

Research Article

Comparative Study of Kinetic oxidation of D-Glucose and D-Fructose by N-Bromosaccharin in Aqueous Acetic Acid medium in the presence of CTAB

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Abstract

Kinetic study of N-Bromosaccharin oxidation of D-Glucose and D-Fructose in aqueous acetic acid medium in the presence of CTAB (Cetyl Trimethyl Ammonium Bromide) has been investigated Iodometrically. The reaction follows first-order kinetics in the substrate, CTAB, and H⁺ ion. The oxidation exhibits first-order dependency at lower concentrations of the substrate while at higher concentrations the reaction follows zero-order kinetics. Binding parameters have been calculated by analyzing the data using the model suggested by Menger Portnoy and Piszkiwicz's model. The effect of temperature on the reaction has been investigated in the temperature range of 40⁰ to 70⁰C. The proposed mechanism and the derived rate law agree with the observed kinetics. The stoichiometric studies for D-glucose and D-fructose systems revealed that one mole of substrate consumed one mole of oxidant.

Keywords: N-Bromosaccharin, D-Glucose, D-Fructose, CTAB, Kinetic oxidation, Stoichiometry

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Introduction

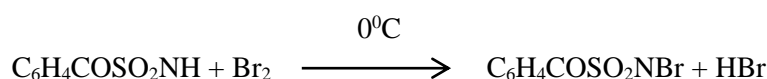
The present study incorporates the oxidative kinetics of Carbohydrates viz. Glucose and Fructose by N-Bromosaccharin in aqueous acetic acid medium in the presence of CTAB. The N-Bromosaccharin oxidation of secondary alcohols and cyclic alcohols in the presence of added saccharin [1], D-Galactose [2], some 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 explored by different workers. The kinetic oxidation of carbohydrates by different oxidants like Bromine [12], N-bromoacetamide [13], Chloramine-T [14], Bromamine-B [15], N-Chloro-mono/di-substituted benzene sulfonamides [16], N-bromosuccinimide [17], N-bromonicotinamide [18], Permanganate ion [19], Potassium iodate [20], Vanadium(V) [21], Gold (III) [22] N-bromo aryl sulphonamides [23], Potassium ferricyanide [24] have been reported.

A review of the literature reveals that different catalysts were also employed to probe into a mechanistic pathway of these compounds, but ambiguity still exists there. There is no mechanistic studies report to look over 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 scavenger for Br.

Experimental

Materials

All the reagents, D-Glucose, D-Fructose, Cetyl Trimethyl Ammonium Bromide, Perchloric Acid, Acetic Acid, Mercuric Acid, Sodium Perchlorate, Sodium Thiosulphate, Starch, Potassium Dichromate and Potassium iodide were supplied by Merck and were used as received. The stock solutions were prepared with doubly distilled deionized water. Sodium thiosulphate solution was standardized by titration against Potassium dichromate solution using starch as an indicator. N-Bromosaccharin was prepared by the method suggested by Bacchawat and Mathur [25].



Kinetic measurements

The reaction was studied at a constant temperature of 60°C ($\pm 1^\circ\text{C}$). The rate of reaction was followed by the estimation of the unreacted N-bromosaccharin iodometrically. The data were fed into different rate equation formulas. The rate constant evaluated from the first-order rate equation was obtained fairly. The kinetics runs were followed up to 80% completion.

Stoichiometry and Product Analysis

The stoichiometry studies for Glucose-NBSA & Fructose-NBSA systems were carried out at experimental temperatures. The various experiments were performed with different [NBSA]/[Glucose] and [NBSA]/[Fructose] ratios under the condition of [NBSA] \gg [Glucose] and [NBSA] \gg [Fructose].

The studies of stoichiometry revealed that 1 mole of Glucose consumed 1 mole of oxidant yielding corresponding aldonic acid as the final oxidation product & 1 mole of Fructose consumed 1 mol of oxidant yielding corresponding ketonic acid as the final oxidation product. The reduction product of N-bromosaccharin was qualitatively identified as saccharin.



