Oxidation of monosaccharides by $N$-metallo-$N$-haloarylsulfonamides: a review

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Mechanism of oxidation of monosaccharides such as erythrose and threose series pentoses and hexoses, 6-deoxyhexoses, uranic acids and aminosugars are studied with mild oxidizing agents such as $\text{Cl}^+$, $\text{Br}^+$ or $\text{I}^+$ in detail. The product profile was confirmed by HPLC and GLC-MS data. Based on the available data, general mechanism for the oxidation of monosaccharides has been reported.

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1. Introduction
Carbohydrates including sugars are one of the major groups of organic matter to occur naturally. Carbohydrates and its oxidative products play a key role as intermediates for the synthesis of many organic molecules. In this context, a number of authors have developed many oxidation procedure for carbohydrates with various oxidants. Although the oxidation of monosaccharides were studied by several workers$^2,3,11$, clear information or an overall view is lacking. In our laboratory we have studied extensively in detail and published several papers$^5,12-17$ on the oxidation of varieties of monosaccharides. This prompted me to document an overall view on the oxidation of monosaccharides with various oxidants. Herein, report the oxidation of monosaccharides such as erythrose and threose series pentoses and hexoses, 6-deoxyhexoses, aminosugars and uronic acids with all available $N$-metallo-$N$-haloarylsulfonamides in alkaline medium. The details of experimental procedure can be found from our previously published papers$^5,12$. The product profile of the above monosaccharides are discussed. Based on these data, a general mechanisms for the oxidation of the monosaccharides have been proposed.

$N$-Metallo-$N$-haloarylsulfonamides (1) as oxidants:
The $N$-metallo-$N$-haloarylsulfonamides (1) are a class of compounds capable of producing halonium cations, hypohalites and $N$-anions which behave both as bases and as nucleophiles, depending on the reaction conditions. The subject has been extensively reviewed and well studied$^1-5$. These oxidants contain a strongly polarized $N$-linked halogen which is in the +1 state ($X = \text{Cl}$ or $\text{Br}$ or $\text{I}$, bonded to nitrogen is positive). Since these oxidants react with a wide variety of functional groups, they are used as reagents in analytical chemistry$^5-7$. We have demonstrated that these oxidants can be used as mild$^5$, specific and selective oxidations can be carried out. Therefore, we employed these oxidants as effective and studied with several possibilities by changing $R$ and $X$ in 1 to get the detailed information of the proposed studies. It is also noted that $\text{RNX}^-$ is the active
species under the present experimental conditions. The details regarding the active species can be found from the papers published elsewhere.8-10.

RNX Na

\[ R = \text{SO}_2^- \quad \text{CH}_3\text{SO}_2^- \]

\[ X = \text{Cl or Br or I} \]

2. Oxidation of erythrose series pentoses and hexoses by 1 in alkaline medium

2.1. HPLC and GLC-MS analysis of products:

HPLC and GLC-MS analysis of the products indicated that D-mannose, D-glucose, D-fructose, L-arabinose and D-ribose were oxidized to a mixture of aldonic acids consisting of arabinonic, ribonic, erythronic and glyceric acids. In the case of hexoses, besides these acids, small portions of hexonic acids were formed (Fig. 1). Incubation of sugars with alkali alone, under the reaction conditions, did not degrade the sugars to significant extent. The oxidation products of sugars were also analyzed at 0.5, 1, 2, 4, 8, 16 and 24 h. The relative proportions of various aldonic acids formed (see Fig. 1 and Table 1) 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 h), revealing that the lower-carbon aldonic acids were not derived from the initially formed six-carbon aldonic acids. Consistent with these data, D-gluconic, D-mannonic, D-galactonic, D-ribo- and D-arabinonic acids were not oxidized by 1.

