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# Oxidation of erythrose series sugars by sodium *N*-chlorobenzenesulphonamide in alkaline medium : A kinetic study

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The kinetics of oxidation of D-glucose, D-mannose, D-fructose, D-arabinose, and D-ribose, with sodium *N*-chlorobenzenesulphonamide (chloramine-B or CAB) in alkaline medium have been studied at 35°C and the rate law, rate = $k'$ [CAB] [Sugar] $[OH^-]^2$ is observed. The rate of reaction is influenced by a change in ionic strength of the medium, and the dielectric effect is negative. The solvent isotope studies in $D_2O$ show that the rate is almost doubled in heavy water. HPLC and GLC-MS analyses of the products indicated that the erythrose-series sugars are oxidized to a mixture of aldonic acids consisting of arabinonic, ribonic, erythronic, and glyceric acids in varying proportions. Based on these data, a mechanism involving the aldo-enolic anions of pentoses and keto-enolic anions of hexoses is suggested.

Aromatic *N*-halosulphonamides are mild oxidants[1,2] containing a strongly polarized *N*-linked halogen which is in the +1 state. The prominent member of this class of oxidants is sodium *N*-chloro *p*-toluenesulphonamide (chloramine-T, or CAT). The benzene analogue, chloramine-B ($C_6H_5SO_2NClNa.1.5H_2O$ or CAB) is easy to prepare and shows similar properties.

A review of literature shows that kinetic studies with this reagent are meagre. Hence, in the present investigations, a detailed study of the kinetics of oxidation of a few monosaccharides by CAB in alkaline medium at 35°C is reported.

Previously, it was reported[3-7] that the oxidation of sugars with CAB and sodium *N*-bromo-*p*-toluenesulphonamide (BAT) in alkaline solutions yield the aldonic acids for aldoses, and arabinonic acid for fructose.[3-7] However, in the present study a detailed product analysis has been made using HPLC and GLC-MS techniques. It is seen that erythro-series sugars (both pentoses and hexoses) are oxidized to a mixture of aldonic acids consisting of arabinonic, ribonic, erythronic and glyceric acids, whereas in the case of hexoses, oxidation occurs mainly with the cleavage of C1-C2 and C2-C3 bonds. Pentoses are oxidized mainly through the cleavage of C1-H and C1-C2 bonds.

## Materials

D-Glucose, D-mannose, D-fructose, D-arabinose, D-ribose, D-gluconic acid, D-galactono-1,4-lactone, D-ribono-1,4-lactone were purchased from Sigma Chemical Co.(st. Louis, MO). D-Manno-1,4-lactone, D-xylo-1,4-lactone, and D-arabino-1,4-lactone were from Pfanstiehl (Waukegan, IL). Chloramine-B was prepared by passing $Cl_2$ gas through a suspension of benzenesulphonamide[8] in 4.0 *M* NaOH for 1 hr at 343K. The product was collected, dried and recrystallized from water [mp 170°C with decomposition]. Its purity was checked by iodometry for its active chlorine content and also by its $^1H$ and $^{13}C$-NMR spectra. The aqueous solution of CAB was standardized iodometrically and stored in brown bottles to minimize its photochemical deterioration. All other reagents were prepared from analytical grade chemicals. A concentrated aqueous $NaClO_4$ was used to maintain a high ionic strength to swamp the reaction mixture. The solvent isotope studies were performed with $D_2O$ (99.4%) supplied by the Bhabha Atomic Research Centre, Bombay, India.

Triply distilled water was used in the preparation of aqueous solutions.

### *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 CAB concentration. A mixture of sugar, alkali and $NaClO_4$ solutions and a solution of CAB were equilibrated separately at 35°C for 15 min. The reaction was initiated by the rapid addition of CAB to this mixture. The progression of oxidation was monitored, for two half-lives, by iodometric determination of unconsumed CAB at various time periods. First order rate constants ($k_{obs}$) were calculated from the plots of log $[CAB]_0$ vs. time 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.

### *Stoichiometry and product analysis*

The reaction mixtures containing sugar, alkali with an excess of CAB were kept for 24 hr at 35°C. The unconsumed CAB was then determined iodometrically, and from this data, the number of moles of the oxidant consumed per mole of sugar was calculated.

The oxidation products were analyzed by Dionex BioLC HPLC coupled to pulsed amperometric detection using a CarboPac PA1 high-*p*H anion-exchange column (4 × 250 mm)[9]. An isocratic elution with 0.2 *M* NaOH was used. Further, the reaction mixture was extracted with diethyl ether to remove benzenesulphonamide and passed through Ag 50W-X12 ($H^+$) and Ag 4-X4 (base) resins. The Ag 4-X4 resins were eluted with 1 *M* pyridine/1 *M* acetic acid, *p*H 5.2 and lyophilized. The products were converted into their trimethylsilyl derivatives and then analyzed by GLC-MS.

