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Mechanistic aspects of oxidation of dextrose by *N*-bromophthalimide in acidic medium: a micellar kinetic study

Minu Singh

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Abstract Kinetic investigations of oxidation of dextrose by *N*-bromophthalimide (NBP) in acidic medium in the presence of mercuric(II) acetate as a scavenger have been studied. In both the absence and presence of surfactants, the oxidation kinetics of dextrose by NBP shows a first-order dependence on NBP, fractional order on dextrose, and negative fractional order dependence on sulfuric acid. The determined stoichiometric ratio was 1:1 (dextrose:NBP). The variation of $Hg(OAC)_2$ and phthalimide (reaction product) have an insignificant effect on reaction rate. Effects of surfactants, added acrylonitrile, added salts, and solvent composition variation have been studied. Activation parameters for the reaction have been evaluated from Arrhenius plot by studying the reaction at different temperature. The rate law has been derived on the basis of obtained data. A plausible mechanism has been proposed from the results of kinetic studies, reaction stoichiometry and product analysis. The role of anionic and non-ionic micelle was best explained by the Berezin's model.

Keywords Kinetics · Oxidation · Dextrose · *N*-Bromophthalimide · Micellar kinetics

Introduction

The application of N-halo compounds in the field of organic synthesis is very extensive, such as oxidation reactions, deprotection and protection of different functional groups, halogenations of saturated and unsaturated compounds, acylation of alcohols, phenols, amines or thiols, epoxidation of alkenes, aziridination etc.

M. Singh (✉)
Department of Chemistry, Kalyan Post Graduate College, Bhilai Nagar, Durg 490006, Chhattisgarh, India
e-mail: minu_0511@yahoo.co.in

[1–3]. The diverse nature of the chemistry of these compounds is due to their ability to act as sources of halonium cations, hypohalite species and nitrogen anions, which act both as bases and nucleophiles [4].

Carbohydrates make up most of the organic matter on Earth because of their extensive roles in all forms of life. First, carbohydrates serve as energy stores, fuels, and metabolic intermediates. Second, ribose and deoxyribose sugars form part of the structural framework of RNA and DNA. Third, polysaccharides are structural elements in the cell walls of bacteria and plants. In fact, cellulose, the main constituent of plant cell walls, is one of the most abundant organic compounds in the biosphere. Fourth, carbohydrates are linked to many proteins and lipids, where they play key roles in mediating interactions among cells and interactions between cells and other elements in the cellular environment. Monosaccharides are the major source of fuel for metabolism, being used both as an energy source (glucose being the most important in nature) and in biosynthesis.

This study will enable to understand the complicated biological reaction in living systems and will also help to understand the catalytic activity of surfactants along with oxidative capacity of NBP in acidic medium. Kinetic studies of oxidation of different types of organic substrate by NBP have also been investigated by different workers [5–17] to explore the effect of the substituent on the redox activity of NBP. In the search for more environmental friendly processes, the use of self-assembled surfactant structures opens up a whole range of new possibilities. This organized media, such as vesicles or micelles can enhance/decrease the reaction rate and selectivity [18]. The unique ability of micelles to solubilize organic substrates in water and to catalyze chemical reactions forms the basis for their use as a medium for investigating organic and bioorganic processes [19–28]. In this regard, micellar effect as a powerful probe has been utilized by different workers to explore the redox activity of NBP.

The present paper deals with the micellar effects on NBP oxidation of dextrose in the presence of acidic medium. The micellar effects have been studied to substantiate the proposed reaction mechanisms.

Experimental

Materials and methods

Analytical reagent grade chemicals and triple distilled water were used throughout the investigation. The solution of NBP (Aldrich, 95 %) was prepared in 80 % acetic acid (AR, S.D. Fine-Chem Limited, Mumbai, India) and stored in a black-coated flask to prevent any photochemical deterioration. The prepared solution of NBP was standardized by reported method [29]. Solution of dextrose (freshly prepared), sodium dodecylsulfate, tritonX-100, and phthalimide (all are, S.D. Fine-Chem Limited, Mumbai, India) were prepared with triple distilled water. Freshly prepared starch solution used as an indicator. Mercuric acetate (S.D. Fine-Chem Limited, Mumbai, India) solution was acidified with 20 % acetic acid and sulfuric acid (AR, s. d. fine chem. limited, Mumbai, India) was diluted with triple distilled water for

the present investigation. All the kinetic measurements were carried out at constant temperature 40 °C.

