Study Of Micellar Catalysed Oxidation of Saccharides By N-Bromosuccinimide

Gorelal Vishwakarma[1] and K.N. Sharma[2]
[1]*Department of Chemistry, A.P.S. University, Rewa (M.P.) India.*
[2]*Department of Chemistry, Govt. Girls P.G. College, Rewa (M.P.) India.*

***Abstract*—Micellar catalyzed oxidation of certain monosaccharides in aqueous acetic acid medium were discussed with an emphasis of correlation of structure and reactivity. The reaction obeyed first-order kinetics in [NBS], and less than unit order in [H^+]. The reaction was observed to proceed through formation of 1:1 intermediate complex between HOBr, and H_2O^+ Br reacting species of oxidant, and substrate. The reaction is initially catalyzed by micellar CTAB at optimum concentration. Two mechanisms-one pathway is independent [H^+], and the other on dependent [H^+], with involvement of water molecule in slow step are discussed. The derived rate law was verified graphically in consistent with the experimental results.**

***Index Terms*—L-arabinose, D-glucose, N-Bromo succinimide, Micellar, oxidation.**

I. INTRODUCTION

Most of the monosaccharides (L-arabinose, and D-glucose) possesses five or six- carbon chains in their structures regarded as pentose and hexose. The mono saccharides biologically important compounds are quite often used as with basic need of life in food, and paper industries in addition to textile, and pharmaceuticals. They are distinguished by their stereochemistry (i.e., the relative orientation of OH groups, attached to C-atoms). Their complex mechanisms of reactions are tremendously difficult in understanding, However, presence of -CHO, -CH_2OH groups etc. are smoothly oxidized to -COOH group and aldehyde involving C-C fission by transfer of electrons to the oxidant exhibiting two types mechanism- heterolytic and homolytic oxidation under suitable conditions. Many protocols regarding review of literature available indicate that kinetics of oxidation of mono saccharides have been investigated widely with a variety of occupants [1-7] in various media.

The micellar are surfactant enzyme catalysts used in various biochemical, and industrial processes, and also in research, soap, and detergents, food, and pharmaceuticals. They own midway activity between homogeneous, and heterogeneous catalysts and very effective when used under CMC. One such cationic cetyltrimethylammonium bromide (CTAB) micellar as catalyst was used recently in exploring the oxidation kinetics of several organic compounds with different oxidizing agents. [8-11] No-Bromo succinimide (NBS) is a potent halo versatile oxidant [12]. It is generally accepted in polar solvent / acid media yielding HOBr, and H_2O^+Br attacking species. There seems to be a few reports on the oxidation aspects of NBS. [13-16] published in recent past. However, such studies of mechanism of mono saccharides with NBS appeared to be scanty, and has not yet been established. But little attention has been paid so far to explore activity of micellar (CTAB) as catalyst in NBS oxidation. This fact prompted us to undertake the present investigation which constitute the kinetic study of micellar CTAB catalysed oxidation of L-arabinose, and D-glucose by NBS in aqueous acetic acid media.

II. EXPERIMENTAL (MATERIALS)

Analytical reagent grade or high purity chemicals were used mostly. NBS was synthesized and its solution was prepared in acetic acid (CDH), and standardized by literature method [17]. L-arabinose and D-glucose (A.R., BDH) were used after their dissolution in double distilled water. The aqueous solution of micellar CTAB (Sigma Aldrich) was used after purification.

KINETICS STUDIES

The reactions were initiated (in a thermostat ± 0.1^0 C) by mixing-by-mixing requisite amount of NBS to other reagents substrate solvent & H^+ of the reaction vessel equilibrated separately at 45^0 C. The progress of the micellar catalyzed NBS-saccharide reaction was monitored by measuring values of unconsumed NBS iodometrically a given instant of time, using starch as indicator. The k_{obs} values are reproducible with a precession of ± 3% error.