## Results

### *Effect of reactant concentrations*

The reactions were carried out with varying concentrations of CAB using constant $[HO^-]$ and high $[S]_0$ (S = Sugar). The plots of log [CAB] vs. time were linear ($r > 0.9985$, $s \leq 0.04$), indicating a first order dependence of reaction rate on $[CAB]_0$ (Table I). The pseudo-first order rate constants ($k_{obs}$) obtained with different $[CAB]_0$ were identical within the limits of experimental error, confirming the first order dependence of the rate on $[CAB]_0$. These values slightly decreased at higher $[CAB]_0$, which could be due to a side reaction of CAB involving the $ClO^-$ ion. The $k_{obs}$ values increased with increase in $[S]_0$ (Table I). The plots of log$k_{obs}$ vs. log $[S]_0$ were linear ($r > 0.9989$, $s \leq 0.04$) with unit slopes. The second order rate constants, $k_2 = k_{obs}/[S]_0$ were constant

Table I—Effect of reactant concentrations on the rate of oxidation of sugars by CAB at 35°C. $[HO^-] = 10.0 \times 10^{-2}$ *M*. I = 0.4 *M*

| $10^3[CAB]_0$ (*M*) | $10^2[S]_0$ (*M*) | $10^4 k_{obs}$ (sec$^{-1}$) | | | | |
|---|---|---|---|---|---|---|
| | | D-Mannose | D-Glucose | D-Fructose | D-Arabinose | D-Ribose |
| 1.5 | 5.0 | 2.50 | 6.66 | 17.50 | 20.90 | 35.5 |
| 2.0 | 5.0 | 2.60 | 6.80 | 17.60 | 21.66 | 35.98 |
| 2.5 | 5.0 | 2.66 | 6.88 | 17.66 | 21.73 | 36.2 |
| 3.0 | 5.0 | 2.78 | 6.78 | 17.75 | 21.68 | 36.38 |
| 3.5 | 5.0 | 2.60 | 6.55 | 17.70 | 21.77 | 36.18 |
| 4.0 | 5.0 | 2.89 | 6.93 | 17.88 | 21.86 | 36.50 |
| 4.5 | 5.0 | 3.03 | 7.20 | 17.65 | 22.05 | 36.63 |
| 5.0 | 5.0 | 3.20 | 7.38 | 17.80 | 22.22 | 36.90 |
| 2.0 | 0.8 | 0.41 | 1.12 | 2.80 | 3.50 | 5.15 |
| 2.0 | 1.0 | 0.53 | 1.40 | 3.52 | 4.33 | 7.20 |
| 2.0 | 2.0 | 1.16 | 2.75 | 6.90 | 8.48 | 14.20 |
| 2.0 | 3.0 | 1.66 | 4.20 | 10.50 | 13.03 | 21.80 |
| 2.0 | 4.0 | 2.22 | 5.40 | 13.50 | 17.30 | 29.30 |
| 2.0 | 5.0 | 2.60 | 6.80 | 17.60 | 21.66 | 35.98 |
| 2.0 | 6.0 | 3.48 | 8.44 | 21.40 | 26.90 | 46.93 |

within the experimental error (Table I), demonstrating a first-order dependence of rates on $[S]_0$. Plots of $k_{obs}$ vs. $[S]_0$ passed through the origin ($r > 0.9996$, $s \leq 0.01$), indicating that the intermediates formed with the oxidant have only transient existence.

*Effect of alkali concentrations.*

At constant $[CAB]_0$ and $[S]_0$, values of $k_{obs}$ increased with an increase in [NaOH] (Table II). The order of reaction in hydroxide ions was calculated from the slope of plots of log $k_{obs}$ vs. log $[HO^-]$ ($r > 0.9984$, $s \leq 0.04$). The data demonstrated that the reactions follow second order dependence on $[HO^-]$.

*Effect of benzenesulphonamide and chloride ions*

Addition of benzenesulphonamide to the reaction mixtures had no significant effect on the rates. This indicates that the product, benzenesulphonamide, was not involved in pre-equilibrium with the oxidant. Addition of NaCl to the reaction mixtures had no effect on the rates suggesting that the free chloride ion was not formed before the rate limiting step.

*Effect of ionic strength*

Addition of $NaClO_4$ increased the rate of reaction. The plots of log $k_{obs}$ vs. $I^{1/2}$ (I = the ionic strength of medium) were linear with fractional slopes of about 0.6 (Figure 1).

*Effect of solvent composition*

The solvent composition of the medium was varied by adding methanol (0-40%). The rate decreased with an increase in methanol content. The plots of log $k_{obs}$ vs. 1/D (D = dielectric constant of the medium) were linear with negative slopes (Figure 2 )