Procedure and kinetic measurements

Solutions of the oxidant and reaction mixtures containing known quantities of the substrates (i.e., dextrose), surfactants, acid, and other necessary chemicals were separately thermostated (±0.1 °C). The reaction was initiated by mixing the requisite amounts of the oxidant with the reaction mixture. Progress of the reaction was monitored by following the rate of disappearance of NBP by an iodometric determination method. The pseudo first order rate constants (k_{obs}) were calculated as usual. Under the experimental conditions, the possibility of decomposition of the surfactants by NBP was investigated and the rate of decomposition in this path was found to be kinetically negligible. To circumvent the solubility problem, sulfuric acid was used to follow the effects of the anionic surfactant (SDS) and non-ionic surfactant (TX-100). The pseudo-first order rate constants (k_{obs}) were reproducible within the experimental error limit.

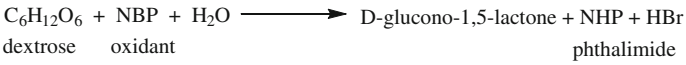
Product identification and stoichiometry

The reaction mixture is [NBP] ≫ [dextrose] were kept in presence of $Hg(OAc)_2$, H_2SO_4, surfactants and acetic acid at room temperature for 72 h. Determination of unconsumed NBP indicated that one mole of dextrose is oxidized by 1 mol of NBP. This result showed 1:1 stoichiometry according to equation for dextrose could be formulated as in Scheme 1.

Under the kinetic conditions, [dextrose] ≫ [NBP], the oxidized reaction mixture was completely neutralized by sodium bicarbonate and then extracted with ether. The aqueous layer was used to detect and estimate the main product, lactone of gluconic acid. The oxidation product of dextrose was detected by $FeCl_3$-HCl blue test, paper chromatography, and dinapthol-sulfuric acid test.

(i) *$FeCl_3$-HCl blue test* [30, 31]: After the kinetic experiment was completed, a part of the oxidized reaction mixture was treated with alkaline hydroxylamine solution. To the other part of the reaction mixture, barium carbonate was added to make the solution neutral [32]. $FeCl_3$ solution that had been colored violet with phenol when added to this reaction mixture gave a bright-yellow coloration [33], indicating the presence of gluconic acid. It is concluded that lactone, formed in the rate-determining step, is hydrolyzed to gluconic acid in neutral medium in a fast step.

(ii) *Paper chromatography* [34]: Generally, paper chromatographic technique is used to identify the oxidation products of carbohydrates. Therefore, paper



Scheme 1 Stoichiometry of the reaction

chromatography was carried out using *n*-butanol-acetic acid–water (4:1:5) as eluent to confirm the lactone formation. Silver nitrate, sodium hydroxide, and sodium thiosulfate were used as detectors.

(iii) *Dinapthol-sulfuric acid test* [35]: The test was carried out by treating a little amount of the final reaction mixture with a few drops of *β*,*β*'-dinapthol solution in concentrated sulfuric acid and then heating for an hour in a water bath at 85 °C. It did develop a characteristic green fluorescence of gluconic acid.

Determination of CMC values

Surfactants are made up of a hydrophilic headgroup and a hydrophobic tail. In aqueous solution the hydrophobic surfactant tail is encapsulated by a highly structured water layer, which is one or two molecules thick. This structured layer has extremely low entropy compared to bulk water. Above the critical micelle concentration (CMC), the surfactants aggregate into micelles or differently shaped assemblies. This surfactant self-assembly destroys the ice-like water layer and results in a positive entropy change, stabilizing the assemblies. Nonionic surfactants generally have a hydrophilic poly(ethylene oxide) or carbohydrate headgroup. Micelles formed by nonionic surfactants contain a hydrophobic core and a hydrophilic palisade layer, which contains water-swollen poly(ethylene oxide) chains, while anionic surfactants can have phosphate, sulfate, sulfonate, or carboxylate headgroups. Micelles generally appear approximately spherical at surfactant concentrations close to the CMC, and this shape is geometrically constrained. Increasing surfactant concentrations and addition of salts results in micellar growth and change of shape to ellipsoidal [36]. CMCs are also affected by the temperature, pressure, and added solubilizates, reduced by a factor proportional to the mole fraction of the solubilizate in the micelle and increased by the reduction of hydrophobic interaction/decrease the ionic strength. CMC value of surfactants (SDS, TX-100) in the presence and absence of substrate and oxidants were determined from plots of the specific conductivity (κ) versus surfactant concentration using conductometric determination method and carried out with a digital conductivity meter, model 611E at 400 °C. The values of CMC of surfactants are sensitive to the nature of the reactants and also depend upon reaction conditions. The break point of nearly two straight-line portions in the plot is taken as an indication of micelle formation, and this corresponds to the CMC of surfactant (Table 1).