2.2. Mechanism:

In the proposed mechanism (Scheme I) the anion \( E^- \) of sugars (keto-isomer in the case of hexoses and aldo isomer in the case of pentoses) react with 1 to form intermediates \( X_1 \) and \( X_2 \). In the case of anions \( (E^-) \) from hexoses, the loss of hydrogen occur at either C-1 or C-3 to form \( X_1 \) and \( X_2 \). The formation of \( X_2 \) accompanies epimerization at C-2 and C-3, \( X_1 \) and \( X_2 \) then can undergo cleavage of C-C bonds between C-1 and C-2, the former giving arabinonic acid and the later 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

![Fig. 1. HPLC analysis of the products formed by the oxidation of sugars by 1 in the presence of NaOH at 30°: (1) glyceric acid, (2) erythronic acid, (3) arabinonic acid, (4) ribonic acid, (5,6) hexonic acids. Man, Glc, Fru, Ara and Rib respectively represent chromatograms of the oxidation products of 1 with D-mannose, D-glucose, D-fructose, L-arabinose and D-ribose. The skewed shoulder on tailing edge of the peak 2 represents a small amount (2-4%) of threonic acid.](image)

| Sugar       | Mole of 1 consumed per mole of sugar | Arabonic acid | Ribonic acid | Erythronic acid and threonic acid | Glyceric acid | Hexonic acid |
|-------------|-------------------------------------|---------------|--------------|-----------------------------------|--------------|-------------|
| D-Mannose   | 2.5                                 | 36            | 19           | 35                                | 4            | 6           |
| D-Glucose   | 2.8                                 | 35            | 21           | 36                                | 3            | 5           |
| D-Fructose  | 2.9                                 | 30            | 20           | 40                                | 8            | 4           |
| L-Arabinose | 2.2                                 | 28            | 8            | 49                                | 14           | –           |
| D-Ribose    | 1.7                                 | 30            | 8            | 48                                | 14           | –           |

*Based on the peak areas normalized using response factors obtained by analyzing standard aldonic acid solutions.*
ribonic acids as in the case of X. The cleavage of C-C bonds between C-2 and C-3 in X, and the breaking of C-C bonds between C-1 and C-2 in X yield aldo-tetrose without epimerization at C-4 (hexoses) or at C-3 (pentoses). The aldo-tetrose further oxidizes to yield erythronic acid and a minor proportion of threonic acid (Table 1). 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.

3. Oxidation of threose series pentoses and hexoses by 1 in alkaline medium

3.1 HPLC and GLC-MS analysis of products

Product analysis of D-gulose, D-idose, L-sorbose, D-galactose, D-talose, D-tagatose, D-xyllose and D-lyxose revealed that all xyllose series hexoses gave mainly mixtures of lyxonic and threonic acids with minor proportions of xylonic, xylonic and glyceric acids, whereas all threose-series hexoses gave mixtures of threonic, threonic and glyceric acids with minor amounts of xylonic and xylonic acids. Xylose and lyxose gave mixtures consisting mainly of threonic, threonic and glyceric acids with minor proportions of xylonic acid (Fig. 2a-c and Table 2). The xyllose series hexoses (gulose, idose and sorbose) gave predominantly threonic and glyceric acids with minor proportions of xylonic and xylonic acids (Fig. 2b). On the other hand, all xyllose series hexoses (galactose, talose and tagatose) gave threonic and xylonic acids as predominant products with small amounts of glyceric and xylonic acids (Fig. 2a). All hexoses except sorbose gave minor amounts of xylonic acids (Fig. 2a and b). Furthermore, all threose-series sugars were oxidized by the acid (-95%) (1) glyceric acid (2) threonic acid (-95%) plus erythronic acid (-5%) (3) xylonic acid (4) xylonic acid (5) xylonic acid (6) threonic acid (7) glyceric acid D-galactose D-talose D-tagatose D-gulose D-idose L-sorbose D-xyllose D-lyxose Peak 2 in (a) represents 95-96% threonic acid and 4-5% threonic acid in (a) and (b) were not oxidized by 1. All other sugars were almost quantitatively oxidized.