STOICHIOMETRY AND PRODUCT ANALYSIS

The ascertain stoichiometry of the NBS- aldose reaction [NBS] was taken in slightly excess over [substrate] along with other reagents (in varying ratio) and reaction was allowed to proceed at 45^0C for 36 h. till the reaction is completed. The estimation of residual NBS in different sets showed the stoichiometry of the reaction is consistent with 1:1 ratio as shown in equation (1).

$$\underset{\text{(NBS)}}{RCHO + C_4H_4O_2NBr + H_2O} \rightleftharpoons \underset{\text{(aldonic acid)}}{RCOOH} + \underset{\text{(Succinimide)}}{C_4H_4O_2NH} \quad \ldots\ldots\ldots (1)$$

where, R= $C_4H_9O_4$ for L-arainose and $C_4H_{11}O_5$ for D-glucose respectively. The oxidation products arabinoic acid and gluconic acid were identified by conventional techniques. In this reaction, NBS and aldose act as a two-electron oxidant and a two-electron reductant respectively.

Polymerization of olefinic monomer (acrylonitrile) to the reaction mixture was not observed even under derived temperature, and inert atmosphere. This rules out the free radicals [18] intermediates formation during the oxidation.

III. RESULTS AND DISCUSSION

Under pseudo-first-order conditions with at least [NBS] > [substrate], the individual initial rates were found ∝ to [NBS], and the linear curves passed through the origin for individual kinetic runs with almost unit slope confirming the first-order dependence of the reaction on NBS in the slow phase. Reversible formation of activated intermediates-(aldose-micellar CTAB, HOBr / H_2O^+Br adducts) can be explained in terms of the different architecture of the reactive intermediates involved in the oxidation have been observed in the reaction of aldoses with NBS & catalyst CTAB. Conversely, there is no report of detection of complex with reacting species. The variation of k_{obs} with [substrate] at 45^0 C is shown in Table. 1. The plots of $\frac{1}{k_{obs}}$ $vs.\frac{1}{[aldose]}$ are linear using least square program as shown in Fig. 1. The plots of above figure displayed saturation kinetics also referred to as Michaelis-Menten kinetics. These plots have an intercept and slope values were found less than unity with co-relation coefficient (R^2 =0.999).

The reaction rate increased with increasing [H^+] at constant experimental conditions, the acid dependent rate constants in each case was also characterized by Zucker-Hammett linear plot (ln k_{obs} vs. lg [H^+]) with characteristic fractional values showing 1 to 0 order with respect to H^+.

Table 1: Dependence of k_{obs} on the initial concentration of aldoses

10^3 × [NBS] = 5.00 (a, b) (mol dm^{-3}); [H^+] = 0.025 (a), 0.050 (b) (mol dm^{-3}),

10^3 × [CTAB] = 1.50 (a), 3.33 (b) (mol dm^{-3}); CH_3COOH-H_2O = 25:75 % (v/v),

T = 45^0 C

10^2× [monosaccharide]	10^4 k (s^{-1})	
	L-arabinose(a)	D-glucose(b)
0.80	1.97	-
1.00	2.41	1.68
1.50	3.16	-
1.66	-	2.49
2.00	4.11	2.92
2.50	-	3.45
3.33	4.96	3.95
4.00	5.25	4.14
5.00	5.52	4.50
6.25	5.33	4.63

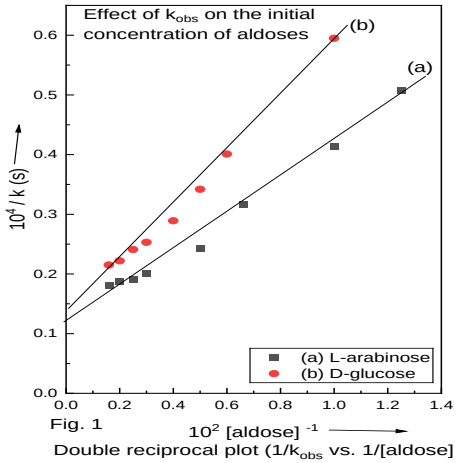


Fig. 1

Double reciprocal plot ($1/k_{obs}$ vs. 1/[aldose]

