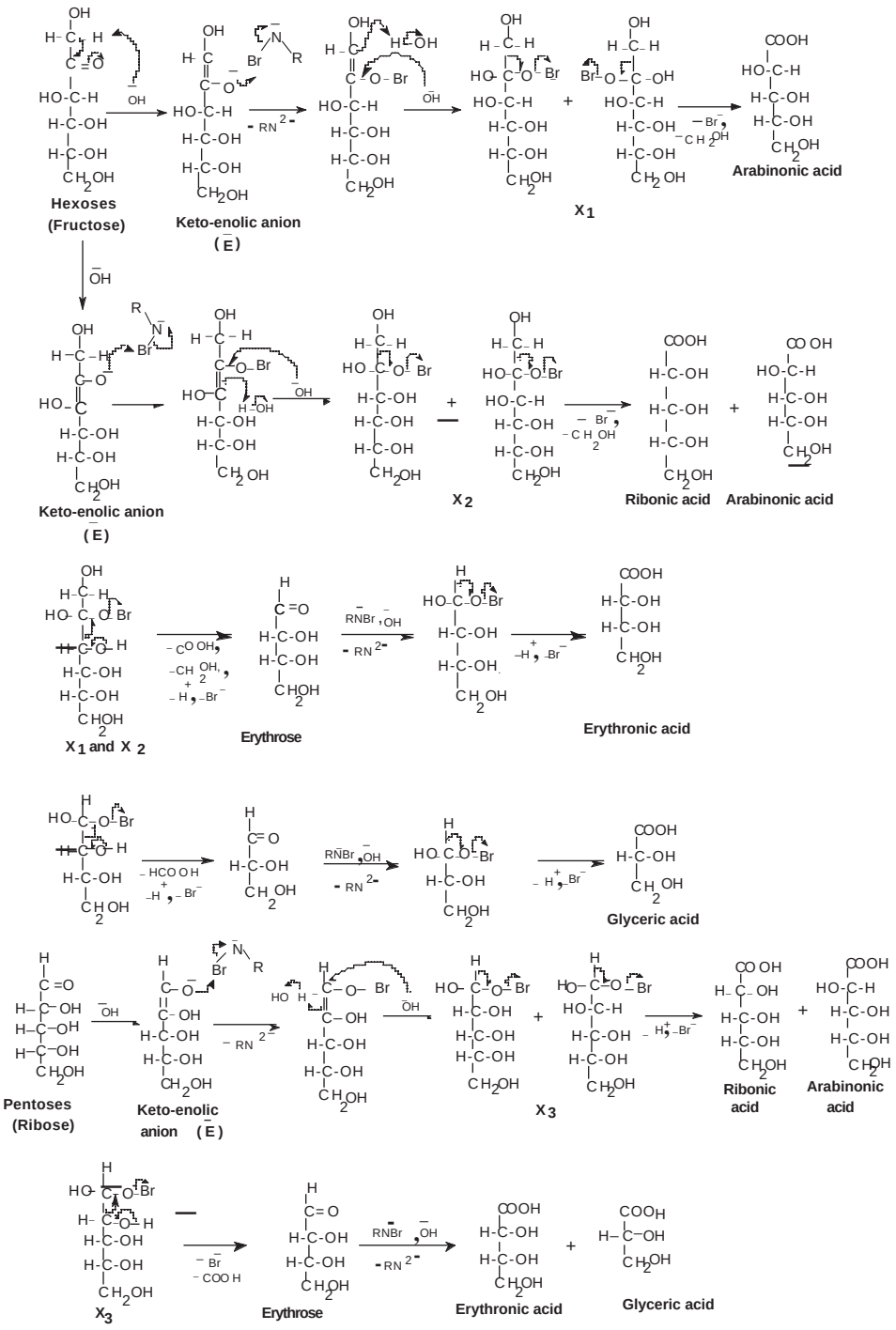
The formation of pentonic acids and erythronic acid by the loss of one and two carbon atoms, respectively, and minor proportions of hexonic acids suggested that these sugars react with BAT or BAB mainly through keto-enolic intermediates. The formations of only minor amounts of hexonic acids suggest that hexoses react extremely slowly with BAT or BAB in the aldo-enolic forms. This conclusion agrees with the formation of only a minor amount of mannonic acid despite the existence of a significant amount of unreacted mannose in the aldose form even after 24 h of incubation with BAT or BAB (Figure 4).