![Fig 2](image)

**Table 2.** HPLC Analysis of the products formed by the oxidation of threose series pentoses and hexoses by 1 in alkaline medium

| Sugar        | Mole of 1 consumed per mole of sugar | Products (approximate mole percentage)* |
|--------------|-------------------------------------|-----------------------------------------|
| D Galactose  | 28                                  | Glyceric acid: 9 Threonic acid: 44 Erythronic acid: 3 Xylonic acid: 32 Lyxonic acid: 12 |
| D Talose     | n d                                 | Glyceric acid: 9 Threonic acid: 45 Erythronic acid: 3 Xylonic acid: 32 Lyxonic acid: 12 |
| D Tagatose   | n d                                 | Glyceric acid: 12 Threonic acid: 47 Erythronic acid: 3 Xylonic acid: 32 Lyxonic acid: 12 |
| D Gulose     | 29                                  | Glyceric acid: 18 Threonic acid: 38 Erythronic acid: 12 Xylonic acid: 32 Lyxonic acid: 7 |
| D Idose      | n d                                 | Glyceric acid: 40 Threonic acid: 40 Erythronic acid: 8 Xylonic acid: 32 Lyxonic acid: 7 |
| L Sorbose    | 27                                  | Glyceric acid: 44 Threonic acid: 44 Erythronic acid: 3 Xylonic acid: 32 Lyxonic acid: 3 |
| D Xylose     | 22                                  | Glyceric acid: 20 Threonic acid: 37 Erythronic acid: 7 Xylonic acid: 32 Lyxonic acid: 36 |
| D Lyxose     | 1 9                                 | Glyceric acid: 25 Threonic acid: 32 Erythronic acid: 12 Xylonic acid: 32 Lyxonic acid: 37 |

*Based on the peak areas
*Peak 2 in Fig. 2 represents 95-96% threonic acid which can be separated by using low flow rate

n d = not determined
except lyxose and galactose were oxidized almost quantitatively by 1; after 24 h incubation with 1 at 35°, 20–25% of lyxose and 5% of galactose remained unoxidized (Fig. 2a-c). The oxidation products were analyzed at 0.5, 1, 2, 4, 8, 20 and 24 h for all the sugars. The relative proportions of various aldonic acids formed were similar at all time-points analyzed.

3.2. Mechanism:

In the proposed mechanism (Scheme 2), the keto-enolic anions (E⁻) of sugars react with 1 to form intermediates $X_1$-$X_3$. For threose-series hexoses, the anions (E⁻) intermediates are predominantly the keto-enolic forms. However, for pentoses, the major reacting species are aldo-enolic anions; probably minor proportions of keto-isomer may also be involved. In the case of anions (E⁻) from hexoses, the loss of hydrogen can occur at either C-1 or C-3 to form C-1-C-2 or C-2-C-3 enediols containing a hypochlorite group at C-2. Since epimerization at C-3 was limited, as
Table 4. HPLC Analysis of the products formed by the oxidation of aminosugars by 1 m alkaline medium

| Aminosugars       | Arabonic acid | Ribonic acid | Erythronic acid | Lyxonic acid | Threonic acid | Glyceric acid | Hexonic acid |
|-------------------|--------------|--------------|-----------------|--------------|---------------|---------------|--------------|
| D-Mannosamine     | 36           | 24           | 32              | -            | -             | 5             | 3            |
| D Glucosamine     | 37           | 20           | 33              | -            | -             | 7             | 3            |
| D-Galactosamine   | -            | -            | 33              | -            | -             | 52            | 10           |

*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 h were similar to those observed at 24 h except that the presence of six-carbon aldonic acid was evident only after 4 h. Similar product profiles were observed even when the reactions were carried out under kinetic conditions.

Scheme 2 (contd.)
evidenced by the formation of only very minor proportions of epimeric pentonic acids from hexoses, it can be concluded that cleavage of the C-1-H bond occurs preferentially as compared with cleavage of the C-3-H bonds to form C-1-C-2 enediols. The enediols thus formed contain polarized double bonds to which hydroxide ion can add at C-2 to form C-2 enediols. The enediols thus formed can undergo cleavage of C-C bonds between C-1 and C-2, the former giving lyxonic acid and the latter forming a mixture of lyxonic and xylonic acids.