This plot has its own significance in arriving at the role of water molecule participation in the mechanism. Kinetics is followed in glacial acetic acid and water solvent composition, in which ratio of water to acetic acid is varied (10% -40% (v/v). it is observed that decrease in dielectric constant of the medium causes enhancement in the rate constants. The plot $\lg k_{obs}$ vs $\frac{1}{D}$ is linear with positive slope, correlated the rate with relative permittivity of the solvent correlated this shows that the reaction is appositive ion-dipolar type. However, the effect of solvent on the oxidation, by Exner's criterion correlation is somewhat found satisfactory.[19] This shows that reaction is positive ion dipolar type. Initially the catalytic oxidation rate increases due to aggregation of micellar (CTAB) with substrate forming active entities and finally showed fraction-order kinetics at its optimum concentration (Table 2). The other influencing factors behind above reasons most probably may be Beregin's model related to hydrophobicity counter ion inhibition and repulsive force between charged [20] surfactant head groups.

Table 2: Dependence of reaction dynamics (k_{obs}) on the [micellar, CTAB]. at 45^0C

10^2 × [mono saccharide] = 1.00 (a), 2.0 (b) (mol dm^{-3});

10^3 × [NBS] = 5.00 (a, b) (mol dm^{-3}); [H^+] = 0.025 (a), 0.050 (b) (mol dm^{-3});

CH_3COOH-H_2O = 25:75 % (v/v),

T = 45^0 C (a, b)

10^3 ×[micellar] (Mol dm^{-3})	10^4 k (s^{-1})	
	L-arabinose(a)	D-glucose(b)
0.80	1.35	-
1.00	1.59	1.17
1.25	-	1.42
1.50	2.41	1.60
2.00	3.19	1.99
2.50	3.57	2.49
3.33	4.68	2.92
4.00	4.89	3.54
5.00	5.07	4.07

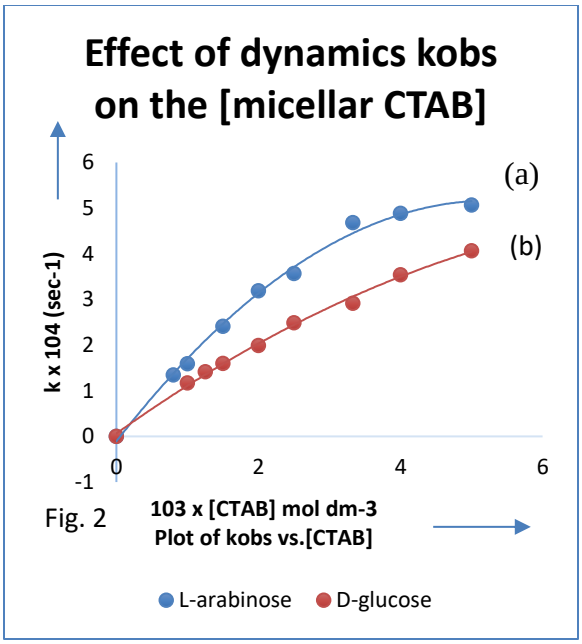


Fig. 2

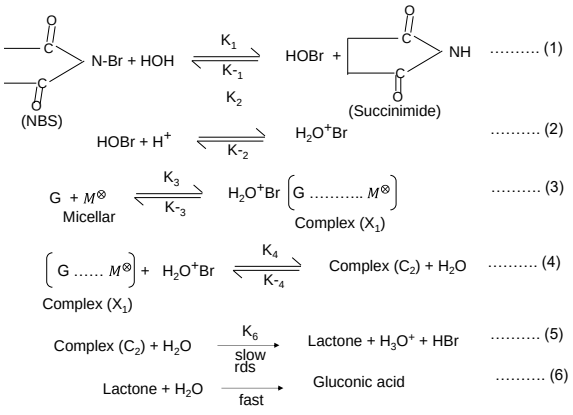
The successive addition of reductant product succinimide slightly retards the oxidation rate whereas the effect of neutral salt and variation in ionic strength is found negligible.