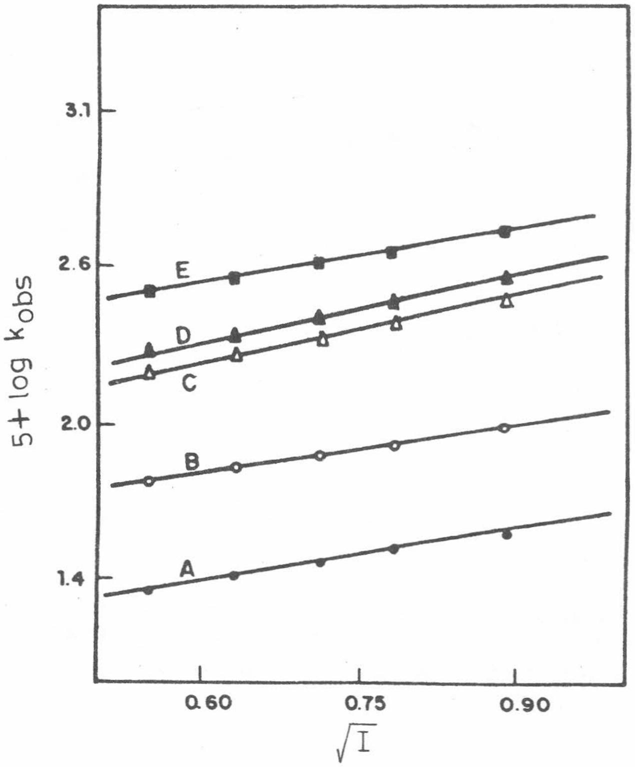


**Figure 1**—Plots of log $k_{obs}$ vs.$(I)^{1/2}$ A=D-Mannose; B=D-Glucose; C=D-Fructose; D=D-Arabinose; E=D-Ribose. $[CAB]_0$=2.0 × $10^{-3}$ mol.dm$^{-3}$, $[S]_o$ = 5.0 × $10^{-2}$ mol.dm$^{-3}$, $[HO^-]$ 10.0×$10^{-2}$ mol.dm$^{-3}$= Temp = 35°C.

*Activation parameters*

To determine the activation parameters, the reaction was studied at four different temperatures (303, 308, 313, and 318 K). The Arrhenius plots of log $k_{obs}$ vs. 1/T (T = absolute temperature) were found to be linear ($r > 0.9980$, $s \leq 0.02$). The activation energies ($E_a$) were calculated from the slopes of the plots. From these values, the thermodynamic parameters $\Delta H^{\#}$, $\Delta S^{\#}$, and $\Delta G^{\#}$ (Table.III) were evaluated.

Table II—Effect of [NaOH] on the rate of oxidation of sugars by CAB at 35°C
$[CAB]_0 = 2.0 \times 10^{-3}$ *M*, $[S]_0 = 5.0 \times 10^{-2}$ *M*, I = 0.4 *M*

| $10^2$[NaOH] (*M*) | $10^4k_{obs}$[sec$^1$] D-Mannose | D-Glucose | D-Fructose | D-Arabinose | D-Ribose |
|---|---|---|---|---|---|
| 4.0 | 0.39 | 1.13 | 2.80 | 3.50 | 5.73 |
| 6.0 | 0.89 | 1.98 | 6.30 | 7.60 | 12.98 |
| 8.0 | 1.60 | 4.20 | 11.22 | 12.78 | 22.89 |
| 10.0 | 2.60 | 6.80 | 17.60 | 21.66 | 35.98 |
| 20.0 | 9.80 | 27.50 | 71.65 | 75.60 | 129.30 |
| 30.0 | 23.30 | 44.50 | 156.80 | 162.5 | 198.90 |

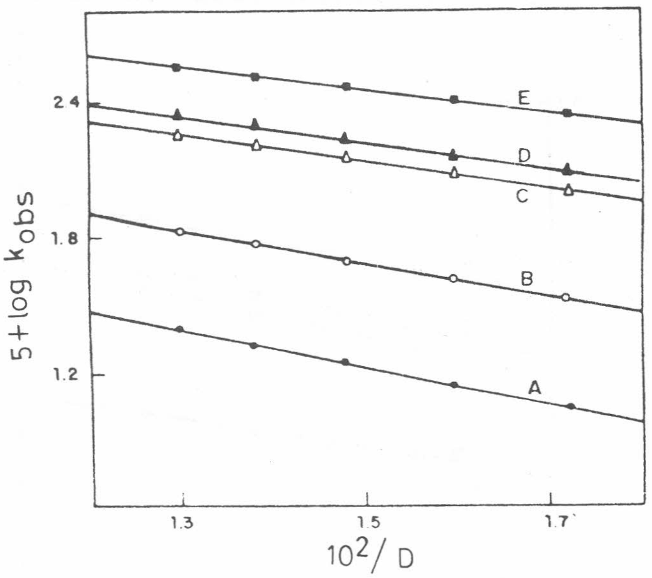


**Figure 2**—Plots of log $k_{obs}$ vs 1/D; A=D-Mannose; B=D-Glucose; C=D-Fructose; D=D-Arabinose; E=D-Ribose. $[CAB]_o$=2.0 X$10^{-3}$ mol.dm$^{-3}$, $[S]_o$ = 5.0 x $10^{-2}$ mol.dm$^{-3}$, $[HO^-]$ = 0.1 *M*; [I]=0.4 mol.dm$^{-3}$ Temp = 35°C.

