

Oxidation of D-Glucose and D-Fructose by N-Bromosaccharin in Aqueous Acetic Acid Medium in Presence of NaLS: A Comparative Study

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Abstract:

The oxidation of D-Glucose and D-Fructose was monitored iodometrically by N-Bromosaccharin in the aqueous acetic acid medium in presence of NaLS (Sodium Lauryl Sulphate). Reaction demonstrated that oxidative species HOBr and $\text{H}_2\text{O}^\oplus\text{Br}$ were involved in the acidic oxidation of Carbohydrates. It was established that respective acids of carbohydrates gluconic acid and arabinoic acid were the oxidation products. Respective acids of carbohydrates were the results of reactive HOBr in acidic conditions. The reaction follows first-order kinetics with respect to HOBr, Glucose, Fructose, and $[\text{H}^+]$ uniformly and is homogeneous.

The Effect of varying salt electrolyte concentration was insignificant showing that the molecular species was involved in the rate-determining step. The Reaction was monitored at 60°C ($\pm 1^\circ\text{C}$) temperature and thermodynamic activation parameters were determined. Binding parameters have been calculated by analyzing the data using the model suggested by Menger Portnoy and Piszkiwicz's model. Kinetic studies, stoichiometry of the reaction and product analysis have been proposed for the oxidation of sugars in the presence of NaLS.

Keywords: Kinetic oxidation, D-Glucose, D-Fructose, NaLS(Sodium Lauryl Sulphate), Stoichiometry.

Introduction:

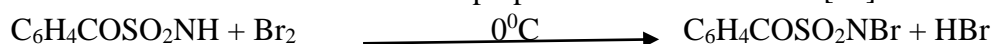
The current work includes the oxidative kinetics of carbohydrates, namely glucose and fructose, by N-Bromosaccharin in the aqueous acetic acid medium in the presence of NaLS(Sodium Lauryl Sulphate). The oxidation of secondary alcohols and cyclic alcohols by N-bromosaccharin in the presence of additional saccharin[1], D-Galactose[2] and certain aldoses (pentoses and hexoses) [3], Glycolic acid [4], Amino acids [5], Benzhydrol [6], Oxoacids [7], Butan-2-ol [8], Propan-2-ol [9], L-Threonine [10], Furfural [11] has been investigated by different researchers. The kinetic oxidation of carbohydrates by various oxidants such as bromine [12], N-bromoacetamide[13], chloramine-T [14], bromamine-B [15], N-Chloro-mono/di-substituted benzenesulfonamides[16], N-bromonicotinamide (NBN) [17]permanganate ion[18], potassium iodate[19], vanadium (V) [20], gold (III) [21]. Potassium ferricyanide [22] and N-bromo aryl sulphonamides [23], N-bromosuccinimide [24] have been reported.

A survey of the literature suggests that various additional catalysts and oxidants were also used to investigate the mechanistic pathway of these compounds, although ambiguity persists. There are no reports of mechanistic research on the catalytic effect of cationic surfactant on the NBSA oxidation of substrates in aqueous acetic acid medium in the presence of Hg (II) acetate as a Br⁻ scavenger.

Experimental:

Materials and methods:

D-glucose, D-fructose, NaLS, perchloric acid, acetic acid, and mercuric acetate as well as sodium perchlorate, sodium thiosulphate, starch, potassium dichromate, and potassium iodide, were all provided by Merck and utilized exactly as received. De-ionized water that had undergone two distillations was used to make the stock solutions. By titrating sodium thiosulfate solution against potassium dichromate solution and using starch as an indicator, the solution was standardized. The procedure recommended by Bacchawat and Mathur was used to prepare N-bromosaccharin.[25]



60⁰C (±1⁰C) was the constant temperature used to study the process. An iodometric estimate of the unreacted N-bromosaccharin was done after determining the rate of reaction. Different rate equation formulas were fed the data. It was fairly feasible to determine the rate constant from the first-order rate equation.

Stoichiometry and Product Analysis:

At experimental temperatures, the stoichiometry studies for the glucose-NBSA and fructose-NBSA systems were completed. Different [NBSA]/[Glucose] and [NBSA]/[Fructose] ratios were used in the experiments under the conditions of [NBSA] >>> [Glucose] and [NBSA] >>> [Fructose].