Results

The kinetics of the oxidation of Carbohydrates by NBSA in the presence of a cationic surfactant CTAB (Cetyl Trimethyl Ammonium Bromide) 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 Reactants

Dependence of rate on the initial concentration of oxidant

The reactions were studied at different initial concentrations of oxidant and constant concentrations of other reactants in the presence of CTAB. In each case, the disappearance of the oxidant obeyed first-order kinetics. The plot of $\log(a-x)$ versus Time is linear (**Figure 1**).

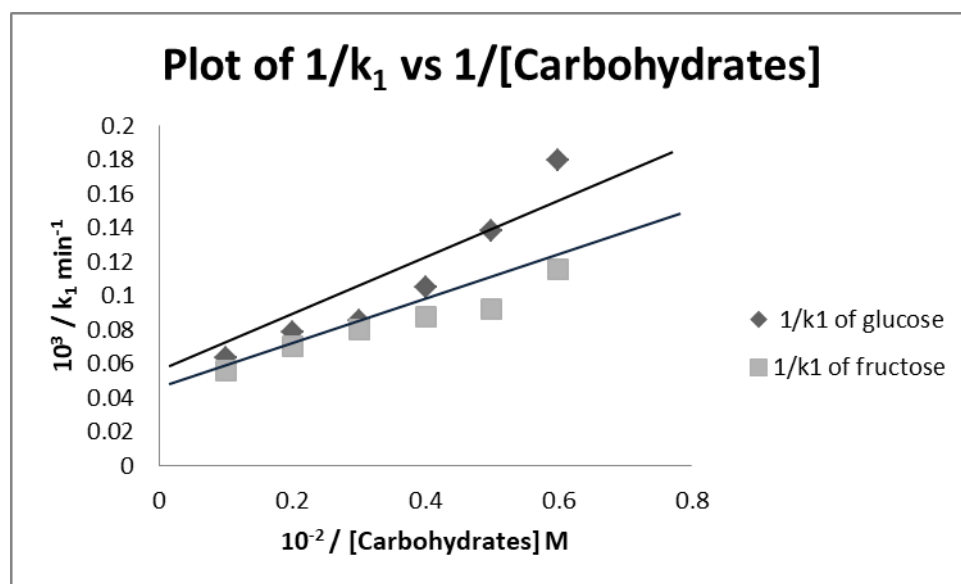


Figure 1 [NBSA] = 2.0×10^{-3} M, [Hg (OAc)₂] = 1.0×10^{-2} M, HOAc – H₂O = 20% (v/v), [CTAB] = 1.0×10^{-2} M
Temp = 60°C

However, there is a slight decrease in the value of the pseudo-first-order rate constant with an increase in the concentration of oxidant (**Table 1**). Such a decrease in rate constant value suggests that N-Bromosaccharin is involved in a pre-equilibrium with some nucleophilic species (probably H₂O) to form some intermediate with lower reactivity. The same deceleration in pseudo-first-order rate constant value was reported in N-bromosaccharin oxidation of Galactose, α -hydroxy acid, Benzyl alcohols & Benzhydrol as mentioned in earlier references.

Table 1 Dependence of rate on the concentration of oxidant

Sr. No.	[NBSA] 10 ³ M	10 ⁻³ k ₁ min ⁻¹ With CTAB	
		[Glucose]	[Fructose]
1.	2.0	7.253	15.57
2.	2.50	6.386	13.12
3.	3.33	5.781	11.52
4.	5.0	3.379	9.95
5.	10.0	1.822	7.51

[Hg(OAc)₂] = 1.0 × 10⁻²M [CTAB] = 1.0 × 10⁻²M HOAc – H₂O = 20% (v/v)
Temp = 60°C [Glucose] = 2.0 × 10⁻²M [Fructose] = 2.0 × 10⁻²M

- Dependence of rate on the concentration of Carbohydrates:

The dependence of the rate on the concentration of Carbohydrates was studied at different initial concentrations of each Carbohydrate and constant concentrations of other reactants in the presence of CTAB. The first-order rate constant increases with an increase in the concentration of Carbohydrates in each case. For each Substrate – NBSA system the plot between k₁ and [Carbohydrate] is initially linear passing through the origin and then bending towards the x-axis at a higher concentration of substrate. The value of (k₂ = k₁/[Carbohydrate]) does not show constancy. The double reciprocal plot between k₁ and [Carbohydrate] is linear with a positive intercept on the y-axis (Figure 1). This confers a shred of kinetic evidence for intermediate complex formation between oxidant and carbohydrate in the pre-equilibrium step.