In the case of aldo-enolic anions from pentoses, hydrogen can be removed only from C-2 to form the C-1-C-2 enediol-anion, which in the presence of I and alkali forms intermediate X3 with epimerization at C-2. The cleavage of C-1-H bonds from X3 gives a mixture of lyxonic and xylonic acids. The cleavage of C-C bonds between C-2 and C-3 in X1 and X2, and the breaking of C-C bonds between C-1 and C-2 in X3 yield aldo-tetrose without epimerization at C-4 (hexoses) or at C-3 (pentoses). The aldo-tetrose further oxidizes to yield threonic acid and a minor proportion of erythronic acid (Table 2). 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. Minor proportions of threonic and glyceric acids could also be formed by the cleavage of C-1-C-2 and C-2-C-3 bonds, respectively, from the keto-enolic form of pentoses through the reaction sequences similar to those outlined for keto-hexoses in Scheme 2.

4. Oxidation of 6-deoxy hexoses by N-metallo-N-haloarylsulfonamides in alkaline medium

4.1. HPLC and GLC-MS analysis of products:

HPLC analysis of products of L-rhamnose, L-fucose and D-fucose indicated a mixture of aldonic acids in varying proportions. The products were identified by comparison of their HPLC retention times with retention times of the saturated aldonic acids. Oxidation of both D-fucose and L-fucose yielded identical products namely, 5-deoxy lyxonic acid, 5-deoxy xylonic acid and 4-deoxy erythronic acid while for L-rhamnose, the oxidation products were 5-deoxy arabinonic acid, 5-deoxy ribonic acid and 4-deoxy erythronic acids. Besides these products, small amounts of 2-hydroxy propanonic acid and 6-deoxy hexonic acids are formed (Fig. 3, Table 3). The oxidation products of 6-deoxy hexoses were also analyzed at 0.5, 1, 2, 4, 8, 16 and 24 h.
The relative proportions of various aldonic acids formed (Fig. 3, Table 3) were similar at all time points analyzed. However, the formation of six-carbon aldonic acids was observed only after 4 h, revealing that the lower carbon aldonic acids were not derived from the initially formed six-carbon aldonic acids.

4.2. Mechanism:

A probable mechanistic picture of the oxidation of L-rhamose is shown in Scheme 3. In alkaline solutions, the enediol anion (S^-) of the sugar reacts with the oxidant in the rate determining step to form an intermediate X. Here the cleavage of C-C bonds between C1 and C2 with epimerization at C3 forms mixture of 5-deoxy pentonic acids. L-Rhamnose gives a mixture of (L-) 5-deoxy arabinonic and (L-) 5-deoxy ribonic acid. The cleavage of C-C bonds between C2 and C3 in X, of 6-deoxy hexose yield (L-) 4-deoxy tetronic acid with no significant epimerization at C4 of the sugars. This explains the formation of (L-) 4-deoxy erythonic acid. The reaction can proceed further with the cleavage of C-C bond between C2 and C3 of (L-) 5-deoxy arabinose to form (L-) 2-hydroxy propanoic acid. A similar scheme can be drawn for the oxidation of L-fucose into a mixture of (L-) 5-deoxy xylonic acid, (L-) 4-deoxy xylonic acid, (L-) 4-deoxy threonic acid and (L-) 2-hydroxy propanoic acid in alkaline medium.

5. Oxidation of amino sugars by N-metallo-N-halosulfonamides in alkaline medium

5.1. HPLC and GLC-MS analysis of products:

The oxidation products analyzed by HPLC and GC-MS indicated that the alkoxy anion (S^-) of the hexosamine formed in a base catalyzed reaction at C-1 carbon is subjected to an electrophilic rate limiting attack by X^+ (1, Cl^+ or Br^+ or I^+) of the oxidant. The hexonic acid formed is decarboxylated with loss of ammonia to form the respective pentoses, which is further converted into the corresponding pentonic acid. The breaking of the bond between C-1 and C-2 carbons in pentose yield tetronic acids (Fig. 4 and Table 4).