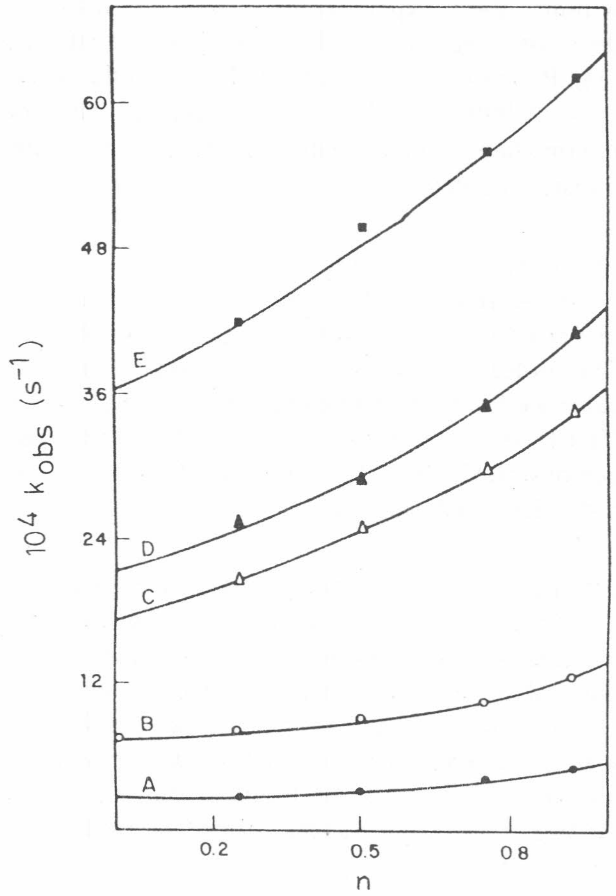


**Figure 3**—Proton inventory plot for the oxidation of erythrose series sugars by CAB in $H_2O$-$D_2O$ mixtures of 308K.

*Solvent isotope studies*

The reactions were performed in pure $D_2O$. The solvent-isotope effects, $k_{obs}(H_2O)/k_{obs}(D_2O)$, were between 0.50 and 0.55 for all sugars. Proton-inventory studies were made in $H_2O$-$D_2O$ mixtures (Table IV). The proton inventory plots, relating the rate constants $k^{n}_{obs}$ to 'n' (n = deuterium atom fraction in $H_2O$–$D_2O$ mixtures) are shown in Figure 3.

*Test for free radicals*

Addition of an aqueous solution of acrylamide to the reaction mixture did not cause polymerization. This suggests the absence of free-radical involvement during the oxidation.

*Analysis of the products*

High-*p*H anion exchange chromatography revealed the formation of similar oxidation products for the erythrose-series sugars studied (Figure 4). A comparison of the HPLC and GLC retention times of the reaction products with those of the standards, indicated that arabinonic acid, ribonic acid, erythronic, and glyceric acids are the oxidation products for all the erythrose-series sugars studied (Table 5); for hexoses, besides these acids, small proportions of hexonic acids were observed. The identities of all the oxidation products were confirmed from their mass fragmentation patterns. Incubation of sugars with alkali

Table III—Activation parameters for the oxidation of sugars by CAB at 35° C

| Sugars | $E_a$ (kJmol$^{-1}$) | $\Delta H^{\#}$ (kJmol$^{-1}$) | $\Delta G^{\#}$ (kJmol$^{-1}$) | $\Delta S^{\#}$ (JK$^{-1}$ mol$^{-1}$) | Log *A* |
|---|---|---|---|---|---|
| D-Mannose | 126.2 | 123.7 | 96.7 | 87.5 | 21.1 |
| D-Glucose | 94.3 | 91.6 | 94.1 | 8.0 | 16.2 |
| D-Fructose | 60.4 | 57.8 | 89.3 | -102.1 | 10.8 |
| D-Arabinose | 85.1 | 82.6 | 91.3 | -28.3 | 15.1 |
| D-Ribose | 81.1 | 78.6 | 90.0 | -37.1 | 14.6 |

Table IV—Proton inventory studies for the oxidation of sugars by CAB in $H_2O$ - $D_2O$ mixtures at 30°C. $[CAB]_0 = 2.0 \times 10^{-3}$ *M*, $[HO^-] = 10.0 \times 10^{-2}$ *M*, $[S]_0 = 5.0 \times 10^{-2}$ *M*, I = 0.4 *M*

| Atom fraction of deuterium (n) | $10^4 k_{obs}$[sec$^{-1}$] | | | | |
|---|---|---|---|---|---|
| | D-Mannose | D-Glucose | D-Fructose | D-Arabinose | D-Ribose |
| 0.00 | 2.60 | 6.80 | 17.60 | 21.66 | 35.98 |
| 0.25 | 3.25 | 8.40 | 21.80 | 26.80 | 44.50 |
| 0.50 | 3.75 | 9.60 | 25.20 | 30.89 | 50.50 |
| 0.75 | 4.45 | 11.25 | 29.80 | 35.78 | 58.00 |
| 0.93 | 5.05 | 12.80 | 33.33 | 40.80 | 65.50 |

alone, under the reaction conditions did not degrade the sugars to significant extents.