- Dependence of rate on Surfactant concentration:

The oxidation of each Carbohydrate with N-bromosaccharin was found out in varying initial concentrations of Cetyl Trimethyl Ammonium Bromide (CTAB) cationic surfactant. The rate [surfactant] profile demonstrates that each oxidation, under study, is a micellar-catalyzed bimolecular process (Figure 2).

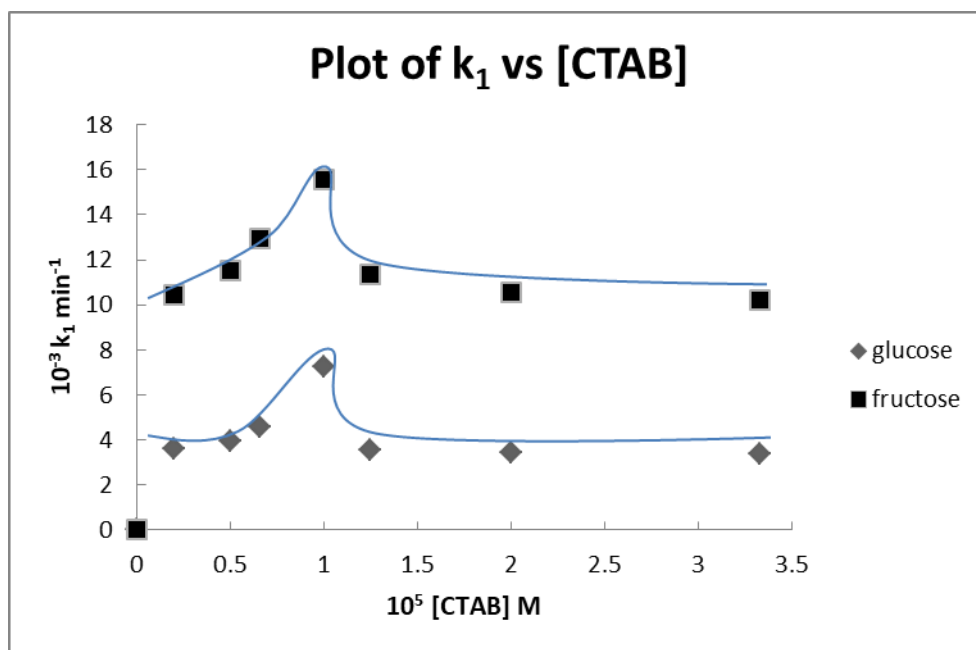


Figure 2 [NBSA] = 2.0 × 10⁻³M, [Carbohydrate] = 2.0 × 10⁻²M, [Hg(OAc)₂] = 1.0 × 10⁻²M, [CTAB] = 1.0 × 10⁻²M, HOAc – H₂O = 20% (v/v) Temp = 60°C

- Dependence of rate on Perchloric acid concentration:

The effect of variation in the concentration of Perchloric acid on the reaction rate was investigated at different initial concentrations of Perchloric acid. With micellar catalyzed reactions, the pseudo-first-order rate constant increases with increasing concentration of acid informing that the reaction under study is acid catalyzed. The plot of log (k₁ – k₂) against log [HClO₄] is linear with a slope value of nearly one confirming the order in Perchloric acid is one. (Figure 3)

- Dependence of rate on Medium:

The effect of variation in the dielectric constant of the medium was investigated with binary mixtures of different compositions of Acetic-Acid and water. The value of the pseudo-first-order rate constant increases

with an increase in the concentration of Acetic acid in the presence of CTAB for both carbohydrates (**Table 2**). The nature of the plot suggests the interaction between dipole and positive ion in the rate-determining step.

