

Kinetics and Mechanism of oxidation of Maltose By N-Bromonicotinamide (NBN)

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ABSTRACT

Kinetics study of oxidation of maltose, by aqueous alkaline solution of N-Bromonicotinamide (NBN) has been carried out in the temperature range 308-323K. The reaction exhibits first order in [KOH] and [Maltose] and zero order about oxidant. Addition of nicotinamide (NA) has no effect. Increase in ionic strength of the medium does not change the rate. Effect of temperature on the rate of oxidation has been followed to show the validity of Arrhenius equation and various activation parameters have been computed. The stoichiometry of the reaction was found to be 1:1. 1,2-enediol is found to be the reactive intermediate. Maltobionic acid is the product of oxidation.

Keywords: Maltose, N-Bromonicotinamide, oxidation, mechanism.

Introduction

Carbohydrates are biologically important substrates. The oxidation of sugars, especially the mono and disaccharides has been the subject of extensive research. Their oxidation can provide new compounds and materials with interesting physicochemical properties. Sugar oxidation occurs under different conditions of pH, temperature and ionic strength giving products that depend on the oxidants used. The kinetics and mechanism of oxidation of monosaccharides and disaccharides have been studied in both acidic and alkaline media, employing different transition metal ions, inorganic acids, complex ions and hydrogen peroxide as oxidants. The results showed that the mechanism may depend on the nature of the substrates, in some cases it involves the formation of

intermediate complex, free radical or transition states. Sheila Srivastava¹ followed the oxidation of dextrose and maltose by acidic solution of sodium periodate catalysed by rhodium(III). Ashok Kumar Singh² investigated the kinetics and mechanism of oxidation of xylose and maltose by potassium iodate in aqueous alkaline medium. Fahim Uddin³ reported the kinetics of maltose and lactose by alkaline iodine solution. Ashok Kumar Singh⁴ investigated the kinetics and mechanism of oxidation of maltose by aqueous alkaline solution of periodate. H. K. Okoro⁵ and E. O. Odebunmi reported the kinetics and mechanism of oxidation of sugar and sugar alcohols by potassium permanganate. E.O. Odebunmi and S.O. Owolude⁶ investigated the kinetics and mechanism of oxidation of some simple reducing sugars by permanganate ion in alkaline medium. Ashok Kumar Singh⁷ followed mechanistic studies of oxidation of maltose and lactose by $[H_2OBr]^+$ in presence of chloro-complex of Rh(III) as homogeneous catalyst. E.O. Odebunmi⁸ followed the kinetics of oxidation of fructose, sucrose and maltose by potassium permanganate in $NaHCO_3/NaOH$ buffer and iridium(IV) complex in sodium acetate/acetic acid buffer. Kinetics and mechanism of the oxidation of disaccharides by Cr(VI) was reported by Viviana Roldán.⁹ N-halo reagents like N-halo derivatives of amines, amides, imides, urea, saccharins, sulfonamides, sulfonimides are widely used in organic synthesis for their potential to promote important reactions such as halogenation, oxidation, and protection as well as formation of C-X, C-O, and C=O bonds. They play a key role in the chemistry of natural compounds¹⁰. Scant reports are available for oxidation of sugars by haloamides. NBN is chosen for the reasons, its easy method of synthesis, handling, rate of oxidation, shelf life and versatility. Our earlier study on the oxidation of amino acids had focused attention on the kinetic aspects of oxidation by NBN¹¹ in aqueous acetic acid medium. In our continuing efforts to exploit NBN as oxidant, the present study investigates the kinetics of oxidation of maltose in aqueous alkaline medium.

Materials and methods

N-Bromonicotinamide (NBN) was prepared by the reported method¹². Standard solution of NBN (m.p. 210°C) was prepared afresh in water and its purity was checked iodometrically. The standard solution of maltose (Aldrich) was always prepared afresh in

double distilled water. The other chemicals used were potassium hydroxide, sodium perchlorate, mercuric acetate etc. All chemicals used were of A.R. grade. Mercuric acetate was added to suppress the formation of free bromine which otherwise would have vitiated the results. Mercuric acetate did not interfere with the results¹³. Ionic strength of the medium was kept at 0.1 mol dm^{-3} by employing concentrated aqueous solution of sodium perchlorate (Merck).

Kinetic measurements

The solution of maltose and oxidant were kept in black coated bottles separately. These solutions were kept in the thermostat to attain the thermostatic temperature. The appropriate quantity of oxidant was added to the substrate containing other reagents and the reaction bottle was shaken well. The reaction was followed potentiometrically by setting up a cell made up of the reaction mixture into which the platinum electrode and reference electrode(SCE) were dipped. The e.m.f of the cell was measured periodically using a Equip-Tronics (EQ-DGD) potentiometer. Different studies such as variation of maltose, oxidant (NBN), potassium hydroxide, sodium perchlorate, nicotinamide and temperature were carried out. The reaction was carried out under pseudo-first order condition ($[\text{maltose}] \gg [\text{NBN}]$). The pseudo-first order rate constants computed from the linear ($r^2 > 0.9990$) plots of $\log (E_t - E_\infty)$ against time. Duplicate kinetic runs showed that the rate constants were reproducible within $\pm 3\%$. The course of the reaction was studied for more than two half-lives.