In contrast to hexoses, pentoses gave significant amounts of corresponding aldonic acids (pentonic acids). From the product profiles, clearly, the major products are formed by the cleavage of C-1–H and C-1–C-2 bonds. Furthermore, since *erythro*-pentulose was not formed to a noticeable extent by the alkali-catalyzed tautomerization of arabinose or ribose, this result together with the above data suggests that pentoses undergo oxidation by BAT or BAB through aldo-enolic intermediates.

The negative entropy change for fructose demonstrates that fructose has a more orderly structure in the transition state and is sterically favored for oxidation by BAT or BAB. HPLC sugar profiles of the reaction mixture at various time points and product profiles demonstrate that, in the case of aldo-hexoses, the fructose isomer formed by the alkali-catalyzed isomerization is the species that reacts with BAT or BAB. The observed faster reaction rate and lower activation energy for fructose (Tables 1 and 3) compared with glucose and mannose agree with the above conclusion. Based on these considerations, a plausible mechanism for the oxidation of sugars by BAT or BAB is proposed in Scheme 2. This general mechanism accounts for the observed kinetics and products of oxidation.

In the proposed mechanism (Scheme 2) the anion E^- of sugars (keto-isomer in the case of hexoses and aldo isomer in the case of pentoses) reacts with BAT or BAB to form intermediates X_1, X_3. In the case of anions (E^-) from hexoses, the loss of hydrogen occurs at either C-1 or C-3 to form C-1–C-2 or C-2–C-3 enediols containing bromoxyl group at C-2. Since these enediols contain polarized double bonds, hydroxide ion can add at C-2 to form intermediates X_1 and X_2. The formation of X_2 accompanies epimerization at C-2 and C-3, then X_1 and X_2 can undergo cleavage of C–C bonds between C-1 and C-2, the former giving arabinonic acid and the latter forming a mixture of arabinonic and ribonic acids. In the case of E^- from pentoses, hydrogen can be removed only from C-2 to form C-1–C-2 enediol anion, which in the presence of alkali forms intermediate X_3 with epimerization at C-2. Breakage of C-1–H bonds from X_3 gives a mixture of arabinonic and ribonic acids as in the case of X_2. The cleavage of C–C bonds between C-2 and C-3 in X_1 and X_2, and the breaking of C–C bonds between C-1 and C-2 in X_3 yield aldotetrose without epimerization at C-4 (hexoses) or at C-3 (pentoses). The aldotetrose further oxidizes to yield erythronic acid and a minor proportion of threonic 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.

Since a common mechanism is operative, a comparison of the rates of oxidation of sugars by BAT and BAB was desirable. If the values of standard rate constants



Scheme 2. Reaction mechanism scheme.

(k_{obs}) are taken into consideration (Table 1), then D-fructose and D-ribose have the highest rates while D-mannose and L-arabinose react slowly among the the two classes of sugars hexoses and pentoses, respectively. Isbell and coworkers[20] in their tritium exchange experiments observed the rate sequence ribose > lyxose > xylose > arabinose. Dewit et al.[21] studied the behavior of monosaccharides in aqueous alkaline solution through UV absorption spectroscopy, by monitoring the band at 310 nm. The rates of enediol formation are xylose > arabinose > ribose. Gleason and Barker[22] noted that the rates of oxidation of pentoses by oxygen in presence of alkali are dependent on the medium. In dilute KOH solution, the relative rate was, xylose > ribose > arabinose > lyxose, while in the presence of concentrated alkali it was ribose > lyxose > xylose > arabinose. However, using the p^{k_a} values of the pentoses, relative rates for the oxidation of pentoses, were calculated as xylose > ribose > lyxose > arabinose. The difference 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 coworkers[20] proposed that aldoses and ketoses generally yield mixtures of *Z* and *E* enediols, the proportion of which differs from sugar to sugar. We believe that the trend reflects the probability of *E* enediol formation, which is more stable than the *Z* isomer. The probability is greatest with D-ribose while D-mannose has the least tendency to form the trans isomer. It appears in general that, the probability of *E* enediol formation in the case of pentoses is greater than that of hexoses with the exception of D-glucose.