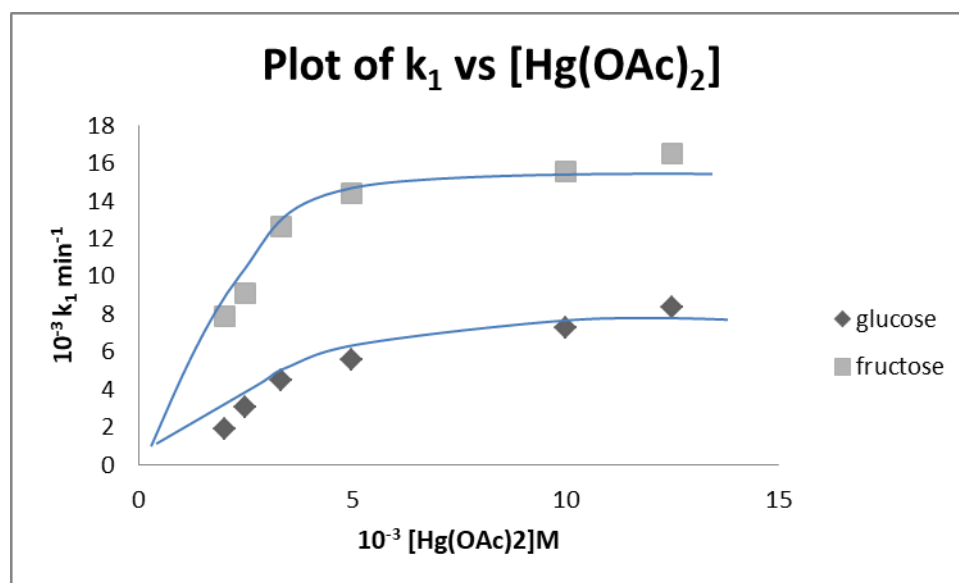


Figure 3 [NBSA] = 2.0×10^{-3} M, [Carbohydrate] = 2.0×10^{-2} M, [Hg(OAc)₂] = 1.0×10^{-2} M, [CTAB] = 1.0×10^{-2} M, HOAc – H₂O = 20% (v/v) Temp = 60°C

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 CTAB	
			[Glucose]	[Fructose]
1.	10	15.50	4.059	12.543
2.	20	17.17	7.253	15.576
3.	30	19.15	9.600	16.032
4.	40	21.98	11.455	17.196
5.	50	25.64	13.310	18.450
6.	60	30.36	14.240	18.850

- Dependence of rate on Mercuric acetate:

The plot of k_1 versus [Mercuric acetate] is obtained linear passing through the origin and then bends towards the x-axis i.e. at a higher concentration range of Mercuric acetate, the pseudo-first-order rate constant remains almost constant (Figure 3). The present investigations were carried out at a concentration of Mercuric acetate which does not affect the oxidation rate. Thus, under the concentration range used Mercuric acetate acts as a trapping agent for Br⁻.

- Dependence of rate on Saccharin:

The effect of addition of Saccharin to the reaction mixture was studied at different concentrations of concentration of Saccharin shows retardation effect (**Table 3**), the retarding effect of Saccharin may be attributed to its involvement in pre-equilibrium hydrolysis of oxidant.

Table 3 Dependence of rate on the concentration of Saccharin

S. No.	[Saccharin] 10 ⁻³ M	10 ⁻³ k ₁ min ⁻¹ With CTAB	
		[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] = 1.0×10^{-2} M [CTAB] = 1.0×10^{-2} M HOAc – H₂O = 20% (v/v)
Temp = 60°C [Glucose] = 2.0×10^{-2} M [Fructose] = 2.0×10^{-2} M

- Dependence of rate on Sodium perchlorate:
Sodium perchlorate has no significant effect on oxidation rate in the presence of CTAB.

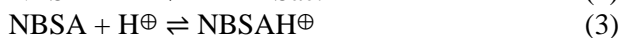
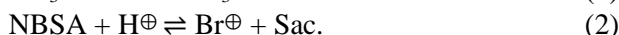
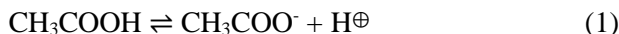
Mechanism

Based on observed kinetic results, Stoichiometry, and product analysis a probable mechanism for oxidation of Glucose and Fructose by N-bromosaccharin in the presence of CTAB has been proposed.