According to stoichiometric study findings, one mol of glucose consumed one mole of oxidant, producing corresponding aldonic acid as the final oxidation product, while one mole of fructose consumed one mole of oxidant, producing corresponding ketonic acid as the final oxidation product. Saccharin was qualitatively identified as N-bromosaccharin's reduction product.



Results:

The kinetics of the oxidation of Carbohydrates by NBSA in the presence of an anionic surfactant NaLS (Sodium Lauryl Sulphate) was investigated at several initial concentrations of the reactants. The reaction rate was determined by the fixed concentration of N-Bromosaccharin.

Dependence of rate:

- **On the initial concentration of oxidant:** In the presence of NaLS, the reactions were examined at various initial oxidant concentrations and constant concentrations of the other reactants. Each time, the oxidant disappeared according to first-order kinetics. The plot of log (a-x) versus Time is linear. (Fig. 1)

The value of the pseudo-first-order rate constant does, however, slightly decline as oxidant concentration rises (Table 1). This drop in rate constant value shows that N-bromosaccharin is forming an intermediate with decreased reactivity in a pre-equilibrium with a nucleophilic species, most likely H₂O. According to

earlier publications, the pseudo-first-order rate constant value for the N-bromosaccharin oxidation of Galactose, α -hydroxy acid, Benzyl alcohols, and Benzhydrol showed the similar slowdown.

Table 1 Dependence of rate on the concentration of oxidant

Sr. No.	[NBSA] 10 ³ M	10 ⁻³ k ₁ min ⁻¹ With NaLS	
		[Glucose]	[Fructose]
1.	2.0	7.64	10.38
2.	2.50	7.18	9.45
3.	3.33	6.87	8.59
4.	5.0	4.21	5.06
5.	10.0	2.65	2.65

[Hg(OAc)₂] = 1.0 x 10⁻²M [NaLS] = 1.0 x 10⁻²M HOAc – H₂O = 20% (v/v) Temp = 60^oC
 [Glucose] = 2.0 x 10⁻²M [Fructose] = 2.0 x 10⁻²M

▪ **On the concentration of Carbohydrates:**

At different initial carbohydrate concentrations for each carbohydrate and constant concentrations for the other reactants, while NaLS was present, the rate dependency on carbohydrate concentration was investigated. In each scenario, the first-order rate constant rises as the concentration of carbohydrates does. The curve between k₁ and [Carbohydrate] for each Substrate-NBSA system starts out linear, passing through the origin, and then bends in the direction of the x-axis at greater substrate concentrations. There is no consistency in the value of (k₂ = k₁/ [Carbohydrate]). According to Figure 1, the double reciprocal plot between k₁ and [Carbohydrate] is linear and has a positive y-axis intercept [Fig.1]. In the pre-equilibrium step, this provides a sliver of kinetic evidence for the development of an intermediate complex between the oxidant and the carbohydrate.