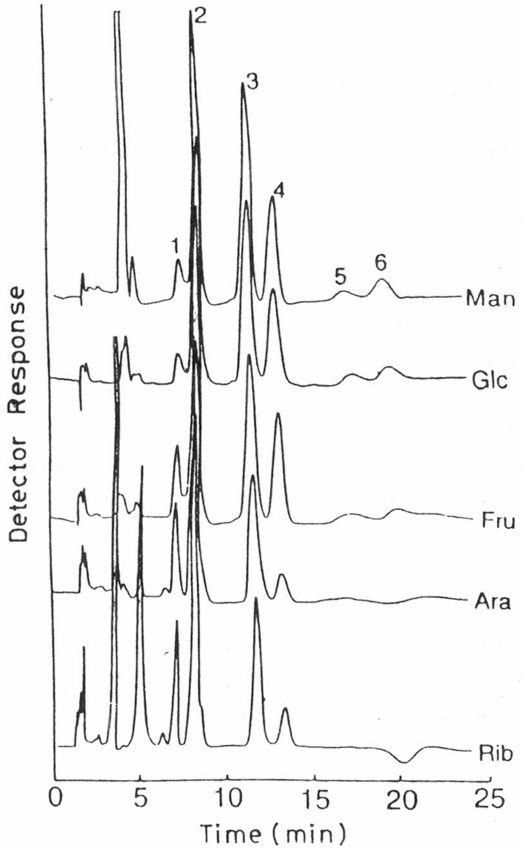


Figure 4—HPLC analysis of the products formed by the oxidation of sugars by CAB in alkaline medium at 35°C. 1, Glyceric acid; 2, Erythronic acid; 3, Arabinonic acid; 4, Ribonic acid; 5 and 6, Hexonic acids. Man, Glc, Fru, Ara and Rib respectively represent reaction of CAB with D-mannose; D-glucose; D-fructose; D-arabinose; D-ribose. The skewed shoulder on the tailing edge of the peak 2 represents a small amount (2-4% of threonic acid).

The oxidation products of sugars were also analyzed at 0.5, 1, 2, 4, 8, 16 and 24 hr. The relative proportion of various aldonic acids formed (Figure 4 and Table V) were similar at all time points analyzed (except, in the case of hexoses, the formation of six-carbon aldonic acids was observed only after 4 hr), revealing that the lower-carbon aldonic acids were not derived from the initially formed six-carbon aldonic acids. HPLC analysis of reaction mixtures at various time points further indicated that, whereas 15-20% of glucose was isomerized into fructose within 30 min, only ~ 5% of mannose was isomerized to fructose at 30 min. Under similar conditions, 10-15% of fructose was isomerized to glucose. Parallel to this observation, a significant amount of mannose (retention time 4.25 min, Figure 4) was not oxidized by CAB even though under similar conditions glucose and fructose (retention times 4.5 and 5.0 min, respectively) were almost completely oxidized. Even after 24 hr only a small proportion of mannonic acid was formed (Figure 4 and Table V). The product profile suggest that hexoses undergo oxidation by CAB in the keto(fructo)-enolic form but not in the aldo-enolic form. In the case of pentoses, the peaks with retention times 3.8 min and 5.1 min (Figure 4) corresponded, respectively to arabinose and ribose. Whereas only a small proportion of arabinose was epimerized to ribose, a significant amount of ribose was epimerized to arabinose. Parallel to this observation, ribose was found to be oxidised by CAB faster than arabinose (Table I). The pentoses react with CAB in the aldo-enolic form. This conclusion agrees with the formation of significant amounts of arabinonic and ribonic acids from arabinose and ribose.

Table V—HPLC analysis of the products formed by the oxidation of sugars by CAB in alkaline medium

| Sugar | Mole of CAB consumed per mole of sugar | Product (mole percentage)[a] | | | | |
|---|---|---|---|---|---|---|
| | | Arabinonic acid | Ribonic acid | Erythronic acid Threonic acid[b] | Glyceric acid | Hexonic acid |
| D-Mannose | 2.4 | 36 | 19 | 35 | 4 | 6 |
| D-Glucose | 2.8 | 35 | 21 | 36 | 3 | 5 |
| D-Fructose | 2.8 | 30 | 20 | 40 | 8 | 4 |
| D-Arabinose | 2.2 | 28 | 8 | 49 | 14 | – |
| D-Ribose | 1.7 | 30 | 8 | 48 | 14 | – |

[a] Based on the peak areas normalized using response factors obtained by analyzing standard aldonic acid solutions. The mole proportions of products formed at 0.5, 1, 2, 4, 8 and 16 hr were similar to those observed at 24 hr, except that the presence of six-carbon aldonic acids was evident only after 4 hr. Similar product profiles were observed even when the reactions were carried out under kinetic conditions.

[b] The shoulder at the tailing edge of the peak 2 in Figure 4 represents threonic acid (2-4% of total aldonic acids formed).