IV. MECHANISM

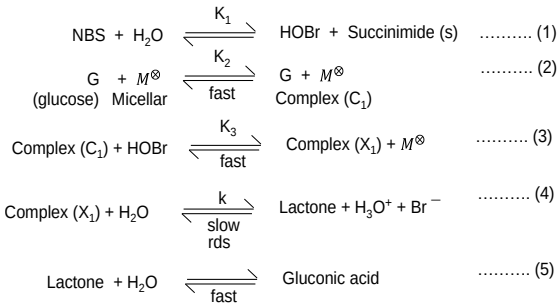
Based on the kinetic evidence as detailed above, the two schemes of appropriate reaction mechanism might be proposed in the following ways:

Scheme-1

(Acid dependent paths)



Scheme-2
(Acid independent path)



The rate was deduced as:

$$k = \frac{k\,K_1K_2K_3[G][M^{\otimes}][H_2O]}{[S] + K_1 + K_1K_2K_3[G][M^{\otimes}]} \quad \ldots.(6)$$

The rate law is therefore be written as:

$$k_{obs} = \frac{k\,K_1K_2K_3\,[G]\,[M^{\otimes}]}{[S] + K_1 + K_1K_2K_3[G][M^{\otimes}]} + \frac{K_2K_3K_4K_6\,[G][M^{\otimes}][H^+]}{K_{-2}K_{-3}K_{-4} + K_{-2}K_{-3}K_{-6} + K_3K_4K_6\,[G][M^{\otimes}]} \quad \ldots(7)$$

The first term is for acid independent path at and second term is for acid dependent path. The equation (7) explains both the rate law for first-order. kinetics in [NBS], and fractional order to substrates and micelles. The double reciprocal lots of $\frac{1}{k_{obs}}$ vs $\frac{1}{[aldehyde]}$ with non-zero intercept on ordinate axis which explains all data. The two monosaccharides studied reveal the order of reactivity as:

L-arabinose> D-glucose.

The above reactivity order correlates with chain length i.e., pentose is oxidized at a faster rate as compared to hexose. i.e., with increase in chain length reaction rate decreases. The percentage composition of -CHO form has lowest in D-glucose (0.022) structure rather than L-arabinose (0.22), highest, that is why, the rate of oxidation. The reason may be that L-arabinose is oxidized through the pyranose structure. The kinetic results suggest that interaction of H_2O^+Br, the cationic oxidant and HOBr with neutral molecule of substrate in rate limiting step is supported by dielectric constant of the medium. The micellar CTAB catalyzed the reactions follow AC-2 path and participation of water molecule as proton abstracting agent. The pyranose structure is favored thermodynamically. The reactions under investigation also observe E^a is lowest for fastest reaction (Table 3.). The approximate constant $\Delta G^{\neq}$ values, suggesting that the reactions essentially follow the similar mechanism. The large negative of $\Delta S^{\neq}$ for the reactions is due to compactness of transition state as compared to ground state, causing a restriction on the freedom consequently loss of entropy was observed in the investigation reaction. Overall reactions are governed by enthalpy controlled.

Table 3: Activation parameter for the micellar catalyzed oxidation of monosaccharides by N-bromo succinimide in aq. acetic acid

Substrate	E^a kJ mol^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	$-\Delta S^{\#}$ JK^{-1} mol^{-1}	$\Delta G^{\#}$ kJ mol^{-1}
L-arabinose	36.38	36.42	162.05	88.37
d-glucose	43.86	39.35	156.98	89.66

Temperature range 40^0 – 55^0C. The entropies of activation are referred to the 1 M. standard state.