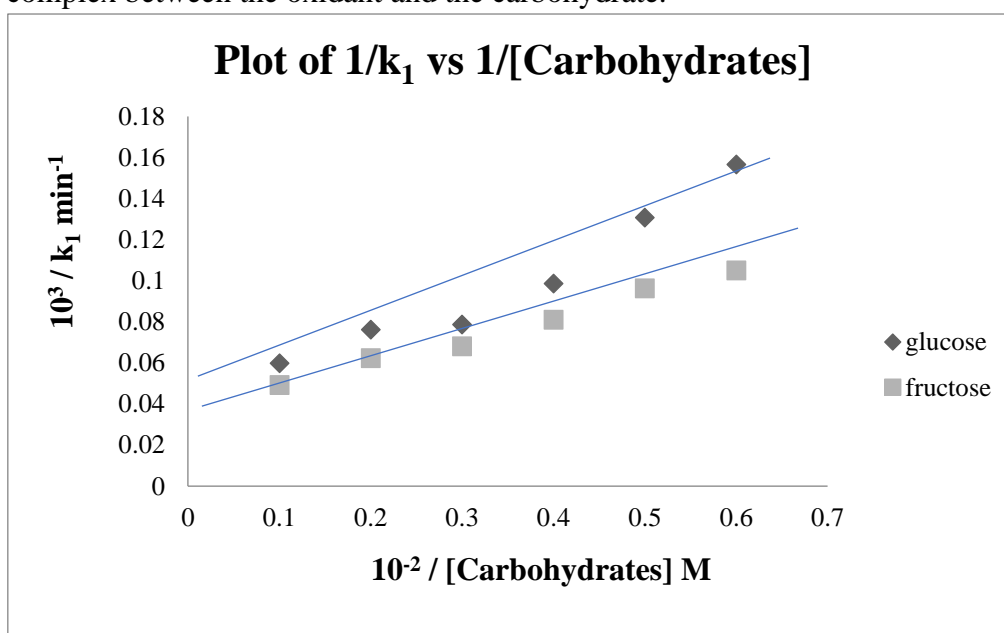


Figure 1. [NBSA] = 2.0 x 10⁻³ M, [Hg(OAc)₂] = 1.0 x 10⁻²M, HOAc – H₂O = 20% (v/v), [NaLS] = 1.0 x 10⁻²M Temp = 60^oC

▪ **On Surfactant concentration:**

Various initial concentrations of the anionic surfactant Sodium Lauryl Sulphate (NaLS) were used to study the oxidation of each carbohydrate with N-bromosaccharin. Each oxidation under study is a micellar-catalyzed bimolecular reaction, as shown by the rate [surfactant] profile (Fig. 2).

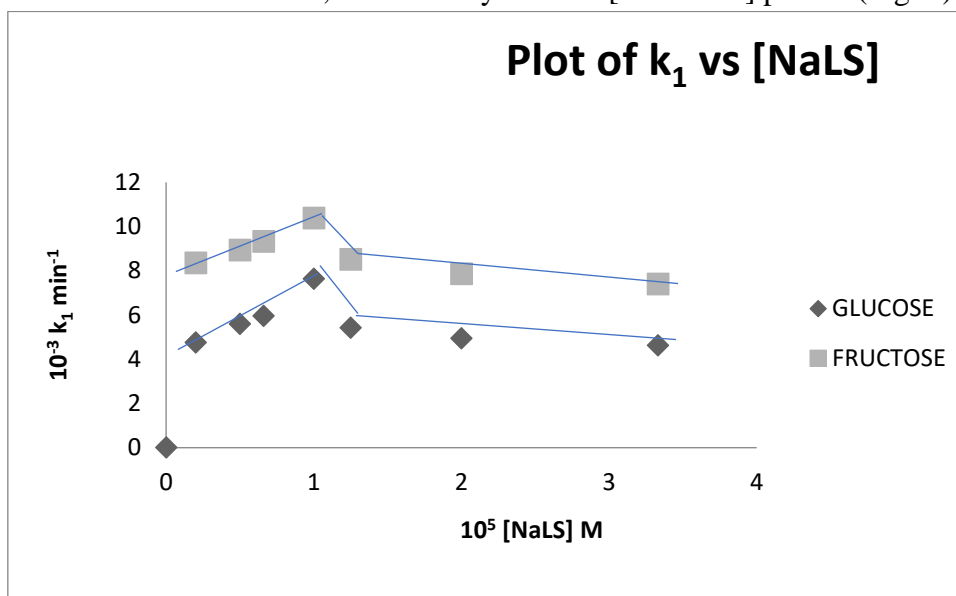


Figure 2 [NBSA] = 2.0 x 10⁻³M, [Carbohydrate]= 2.0 x 10⁻²M, [Hg(OAc)₂]=1.0 x 10⁻²M, [NaLS] = 1.0 x 10⁻²M, HOAc – H₂O =20% (v/v) Temp = 60^oC

▪ **On Perchloric Acid concentration:**

At various initial concentrations of perchloric acid, the effect of variations in perchloric acid concentration on the reaction rate was examined. When an acid concentration is increased in a reaction involving micellar catalysts, the pseudo-first-order rate constant rises, indicating that the reaction is acid catalyzed. The relationship between log ((k₁ – k₂) and log [HClO₄] is linear, with a slope value nearly one, confirming that the order in perchloric acid is one.