## Discussion

The identical orders observed for the oxidation of sugars by CAB suggest a common mechanism for the oxidation process. The organic haloamines (RNClNa where R=$C_6H_5SO_2$ - for CAB) behave like strong electrolytes in aqueous solutions,[10] and the several equilibria present are predominantly *p*H dependent[11,12]. Bishop and Jennings[10], and Morris *et al.*[13] have formulated the following reactions for CAB in aqueous solutions:

$$\mathrm{RNClNa} \rightleftharpoons \mathrm{RNCl^- + Na^+} \qquad \ldots(1)$$

$$(\mathrm{R = C_6H_5SO_2^-})$$

In acidic solutions, the anion is protonated to form monochloroamine-B (RNClH):

$$\mathrm{RNCl^- + H^+} \rightleftharpoons \mathrm{RNClH} \qquad \ldots(2)$$

RNClH undergoes disproportionation and/or hydrolysis as follows:

$$\mathrm{2\,RNClH} \rightleftharpoons \mathrm{RNH_2 + RNCl_2} \qquad \ldots(3)$$

$$\mathrm{RNClH + H_2O} \rightleftharpoons \mathrm{RNH_2 + HOCl} \qquad \ldots(4)$$

The dichloramine-B can undergo hydrolysis according to equation (5):

$$\mathrm{RNCl_2 + H_2O} \rightleftharpoons \mathrm{RNClH + HOCl} \qquad \ldots(5)$$

Therefore, the oxidizing species in acidic solutions of CAB are RNClH, $RNCl_2$ and HOCl.

In alkaline medium, however, the anions, $RNCl^-$ and $ClO^-$, are dominant, and the following equilibria have been reported[14].

$$\mathrm{RNCl^- + H_2O} \rightleftharpoons \mathrm{RNH_2 + ClO^-} \qquad \ldots(6)$$

$$\mathrm{RNCl^- + H_2O} \rightleftharpoons \mathrm{RNHCl + HO^-} \qquad \ldots(7)$$

$$\mathrm{RNHCl + HO^-} \rightleftharpoons \mathrm{RNH_2 + ClO^-} \qquad \ldots(8)$$

Equations (6) and (8) indicate a retardation of rate by the product, benzene sulphonamide, while a decrease in rate by alkali is expected from equation (7). Since neither of these have been observed in this present studies, it is likely that the anion, $RNCl^-$, is the active oxidant. In alkaline solutions, sugars undergo enolization to form enediol anions ($E^-$). In the absence of other reactants, $E^-$ undergoes rapid epimerization and isomerization (Lobry de Bruyn-Alberda van Ekenstein transformation) to form a complex mixture of aldoses and ketoses.[15] However, in the presence of CAB, $E^-$ reacts with $RNCl^-$ to form intermediates (X), which inturn undergo cleavage to form products. (Table IV).

In view of the observed first order dependence of rate on $[CAB]_0$ and $[S]_0$ and second order dependence on $[HO^-]$, the following reaction sequence (Scheme 1) is proposed for the oxidation of sugars by CAB in alkaline solutions:

$$\mathrm{S + HO^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{E^- + H_2O} \qquad \text{(i) Slow}$$

$$\mathrm{E^- + HO^- + RNCl^-} \xrightarrow{k_2} \mathrm{X} \qquad \text{(ii) Slow \& rds}$$

$$\mathrm{X} \xrightarrow{k_3} \text{Products} \qquad \text{(iii) Fast}$$

**Scheme I**

Assuming steady state conditions for $E^-$, rate law (9) can be derived:

$$\text{Rate}=\frac{d[\text{CAB}]}{dt}=\frac{k_2k_1[\text{S}][\text{HO}^-]^2[\text{CAB}]}{k_1[\text{H}_2\text{O}]+k_2[\text{HO}^-][\text{CAB}]} \qquad \ldots(9)$$

Since there is a second order dependence of rate on $[\text{HO}^-]$, which slightly decreases at higher $[\text{HO}^-]$ the assumption that $k_{-1}\ [\text{H}_2\text{O}]>k_2\ [\text{HO}^-][\text{CAB}]$, at lower $[\text{HO}^-]$where $k_2$ represents the specific reaction rate constant for the rate limiting step, is valid. Thus, rate law (9) is reduced to

$$\text{Rate}=-\frac{d[\text{CAB}]}{dt}=\frac{k_2k_1[\text{S}][\text{HO}^-]^2[\text{CAB}]}{k_1[\text{H}_2\text{O}]} \qquad \ldots(10)$$

which agrees with the experimental observations

$$\text{Rate}=k'[\text{S}][\text{HO}^-]^2[\text{CAB}] \qquad \ldots(11)$$

Scheme I is supported by the following experimental observation :

(i) The rate increases in $D_2O$ medium, since $DO^-$ ion is a stronger base than $HO^-$ ion. The inverse solvent isotope effect $k\ (D_2O)/k\ (H_2O) \approx 2$ and signifies a fast pre-equilibrium ion transfer[16]. Proton inventory plots (Figure 3) could throw some light on the nature of the transition state. From a qualitative point of the curvature of proton inventory plots can be compared with those of standard curves in literature[17-19], and it may be concluded that $HO^-$ ion is involved in the formation of transition state.

(ii) The rate determining step in Scheme I involves negative ions. Therefore, reaction rate is expected to be increased with an increase in the ionic strength (I) of reaction medium. The plots of log $k_{\text{obs}}$ vs $I^{1/2}$ gave straight lines with slopes between 0.6 and 0.8 (Figure 1), even though the strengths employed were beyond the Debye-Hückel range. The theoretical slope of unity has not been realized. This is possibly due to the formation of Bjerrum ion pairs in concentrated solutions[20].

(iii) Plots of log $k_{\text{obs}}$ vs.1/D gave straight lines with negative slopes (Figure 2). Assuming a double sphere model[21] for the reaction, the effect of solvent composition on the rate of a reaction involving two negative ions is given by equation (12).