5.2. Mechanism:

A possible mode of oxidation of D-glucosamine (or D-mannosamine) by 1 in alkaline medium is shown in Scheme 4. The hexosamine reacts with the anion of oxidant in presence of alkali to form 2-aminogluconic acid, which reacts
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\[
\begin{align*}
\text{L-Rhamnose} & \xrightarrow{\text{O}} \text{H-C-} & \text{H} & \text{C} & \text{OH} & \text{H} & \text{C} & \text{OH} \\
& \text{HO-C-H} & \text{HO-C-H} & \text{CH}_3 & \text{HO-C-H} & \text{HO-C-H} & \text{CH}_3 \\
\text{(S\textsuperscript{-})} \\
\text{H-C-} & \text{H} & \text{C} & \text{OH} & \text{H} & \text{C} & \text{OH} & \text{H} & \text{C} & \text{OH} \\
& \text{HO-C-H} & \text{HO-C-H} & \text{CH}_3 & \text{HO-C-H} & \text{HO-C-H} & \text{CH}_3 \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
\text{H} & \text{C} & \text{OH} & \text{H} & \text{C} & \text{OH} & \text{H} & \text{C} & \text{OH} \\
& \text{HO-C-H} & \text{HO-C-H} & \text{CH}_3 & \text{HO-C-H} & \text{HO-C-H} & \text{CH}_3 \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
\text{H} & \text{C} & \text{OH} & \text{H} & \text{C} & \text{OH} & \text{H} & \text{C} & \text{OH} \\
& \text{HO-C-H} & \text{HO-C-H} & \text{CH}_3 & \text{HO-C-H} & \text{HO-C-H} & \text{CH}_3 \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
(\text{L-}) \text{5-deoxyribononic acid} & (\text{L-}) \text{5-deoxyarabinonic acid} & (\text{L-}) \text{5-deoxyarabinose} \\
\text{CH} & \text{O-C-H} & \text{H} & \text{C} & \text{OH} & \text{H} & \text{C} & \text{OH} & \text{H} & \text{C} & \text{OH} \\
& \text{HO-C-H} & \text{HO-C-H} & \text{CH}_3 & \text{HO-C-H} & \text{HO-C-H} & \text{CH}_3 \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
(\text{X}) \\
\text{CH} & \text{O-C-H} & \text{H} & \text{C} & \text{OH} & \text{H} & \text{C} & \text{OH} & \text{H} & \text{C} & \text{OH} \\
& \text{HO-C-H} & \text{HO-C-H} & \text{CH}_3 & \text{HO-C-H} & \text{HO-C-H} & \text{CH}_3 \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
(\text{L-}) \text{4-deoxyerythronic acid} \\
\text{CH} & \text{O-C-H} & \text{H} & \text{C} & \text{OH} & \text{H} & \text{C} & \text{OH} & \text{H} & \text{C} & \text{OH} \\
& \text{HO-C-H} & \text{HO-C-H} & \text{CH}_3 & \text{HO-C-H} & \text{HO-C-H} & \text{CH}_3 \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
(\text{L-}) \text{2-hydroxypropanoic acid} \\
\text{5-deoxyarabinose} \\
\text{CH} & \text{O-C-H} & \text{H} & \text{C} & \text{OH} & \text{H} & \text{C} & \text{OH} & \text{H} & \text{C} & \text{OH} \\
& \text{HO-C-H} & \text{HO-C-H} & \text{CH}_3 & \text{HO-C-H} & \text{HO-C-H} & \text{CH}_3 \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
\text{H} & \text{C} & \text{OH} & \text{H} & \text{C} & \text{OH} & \text{H} & \text{C} & \text{OH} \\
& \text{HO-C-H} & \text{HO-C-H} & \text{CH}_3 & \text{HO-C-H} & \text{HO-C-H} & \text{CH}_3 \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
(\text{L-}) \text{2-hydroxypropanoic acid} \\
\text{Scheme 3}
with the oxidant to form D-arabinose through decarboxylation followed by deamination in the form of \( \text{NH}_3 \) via hydrolysis of intermediate imine. The pentose is further oxidized to arabinonic acid and its epimer ribonic acid. The former predominates over its epimer. This is possibly due to stabilization of transition state, as the preceding intermediate has hydrogen bonding involving hydroxyl hydrogen on C-5 with oxygen on C-2. The C-C bond scission between C-1 and C-2 on pentose yield the tetronic acids. The H and OH groups on C-3 are not significantly isomerized. This explains the formation of erythonic acid. Further, bond breaking between C-2 and C-3 results in the formation of glyceric acid.