▪ **On Mercuric acetate:**

At increasing concentrations of Mercuric acetate, the pseudo-first-order rate constant is essentially constant, as shown in Fig.3 plot of k₁ against [Mercuric acetate], which is derived linearly and bends towards the x-axis. The concentration of Mercuric acetate used in the current experiments had no effect on the rate of oxidation. Therefore, Mercuric acetate serves as a Br⁻ trap under the concentration range utilized.

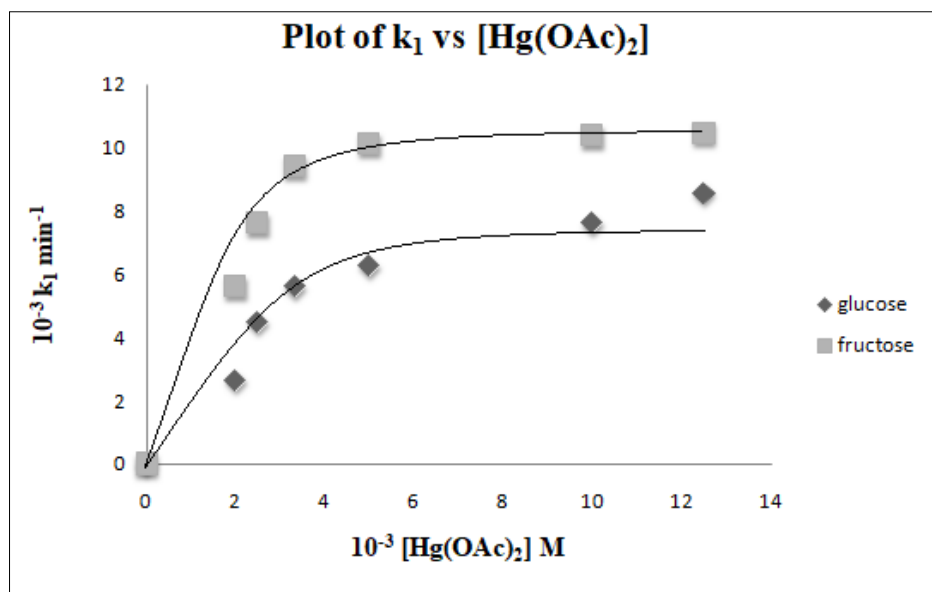


Figure 3 $[\text{NBSA}] = 2.0 \times 10^{-3}\text{M}$, $[\text{Carbohydrate}] = 2.0 \times 10^{-2}\text{M}$, $[\text{Hg}(\text{OAc})_2] = 1.0 \times 10^{-2}\text{M}$, $[\text{NaLS}] = 1.0 \times 10^{-2}\text{M}$, $\text{HOAc} - \text{H}_2\text{O} = 20\% \text{ (v/v)}$ $\text{Temp} = 60^\circ\text{C}$

▪ **On Medium:**

Binary mixes of various proportions of acetic acid and water were used to study the impact of variations in the medium's dielectric constant. For both carbohydrates, the value of the pseudo-first-order rate constant rises when acetic acid concentration rises in the presence of NaLS (Table 2). The plot's design implies that dipole and positive ion contact in the rate-determining step.

Table 2 Dependence of rate on the dielectric constant of the medium

S.No.	HOAc-H ₂ O %(v/v)	10 ³ /D	10 ⁻³ k ₁ min ⁻¹ With NaLS	
			[Glucose]	[Fructose]
1.	10	15.50	6.870	8.365
2.	20	17.17	7.641	10.383
3.	30	19.15	11.466	13.551
4.	40	21.98	12.802	14.376
5.	50	25.64	14.555	16.524
6.	60	30.36	15.150	18.120

$[\text{Hg}(\text{OAc})_2] = 1.0 \times 10^{-2}\text{M}$ $[\text{NaLS}] = 1.0 \times 10^{-2}\text{M}$ $\text{Temp} = 60^\circ\text{C}$
 $[\text{Glucose}] = 2.0 \times 10^{-2}\text{M}$ $[\text{Fructose}] = 2.0 \times 10^{-2}\text{M}$

▪ **On Saccharin:**

The effect of adding saccharin to the reaction mixture was investigated at various concentrations, and the results suggest that saccharin retards the reaction (Table 3). This can be related to saccharin's role in the pre-equilibrium hydrolysis of the oxidant.