V. CONCLUSION

The oxidation of L-arabinose and D-glucose by N-Bromo succinimide (NBS) in aqueous acetic acid catalyzed by an excellent micellar cetyltrimethylammonium bromide (CTAB) was carried out under the kinetic conditions [aldose] >> [NBS], The overall process revealed first-order dependence on [NBS], and fraction-order kinetics trio each with aldose, H^+, and micellar (CTAB). Experimental evidence for occurrence of free radicals has been lacking. Employing HOBr, and H_2O^+Br active species of oxidant, two mechanistic pathways were explained as one acid dependent, and other acid independent paths. The catalysed reaction forms an intermediate complex (1:1) at transition state that disproportionate in rds to yields main products of oxidation as corresponding arabinoic acid and gluconic acid, characterised by modern existing methods. It can be concluded that the reaction is dominated by influence of pentose structure, steric effect, percentage composition of aldehydic group in addition to lengthening of carbon chains and kinetic parameters.

The order of reaction is observed as L-arabinose > D-glucose. The study indicates that enthalpy rather than entropy parameters controls the reaction rate. The

CTAB catalysed reactions follow AC-2 path and participation of water molecule as proton abstracting agent.

The negative values of $\Delta S^{\#}$ shows the presence of symmetrical transition state reducing translational, and rotational freedom that supports the deduced rate law is well in conformity with thermodynamic parameters.

REFERENCES

[1] Fadnis, A.G. and Shrivastava, S.K.: Ann. Quim. Serb., 1986, 82 (1), 5.
[2] Sachdev, Neerja, Singh, Ajay Kumar, Shrivastava, Alka, Katre, Yokraj, Aslam Aftab, and Khan, Parwaz, : Arab. J. Chem., 2014, 1380.
[3] Babu, K. Satish, Rajanna, K.C., Reddy J., Narender, Reddy K., Rajender Rao, Rajeshwar, Y.: Chemical Data Collection. Elsevier B.V., 2019, 100, 332.
[4] Rajput, Surendra Kumar, Sharma, Aarti, Chandraker, and Priyamvada: Ind. Chem. Soc., 2007, 84(8): 777-780.
[5] Shukla, P.C., Tiwari, P.S., Sharma, K. and Sharma, V.K.: Ind. Cou. Chem., 1988, p. 1.
[6] Tomar, Ashish, and Kumar, Arun: J. Indian Chem. Soc., 2007, 84, 1162-1165.
[7] Dwivedi, Surabhi, and Gupta, H.D.: Int. J. Sci. Dev. & Res., 2023, 8(2), 870-874.
[8] Pati, S., Katre, Y.R., and Singh A.K.: J. Surfactant and Detergents, 2007, 10(3), 175-184.
[9] Singh, Neelam, Sharma, K.N., Khan M.U., and Singh, Santosh K.: J. Green and Herbal Chemistry, 2021, Sec. A, 14(4): 344-349.
[10] Agnihotri, Mamta, Khan, M.U., and Tiwari, Saras: Elec. J. Adv. Res. 2020, 6(2), 1-9.
[11] Manna, Kausik,and Panda, Amiya Kumar : J. Surfact. Deterg. 2011, 14, 563-576.
[12] Shukla, Dheerendra Kumar, and Vishwakarma, Umesh : Int. J. Sci. Dev. & Res. 2023, 8(7) :876-880.
[13] Taylor, K. G., and Clark. M.S.: J. Org. Chem., 1976, 41 114.
[14] Langbein, G., and Steinert, B. : Ber., 1962, 95, 1873.
[15] Hiran, B.L; Malkani, R.K., and Rathore, N.: Kinetics and Catalysis, 2005, 26(3), 334-339.
[16] Khan, Nusrat Baby, Khan, Khushboo, and Dwivedi, H.P.: Int. J. Adv. Res. Chem. Sci., 2018, 596, 1-6.
[17] Shrivastava, Seilla, and Gupta, Vandana: J. Indian Chem. Soc., 2006, 83, 1103-1106.
[18] Shlji Kaji, Gaeshi *et al.*: Bull Chem. Soc., Japan, 1985, 58 (2 B): 769-770.
[19] Exner, O.: Collect. Chem. Czech. Commun., 1966, 31, 3222.
[20] Swain C.G., Swain. M.S., Powel. A.L. and Alunni, S.: J. Am. Chem. Soc., 1983, 105, 502.
[21] Bakshi, M.S., and Kaur, U: J. Macro mol Sci., 1999, 36 A: 697-718.