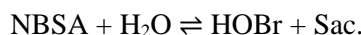
In order to find out the mode of fission during the course of oxidation, the effect of added Acrylonitrilo was investigated. In view of the absence of any effect of radical scavenger, Acrylonitrile, on the reaction rate, it is unlikely that a one-electron reaction giving rise to free radicals is operative in this oxidation.

Nature of oxidant species

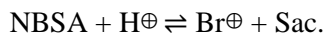
In the aqueous acetic acid medium and in the presence of Perchloric acid, N-bromosaccharin exists as molecular species (NBSA), Hydrolytic product (HOBr), various protonated species, and the Acetyl derivatives according to the following equilibria:



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.



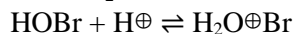
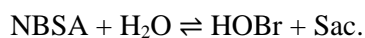
In an aqueous solution, it is difficult to distinguish between Br⁺ and H₂O⁺Br, because they differ only by molecule of Water, but it is well documented that H₂O⁺Br is more effective electrophile than Br⁺.

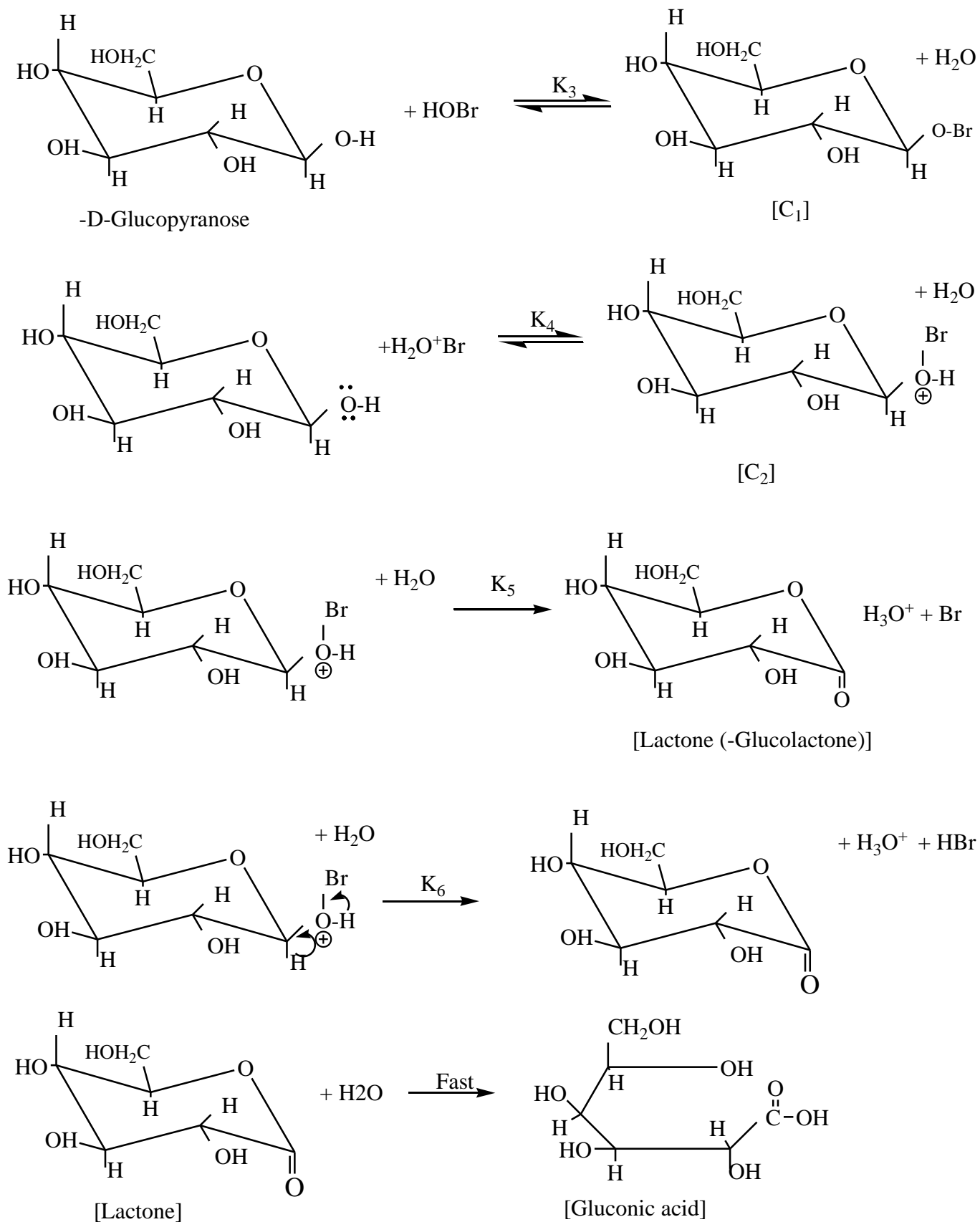
Nature of the substrate

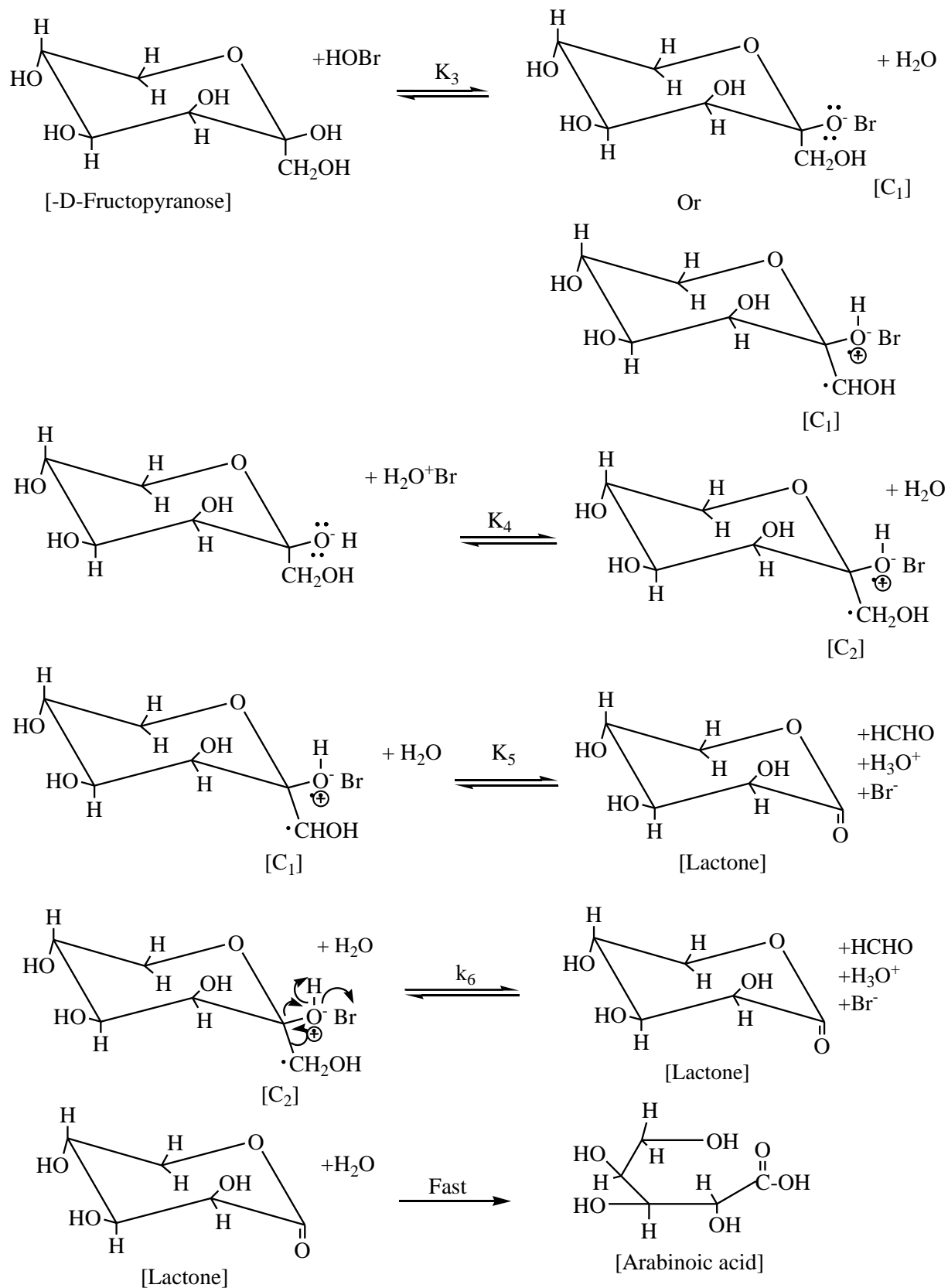
Carbohydrates "D-Glucose and D-fructose" are polyfunctional organic compounds and can exist in both a straight chain and ring form having 5 hydroxyl groups and 1 carbonyl group. Carbohydrates are Nucleophilic in nature. In the present investigation observed acid catalysis suggests protonation of Carbohydrate. If protonated carbohydrate was the active reductant species, the oxidation of Glucose and Fructose would have been faster under similar experimental conditions. The slow oxidation of substrates under similar experimental conditions rules out the protonation of carbohydrates. Hence, the mechanistic step involves interaction between +ve oxidant species and neutral Carbohydrate molecules. Medium effect studies also demonstrate that the slow step is a positive ion-dipole reaction in the present investigation. In the presence of CTAB Michaelis-Menten kinetics in [Carbohydrate] is observed. This demonstrates the formation of Hypobromite ester in pre-equilibrium followed by its decomposition in slow steps. Ahead the rate-determining step incorporates hydride ion transfer as the introduction of the hydroxyl group in Glucose and Fructose enhances the rate of oxidation suggesting the nature of the intermediate.