Table 3 Dependence of rate on the concentration of Saccharin

S. No.	[Saccharin] 10 ⁻³ M	10 ⁻³ k ₁ min ⁻¹ With NaLS	
		[Glucose]	[Fructose]
1.	0.00	7.253	15.576
2.	2.00	7.101	15.510
3.	2.50	6.150	13.125
4.	3.33	4.459	10.470
5.	5.00	2.826	9.337
6.	10.00	1.823	8.865

[Hg(OAc)₂ = 1.0 x 10⁻²M [NaLS] = 1.0 x 10⁻²M HOAc – H₂O = 20% (v/v) Temp = 60^oC
 [Glucose] = 2.0 x 10⁻²M [Fructose] = 2.0 x 10⁻²M

▪ **On Sodium Perchlorate:**

Sodium Perchlorate has no significant effect on oxidation rate in the presence of NaLS.

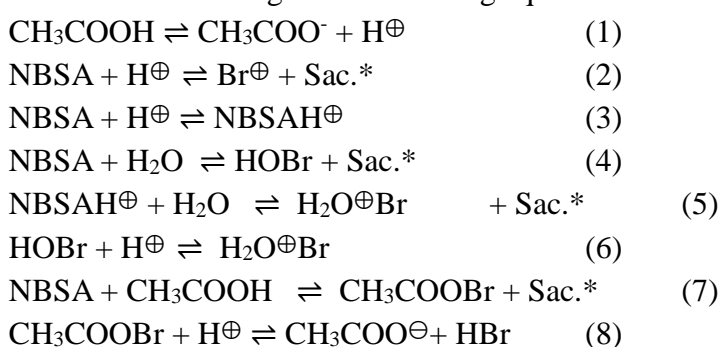
Mechanism:

A potential mechanism for the oxidation of glucose and fructose by N-bromosaccharin in the presence of NaLS has been hypothesized based on observed kinetic data, stoichiometry, and product analyses.

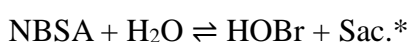
The impact of added Acrylonitrilo was examined to determine the mode of fission during the process of oxidation. In view of the absence of any effect of radical scavenger, Acrylonitrile, on the reaction rate, it is unlikely that a one-electron reaction giving rise to free radicals is operative in this oxidation.

Nature of oxidant species:

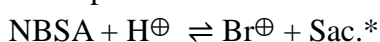
In the aqueous acetic acid medium and in the presence of Perchloric acid, N-bromosaccharin exists as molecular species (NBSA), Hydrolytic product (HOBr), various protonated species, and the Acetyl derivatives according to the following equilibria:



In NBSA oxidation of Carbohydrates, the retarding effect of added saccharin rules out NBSA or NBSAH[⊕] as an active oxidant. On the other hand, it demonstrates a pre-equilibrium hydrolysis of oxidant.



In the presence of mineral acid, HOBr is protonated to H₂O[⊕]Br which now acts as an active oxidant.