A similar mechanism can be drawn for the oxidation of D-galactosamine by \( \text{I} \) into a mixture of D-lyxonic acid, D-threonic acid and D-glycemic acids in alkaline medium.

\[
\text{Scheme 4 (contd.)}
\]
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Scheme 4 (contd.)

Scheme 4

Scheme 5
6. Oxidation of uronic acids by \(N\)-metallo-\(N\)-haloaryl sulfonamides 1 in alkaline medium

6.1. HPLC and GLC-MS analysis of products:

The oxidation of D-glucuronic acid and D-galacturonic acid by 1 leads to the corresponding dicarboxylic acids, namely D-glucaric and D-galactaric acids. In this case also the oxidation was found to be smooth in the presence of NaOH at the C-1 carbon without affecting the C-6 carboxyl group, leading to the formation of the products.

6.2. Mechanism:

A possible mode of oxidation of the uronic acids as illustrated by D-glucuronic to D-glucaric acid is shown in Scheme 5. The sugar reacts in the pyranose form to give the sugar and the corresponding dicarboxylic acids.

7. Rate studies and Conclusion

(i) The observed oxidation rate is lower when \(R = CH_3C_6H_4SO_2\) compared to \(R = C_6H_5SO_2\) in 1. The ratio of \(k_{obs}(C_6H_5SO_2)/k_{obs}(CH_3C_6H_4SO_2) > 1\), indicating the participation of -CH_3 group in the oxidant, which exerts a strong inductive effect pushing up the electron density at the polar N-X bond, thus reducing the electrophilicity of the X atom and hence the observed rate constants (Tables 5 and 6).

(ii) From the Tables 5 and 6 it is seen that, the \(k_{obs} I^+ > k_{obs} Br^+ > k_{obs} Cl^+\). This may be due to the difference in electrophilicities of iodine, bromine and chlorine.

In these reactions electronegativity of halogens play an important role. Iodine has the least electronegativity of 2.2; bromine has a higher electronegativity of 2.7 and chlorine still higher electronegativity of 2.8. As the electronegativity increases, the electropositive nature decreases. Since the positive halogen atoms are the reactive species in these oxidation reactions and the electropositive nature is in the order I > Br > Cl. Therefore, reactivity of \(N\)-metallo-\(N\)-haloaryl sulfonamides is in the order IAB > BAB > CAB in the case of benzene analogues of 1. Similarly in the case of toluene analogues of 1, the reactivity is in the order IAT > BAT > CAT. From the above observation it can be generalized that iodamines are strong oxidising agents than bromamines and chloramines, and bromamines are strong oxidising agents compared to chloramines for the oxidation of monosaccharides.

Conclusion:

The present studies report a detailed investigation on the oxidation of varieties of sugars such as erythrose, threose series pentoses and hexoses, 6-deoxyhexoses, amino sugars and uronic acids with different oxidizing species namely Cl^+, Br^+ or I^+ (1) to ascertain the mechanism involved in this type of redox systems. Furthermore, the product pro-
file has been examined thoroughly. The observed rate constants ($k_{\text{obs}}$) for all the sugars are given in Tables 5 and 6 and the rate of oxidation is carefully observed. With the available data, such as, $k_{\text{obs}}$ values, stoichiometry and product profile (%), a common mechanism in each category of sugar is operating in these molecules. The products of oxidation of all these sugars (monosaccharides) lead to the corresponding acids. In the present studies, it is observed that the change of oxidants from CI+ to I+ did not alter the product profile (%). However, it has been noted that, the oxidation is generally faster with the iodine analogues of 1 than that of bromine or chlorine [$k_{\text{obs}}$ (I) > $k_{\text{obs}}$ (Br) > $k_{\text{obs}}$ (Cl)].

This has been rationalized in terms of the differences in electrophilicity of halonium cations, CI+, Br+ or I+ which are generally the reactive species in these reactions. Also, it is partly due to the moderate differences in the Van der Waal’s radii of iodine, bromine and chlorine.

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