Earlier studies on the oxidation of hexoses and pentoses by CAT and CAB in alkaline medium[6,7] showed the experimental rate law, rate = k [OX] [S] $[HO^-]^2$, which amounts to the involvement of oxidant in a rate limiting step. Substantial primary salt, solvent isotope, ionic strength and dielectric effects were noticed. However, in the present studies it was observed that oxidation was generally faster with the bromine analogues.[23,24] This result has been rationalized in terms of the differences in electrophilicity of halonium cations, Cl^+ and Br^+ which are generally the reactive species in these reactions.[25] Also, it is partly due to the moderate differences in the van der Waal's radii of bromine and chlorine.

EXPERIMENTAL

Materials and Methods. D-mannose, D-glucose, D-fructose, L-arabinose and D-ribose were purchased from Sigma chemicals. BAT and BAB were prepared by the method of Nair et al.[26] The aqueous solutions of BAT and BAB were prepared, iodometrically standardized, and stored in brown bottles to prevent their photochemical deterioration. A concentrated aqueous solution of sodium perchlorate was used to maintain the ionic strength of the reaction mixture. All other chemicals used were of analytical grades of purity. Triply distilled water was used for preparing aqueous solutions. The solvent isotope studies were made with D_2O (99.4%) supplied by Bhabha Atomic Research Center, Bombay (India).

Kinetic Procedure. The reactions were carried in glass stoppered pyrex boiling tubes coated black on the outside. Pseudo first order conditions of $[sugar]_o \gg [oxidant]_o$ were maintained for kinetic runs (oxidant = BAT or BAB). The oxidant and the requisite amounts of sugar, alkali, sodium perchlorate solutions and water (for constant

total volume) were taken in separate boiling tubes and thermostated for 30 min at 30°C. The reaction was initiated by the rapid addition of oxidant (BAT or BAB) to the mixture and its progress was monitored by iodometric estimation of unconsumed oxidant in known aliquots of the reaction mixture at regular intervals of time. The reaction was studied for more than two half lives. Pseudo first order rate constants k_{obs} were calculated from the plots of log $[OX]_o$ vs. time, where OX represent the oxidant and these were reproducible within ±5% error.

Stoichiometry and Product Analysis. The reaction mixture containing 0.01M sugar, 0.02M alkali, and an excess of oxidant (BAT or BAB ~ 0.05M) was kept for 24 h at 30°C. The unconsumed oxidant (BAT or BAB) was determined iodometrically. From these data, the amount of the oxidant consumed per mole of sugar was found to be 3 moles for hexoses and 2 moles for pentoses.

The oxidation products were analyzed by Dionex HPLC (high performance liquid chromatography) with pulsed amperometric detection using a Carbopac PA1 high-pH anion exchange column (4×250 mm)[27] Isocratic elution with 0.2 M NaOH was used. The products arabonic, ribonic, erythronic, threonic, glyceric and hexonic acids were identified by comparison of the HPLC retention times with those of standard aldonic acids and by GLC-MS.

For GLC-MS characterization, the reaction mixture was extracted with diethyl ether to remove *p*-toluenesulphonamide and then passed through AG 50 W-X12 (H^+) and AG-4-X4 (base) resins. The AG 4-X4 resins were eluted with 1M pyridine-1M acetic acid, pH 5.2, and lyophilized. The products were converted into their trimethylsilyl derivatives and then analyzed by GLC-MS (Chart speed = 0.5 mm/min and flow rate = 0.8 ml/min).

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