*Sac. = Saccharin

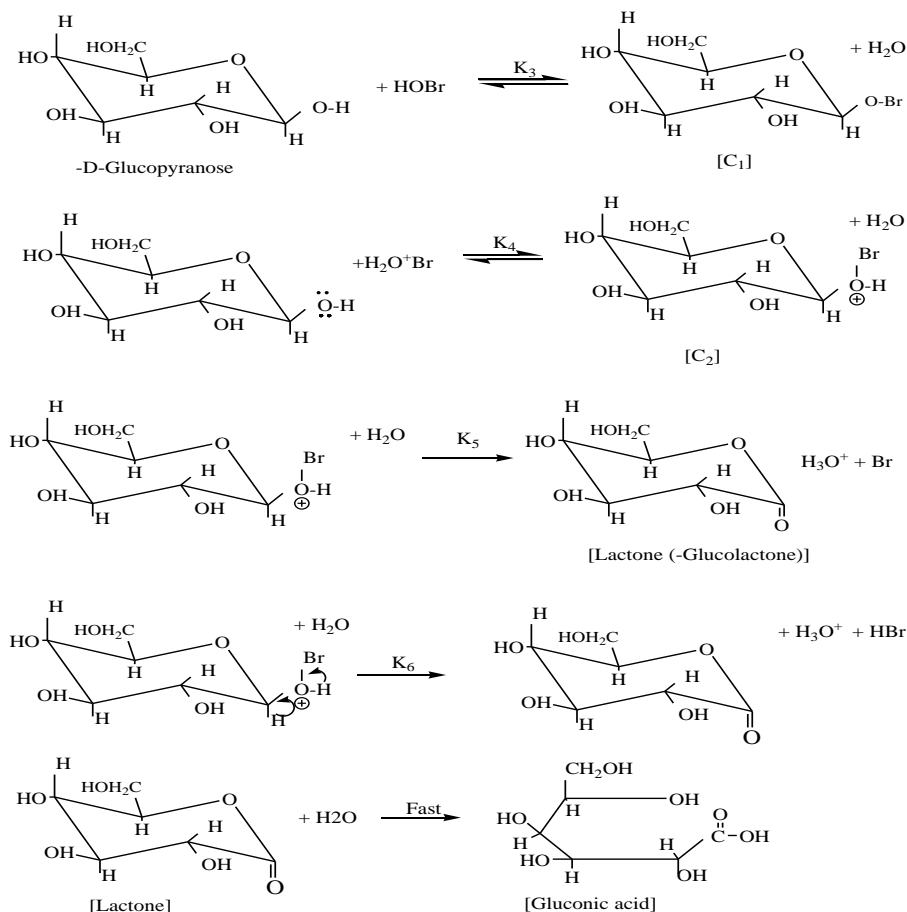
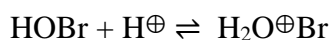
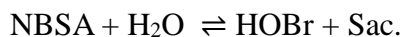
In an aqueous solution, it is difficult to distinguish between Br[⊕] and H₂O[⊕]Br, because they differ only by molecule of Water, but it is well documented that H₂O[⊕]Br is more effective electrophile than Br[⊕].