Stoichiometry

N-Bromonicotinamide was taken in large excess as compared to maltose in different ratios. Reaction mixture containing maltose, potassium hydroxide and N-bromonicotinamide (in excess) were equilibrated for 42 hours at room temperature($\sim 30^\circ\text{C}$). After the reaction was complete, the excess of NBN was determined iodometrically and indicated 1:1 stoichiometry. The overall stoichiometry of the oxidation reaction may be represented as



Product Analysis

In a typical experiment, a mixture of freshly prepared maltose (1 mol dm^{-3}) and NBN (1.5g , 0.2 mol dm^{-3}) was made up to 50 ml with water. The mixture was allowed to stand for 12 hours in the dark to ensure completion of the reaction. The product of oxidation was maltobionic acid. Nicotinamide was the by-product. The product was identified by spot test analysis¹⁴. The product was also identified by the following method. A little of the product was added to 1 ml of 5% sodium bicarbonate solution. Evolution of carbon dioxide with effervescence indicated the presence of acidic group in the compound. Evidence for the formation of an enediol is furnished by observed ability of alkaline solution of carbohydrates to decolorize solution of $2,6\text{-dichlorophenolindophenol}$.

Results

The kinetic results for the oxidation of maltose by N-Bromonicotinamide (NBN) can be summarized as follows. The kinetic studies were carried out under pseudo-first order conditions with $[\text{maltose}] \gg [\text{NBN}]$.

Effect of varying [oxidant]

The constancy of pseudo-first order rate constant at different $[\text{NBN}]$ at constant $[\text{maltose}]$ indicates the reaction exhibits zero order about the oxidant (Table 1).

Table 1- Effect of variation of [NBN] on reaction rate

$[\text{substrate}] = 0.02 \text{ mol dm}^{-3}$ $[\text{KOH}] = 0.06 \text{ mol dm}^{-3}$,
 $[\text{NaClO}_4] = 0.1 \text{ mol dm}^{-3}$, $\text{Hg}(\text{CH}_3\text{COO})_2 = 0.005 \text{ mol dm}^{-3}$, $\text{Temp.} = 308 \text{ K}$

[NBN] 10³ moldm⁻³	k_{obs} 10⁷ sec⁻¹
0.5	7.83
1.0	7.85
1.5	7.86
2.0	7.87
2.5	7.86

Effect of varying [maltose]

At constant [OH⁻], [NBN], the plot of log(E_t - E_∞) (where E_t is the e.m.f. of the cell at time t and E_∞, the corresponding value at the completion of the reaction) Vs time is linear, indicating a first order dependence of rate on [maltose]. The rate constant increases in direct proportionality with the increase in the concentration of maltose, proving the reaction is of first order in [maltose]. (Table 2).

Table 2- Effect of variation of [Substrate] on reaction rate

[NBN]=0.001 mol dm⁻³ [NaOH]=0.06 mol dm⁻³,
 [NaClO₄]=0.1mol dm⁻³, Hg(CH₃COO)₂=0.005 mol dm⁻³, Temp. =308K

[Sub] 10² moldm⁻³	k_{obs} 10⁷ sec⁻¹
2.0	7.86
2.5	8.32
3.0	8.68
3.5	9.04
4.0	9.41

Effect of varying $[\text{OH}^-]$

A scrutiny of table 3 shows that the rate increases proportionally with the increase in $[\text{KOH}]$. The plot of $\log k_{\text{obs}}$ versus $\log [\text{OH}^-]$ was linear with a unit slope indicating first order dependence on [potassium hydroxide] (Table 3).

Table 3- Effect of variation of $[\text{OH}^-]$ on reaction rate

$[\text{NBN}] = 0.001 \text{ mol dm}^{-3}$ [substrate] = 0.02 mol dm^{-3} ,
 $[\text{NaClO}_4] = 0.1 \text{ mol dm}^{-3}$, $\text{Hg}(\text{CH}_3\text{COO})_2 = 0.005 \text{ mol dm}^{-3}$, Temp. = 308 K

$[\text{NaOH}]$ 10^2 mol dm^{-3}	$k_{\text{obs}} 10^7 \text{ sec}^{-1}$
6	7.86
8	8.53
10	9.13
12	9.65
15	10.29

Effect of addition of nicotinamide

The effect of one of the product of the reaction has been studied by adding various concentrations of nicotinamide, keeping concentration of maltose, NBN constant. There is no significant change in the rate of reaction.

Effect of ionic strength

The effect of ionic strength was studied by carrying out investigations in the presence of different amounts of sodium perchlorate. No appreciable salt effect was detected.