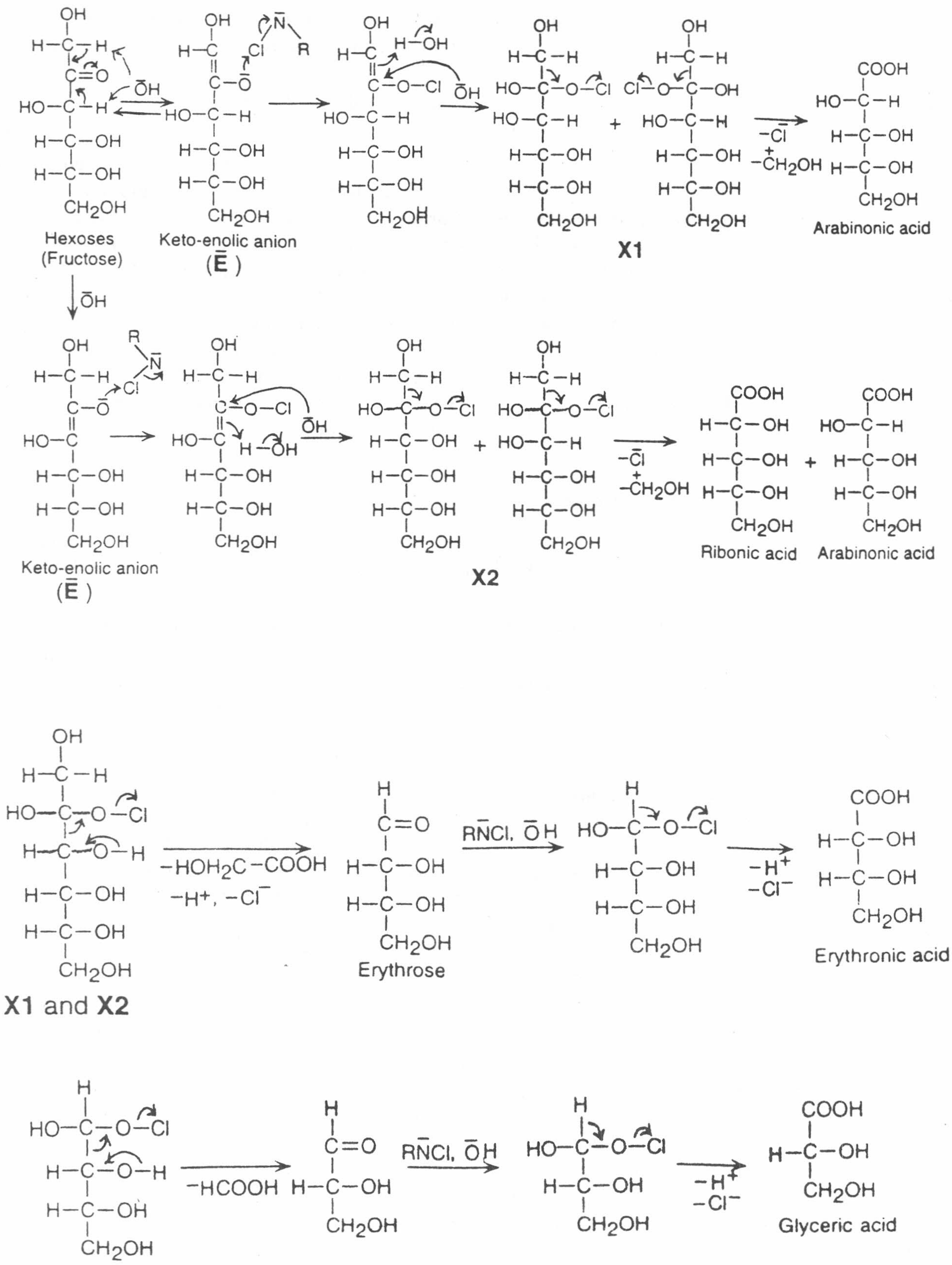
$$\log k=\log k_0-Z_AZ_Be^2/D\,k\,Td_{AB} \qquad \ldots(12)$$

where, $k_0$ is the rate constant in a medium of infinite dielectric constant, $Z_Ae$ and $Z_Be$ are the charges on ions, $d_{AB}$ refers to the size of the activated complex, $k$ is the Boltzmann Constant, and T is the absolute temperature. From the slope of the straight lines in Figure 2, $d_{AB}$ was calculated. The derived values for D-glucose, D-mannose, D-fructose, D-arabinose, and D-ribose are 3.41Å, 2.72Å, 4.02Å, 3.77Å and 4.56Å respectively. These values are comparable with those obtained in similar reactions.[21]