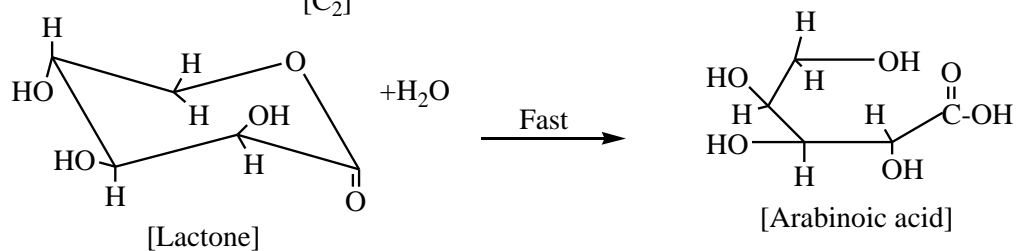
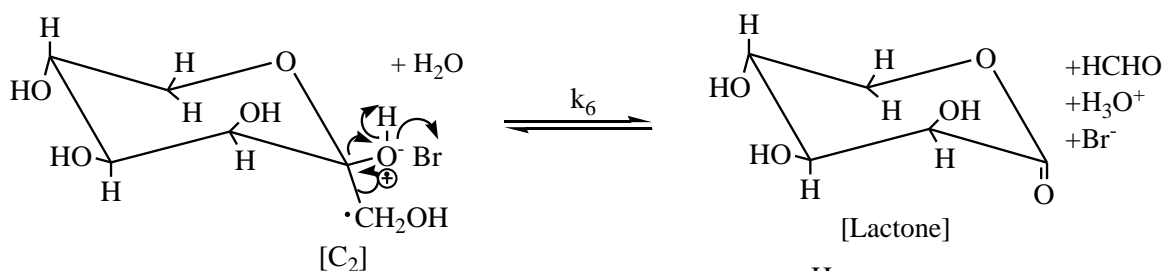
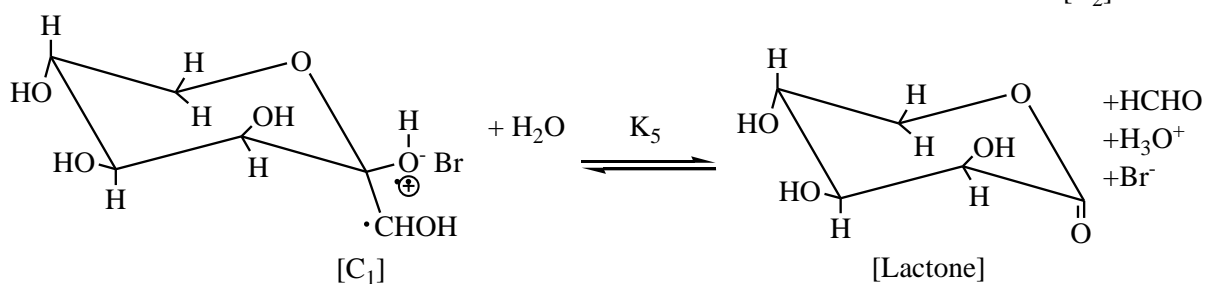
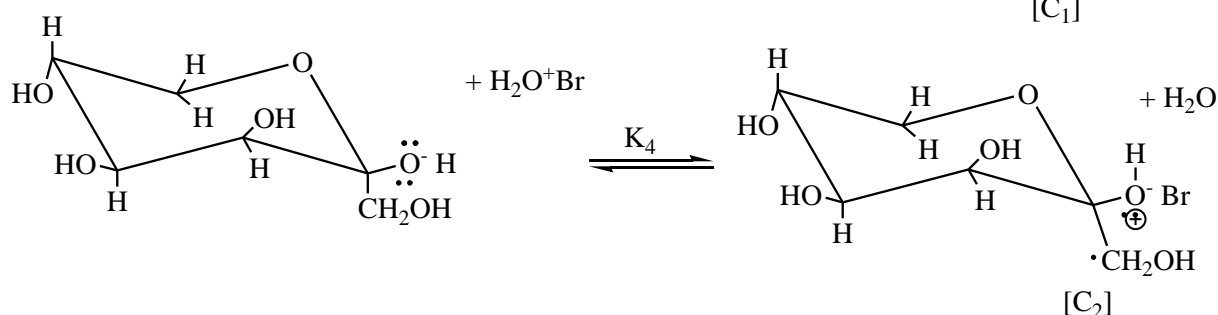
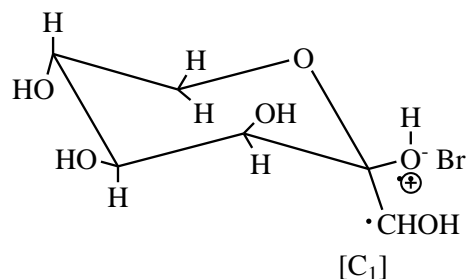
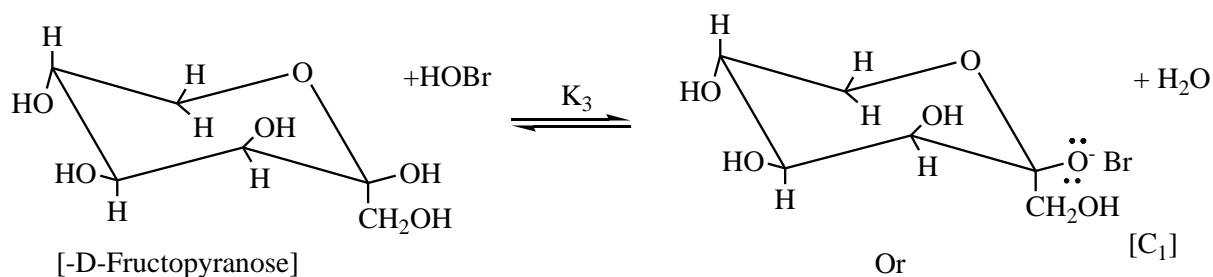
Nature of the substrate:

The polyfunctional organic substances "D-glucose and D-fructose" are carbohydrates with 5 hydroxyl groups and 1 carbonyl group that can exist as a straight chain or a ring. The nature of carbohydrates is nucleophilic. Acid catalysis that was observed during the current experiment points to protonation of carbohydrates. Under comparable experimental circumstances, the oxidation of glucose and fructose would have been more rapid if protonated carbohydrate was the active reductant species. Similar experimental setups result in the slow oxidation of substrates, ruling out carbohydrate protonation. Therefore, the mechanistic step involves interactions between neutral carbohydrate molecules and +ve oxidant species. Additionally, medium-impact experiments show that the slow step in the current study is a positive ion-dipole reaction. Michaelis-Menten kinetics in [Carbohydrate] is shown when NaLS is present.

It demonstrates how hypobromite ester forms in a pre-equilibrium state and then slowly decomposes. The introduction of the hydroxyl group in glucose and fructose increases the rate of oxidation, revealing the nature of the intermediate; therefore the rate-determining phase contains hydride ion transfer ahead. A probable mechanism for the oxidation of D-Glucose and D-Fructose by N-bromosaccharin in the absence of NaLS has been proposed based on the above kinetic measurements, stoichiometry, and product analyses.

Mechanism in the absence of NaLS:





$$\text{Rate} = k_5 [\text{C}_1] + k_6 [\text{C}_2]$$

$$k_{\text{obs}} = \frac{\text{Rate}}{[\text{NBSA}]} = \frac{k_1 k_3 k_5 [\text{Carb.}] [\text{H}_2\text{O}]}{(k_{-3} + k_5) k_{-1} [\text{S}] + k_3 k_5 [\text{Carb.}]}$$

Oxidation of Carbohydrates in the presence of NaLS:

The fact that the rates for each carbohydrate-NBSA system increased in the presence of NaLS suggests that the current study involves biphasic oxidation, in which the reaction takes place in both the micellar and aqueous phases due to the partitioning of the substrate carbohydrate between the two phases. Additional evidence from micellar catalysis also indicates the possibility that concentration and environmental factors may play a role in the faster electron transfer observed in the micellar phase.

The neutral carbohydrate molecule is an active reactant in the kinetic analysis of the oxidation of carbohydrates by NBSA in the absence of NaLS, while HOBr and $\text{H}_2\text{O}^\oplus\text{Br}$ are active oxidant species. The protonated oxidant species $\text{H}_2\text{O}^\oplus\text{Br}$ and the anionic micelle NaLS are electrostatically attracted to one another, which results in the efficient catalysis of oxidation by NaLS.

Table 4 Fighting parameters: Piskiewicz Model [26]

Surfactant	Carbohydrates	N	log [D] ₅₀	10 ³ K _D
NaLS	Glucose	0.87	1.149	1.0
	Fructose	2.00	0.500	1.0

The values of cooperative index “n”, **K_D**, and **log [D]₅₀** derived are given in Table 4.

Positive cooperativity is implied by a value of “n” greater than unity, indicating that the first molecule of the substrate that binds to the surfactant molecule makes it easier for succeeding molecules to bind. If the value is less than unity, it means that the first molecule to bind makes it harder for the subsequent molecules to bind.

The importance of thermodynamic factors lends more weight to the mechanism's proposal. In the presence of NaLS, the value of E_a for glucose drops while the value for fructose increases. A bimolecular process is supported by the values of H, S, and G.

Conclusion:

Based on the results of the kinetic investigation as well as existing literature recommendations, it was determined that among the many active species, HOBr is considered to be an active oxidant. According to the results, NaLS is a good anionic micelle for the oxidation reaction of carbohydrates. Oxidation can occur either acid-dependently or acid-independently when it is catalyzed by an acid. Comparative rate shows faster reaction in Glucose.

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