Effect of added salts

Added salts like BaCl_2 , KCl , Na_2SO_4 and K_2SO_4 do not have any effect on the rate.

Test for free radicals

The possibility of free radical intervention in the NBN oxidation reaction was tested by the following procedure. The reaction mixture containing acrylonitrile scavenger was kept for 24hours in an inert atmosphere and then diluted. On dilution, formation of precipitate was not observed indicating the absence of free radical intervention in the reaction.

Effect of temperature

Increase in temperature increases the rate of oxidation and plot of $\log k_{\text{obs}}$ Vs reciprocal of temperature is linear. The oxidation of maltose by NBN was studied at different temperatures (308to 323K) (Table 4) and the activation parameters were evaluated (Table 5) .

Table 4-Effect of Temperature on reaction rate

[substrate]=0.02 mol dm⁻³ [KOH]=0.06 mol dm⁻³,
 [NBN]=0.001 mol dm⁻³ [NaClO₄]=0.1mol dm⁻³,
 Hg(CH₃COO)₂=0.005 mol dm⁻³

Temperature K	k_{obs} 10⁷ sec⁻¹
308	7.84
313	10.30
318	13.24
323	16.95

Discussion

The possible oxidizing species in alkaline medium are NBNBr, Br₂ and HOBr. The observed zero order dependence of the reaction rate on NBN rules out NBNBr and molecular bromine as the reactive oxidizing species. Addition of nicotinamide having no effect on the rate indicates that HOBr may not be the oxidizing species. H₂OBr may be discarded because of negligible effect of addition of nicotinamide on reaction rate. A careful study of the kinetics of oxidation of maltose shows that the rate expression is of the

Substrate	E _a kJmol ⁻¹	ΔH [#] kJmol ⁻¹	ΔS [#] J K ⁻¹ mol ⁻¹	ΔG [#] kJmol ⁻¹
Maltose	20.96	18.40	- 174.4	72.12

form

$$-\frac{d[NBN]}{dT} = k [\text{maltose}] [\text{OH}^-]$$

which implies that the rate of reaction is independent of the concentration of [NBN], while the reaction is of first order both with respect to maltose as well as alkali. In cases where the concentration of maltose as well as alkali is large as compared to the concentration of [NBN], the rate expression becomes

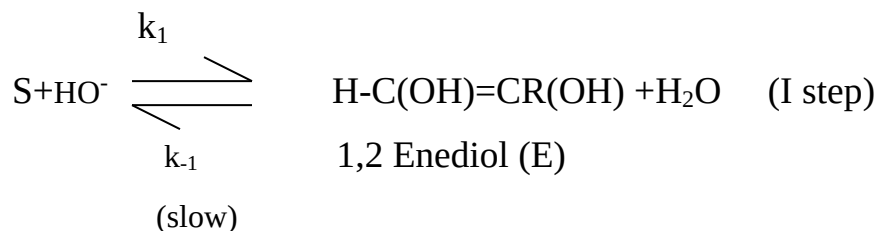
$$\frac{d[NBN]}{dT} = k_s = \Delta\chi/\Delta t$$

where

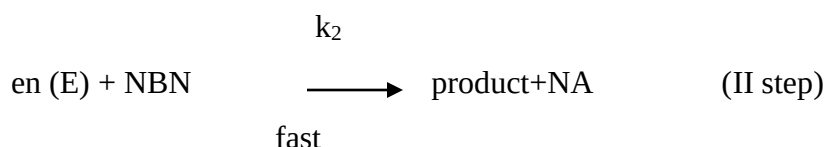
$$k_s = k[\text{maltose}][\text{OH}^-]$$

Mechanism

On the basis of the above experimental results, it appears that the first slow step involves a reaction between hydroxide ion and maltose, leading to the formation of an intermediate reactive form:



where S represents the sugar. The fact that this step is slow explains how the order of the reaction is unity with respect to reducing sugar. Further, this intermediate reactive form, which is called, 1,2 enediol, is subsequently oxidized by NBN to form nicotinamide and maltobionic acid.



{Product- maltobionic acid}

where “ en “ represents 1,2 enediol. The fact that the second step is fast explains the zero order of the reaction with respect to [NBN].

It may be pointed out that in the present study, oxidation by bromine was completely suppressed as the oxidative studies were carried out in presence of mercuric acetate which combines with bromide ions formed in the reaction¹³. Thus kinetics of only NBN oxidation was followed. The involvement of substrate molecule in the rate-determining step leads to different values of k_{obs} for different initial concentrations of maltose.

Conclusions

At the end of this research work, it is inferred that the reaction rates are enhanced by increase in [substrate], [alkali] and temperature. Added nicotinamide has no effect on the rate. 1,2-Enediol form of sugar is the reactive intermediate leading to products. Maltobionic acid is the product of oxidation. Suitable mechanism in compliance with experimental observations was proposed and the rate law was derived. NBN can be used as a better oxidant for the facile oxidation in the grounds of its easy method of synthesis, handling, rate of oxidation, shelf life and versatility.

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