Based on the above kinetic results, stoichiometry, and product analysis a probable mechanism for the oxidation of glucose and fructose by N-bromosaccharin in the absence of CTAB has been proposed.

Mechanism in the absence of CTAB







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

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

Oxidation of Carbohydrates in the presence of CTAB

Increase in rate for each carbohydrate – NBSA system in the presence of CTAB suggests that the present investigation is biphasic oxidation, i.e. the substrate carbohydrate is partitioned between the micellar and the aqueous phase, and hence the reaction proceeds in both phases. Further micellar catalysis also suggests that electron transfer is more rapid in the micellar phase and this may be due to concentration and environmental effects.

Kinetic results for the oxidation of carbohydrates by NBSA in the absence of CTAB, neutral carbohydrate molecule is an active reactant, and HOBr and $\text{H}_2\text{O}^+\text{Br}$ are active oxidant species. The effective catalysis of oxidation by CTAB can be explained by the electrostatic attraction force between the protonated oxidant species $\text{H}_2\text{O}^+\text{Br}$ and the cationic micelle CTAB bringing both reactants closer.

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

Table 4 Fighting parameters: Piszkiwicz Model [26]

Surfactant	Carbohydrates	N	$\log [D]_{50}$	$10^3 K_D$
CTAB	Glucose	1.66	0.602	1.0
	Fructose	1.16	0.862	1.0

A value of “n” greater than unity implies positive co-operativity i.e. the binding of the first molecule of the substrate to the surfactant molecule makes it easier for subsequent molecules to bind. A value less than unity would indicate negative co-operativity i.e. the first molecule bound makes it more difficult for the next one to bind.

The significance of thermodynamic parameters gives additional support to propose the mechanism. The value of E_a for Glucose decreases and for Fructose increases in the presence of CTAB. The value of ΔH^* , ΔS^* , and ΔG^* are in favor of a bimolecular mechanism.

Conclusion

As a result of the findings as well as previous literature suggestions, it was concluded that among the numerous active species, HOBr is considered to be an active oxidant based on the findings of the kinetic investigation. As a result of the findings, it was concluded that CTAB is a useful cationic micelle for the oxidation reaction of carbohydrates. Acids are used to catalyze oxidation, which can proceed in both acid-dependent and acid-independent ways.

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