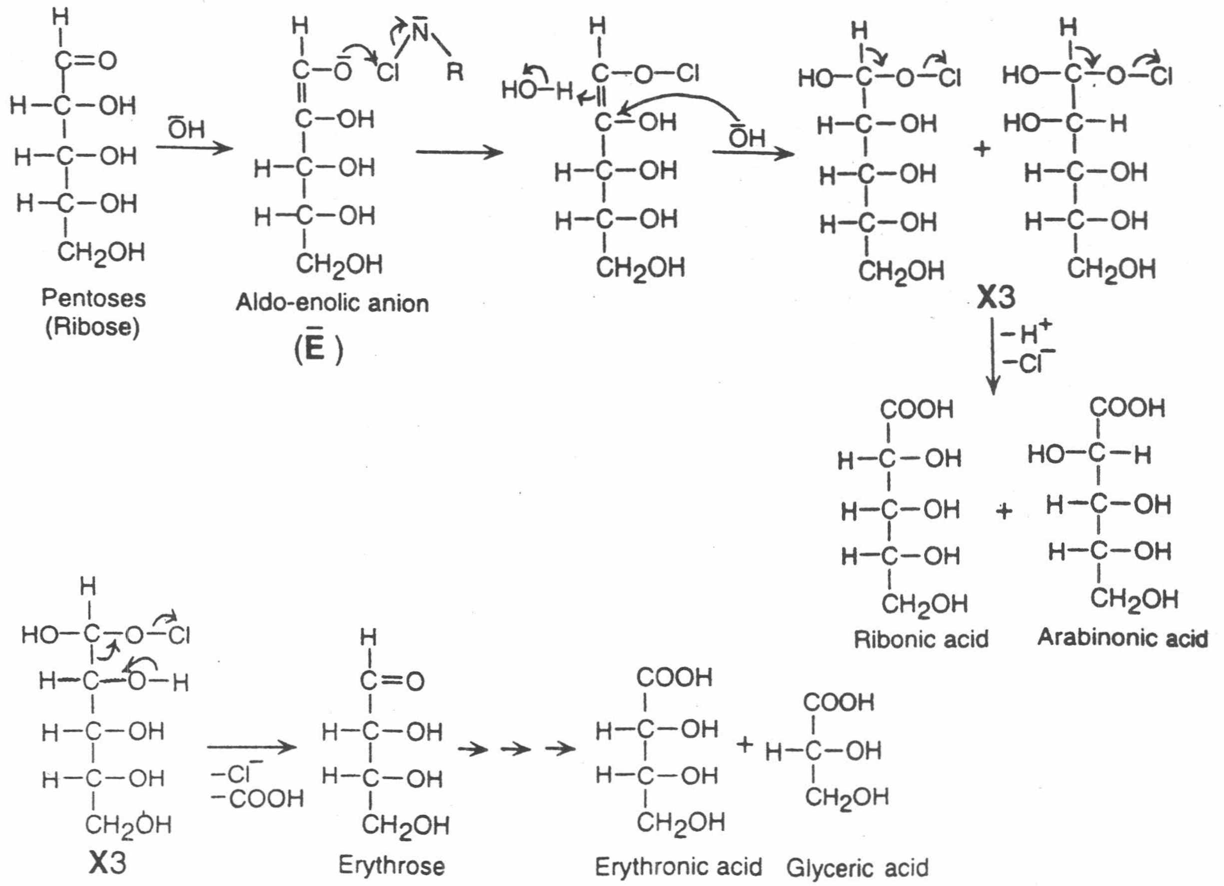
(iv) Scheme I shows that the rate limiting step involves an interaction among three similarly charged ions. Agrawal and Mushran[3] have made a similar observation. Such a sequence requires a high activation energy. The values in Table III agree with this prediction.

The 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 react with CAB. The observed faster reaction rate and lower activation energy for fructose (Tables I and III) compared with glucose and mannose agree with the above conclusion. Based on these considerations, a plausible mechanism for the oxidation of sugars by CAB is proposed in Scheme II. This mechanism accounts for the observed kinetics and products of oxidation.

In the proposed mechanism (Scheme II), the anions ($E^-$) of sugars (keto-isomer in the case of hexoses and aldo-isomer in the case of pentoses) react with CAB to form complexes X1-X3. In the case of anions ($E^-$) from hexoses, the loss of hydrogen can occur at either C1 or C3 to form C1-C2 or C2-C3 ene-diols containing chloroxyl group at C2. Since these ene-diols contain polarized double bonds, hydroxide ion can add at C2 to give intermediates X1 and X2; the formation of X2 accompanies epimerization at C3. X1 and X2 then can undergo cleavage of C-C bonds between C1 and C2, the former giving arabinonic acid and the latter forming a mixture of arabinonic and ribonic



**Scheme II (Contd)**



Scheme II

acids. In the case of E⁻ from pentoses, hydrogen can be removed only from C2 to form C1-C2 ene-diol anion, which in the presence of alkali forms intermediate X3 with epimerization at C2. Breakage of C1-H bonds from X3 gives a mixture of arabinonic and ribonic acids as in the case of X2. The cleavage of C-C bonds between C2 and C3 in X1 and X2, and the breaking of C-C bonds between C1 and C2 in X3 yield aldo-tetrose without epimerization at C4 (hexoses) or at C3 (pentoses). The aldo-tetrose further oxidizes to yield erythronic acid and a minor proportion of threonic acid (Table V). The reaction can proceed further, with the cleavage of C-C bonds between C3 and C4 of hexoses and the breaking of C-C bonds between C2 and C3 of pentoses, to form glyceric acid.

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