Results and discussion

In order to propose a probable reaction mechanism for micelle catalyzed oxidation of dextrose by NBP, it is necessary to study the effect of variation of concentration of different reactants on the rate of reaction. Kinetics due to molecular bromine intervention was removed by the addition of mercury(II) ions, which removed Br^- ions either as $HgBr_2$ or as $HgBr_4^{2-}$. Here, mercuric acetate was added as a scavenger. Oxidation of dextrose by NBP in the presence of SDS and TX-100 were

Table 1 Critical micellar concentration (CMC) values of surfactants at 40 °C

Solutions	CMC of SDS	CMC of TX-100
(i) Water	9.15×10^{-3}	3.20×10^{-4}
(ii) Dextrose	4.29×10^{-3}	3.0×10^{-4}
(iii) NBP	8.20×10^{-3}	2.60×10^{-4}
(iv) Acetic acid% (v/v)	2.26×10^{-3}	1.66×10^{-5}
(v) H_2SO_4	1.57×10^{-3}	1.27×10^{-5}
(vi) Dextrose + NBP + acetic acid% (v/v) + H_2SO_4	2.90×10^{-3}	2.69×10^{-5}

Literature value at 25 °C: (a) SDS = 8.3×10^{-3} mol dm^{-3}; (b) TX-100 = 0.2×10^{-3} mol dm^{-3}

investigated under varying conditions of [dextrose], [NBP], solvent, mercuric acetate, phthalimide, salts, [SDS], [TX-100] and temperature.

Dependence on $[S]_T$ i.e., $[dextrose]_T$

From the plot of k_{obs} vs. $[S]_T$ (cf. Fig. 1; Table 2), it has been established that this shows the first order dependence on $[S]_T$ in both, the absence and presence of SDS and TX-100.

Dependence on $[NBP]_T$

Under the experimental conditions $[dextrose]_T \gg [NBP]_T$, the presence and absence of SDS and TX-100, the rate of disappearance of NBP shows a first order dependence on NBP. The pseudo first order rate constants (k_{obs}) have been evaluated from the linear plot of $\log[NBP]_T$ vs time (t) as usual (Fig. 2; Table 2).

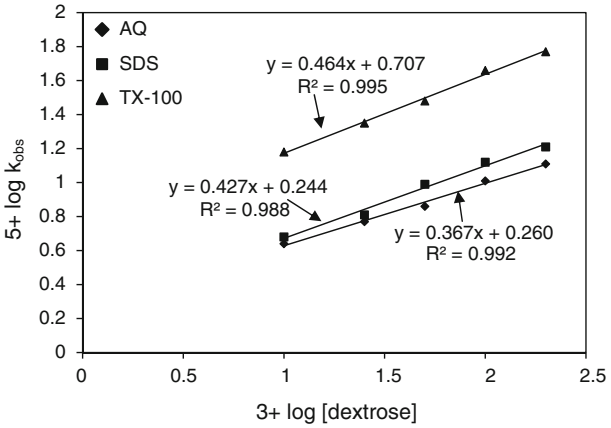


Fig. 1 Plots between log [dextrose] versus log k_{obs} at 40 °C: [NBP] = 2.0×10^{-4} mol dm^{-3}, $[Hg(OAc)_2] = 5.0 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.5 \times 10^{-4}$ mol dm^{-3}, acetic acid (30 %) (v/v). *Filled diamond* without surfactant (aqueous), *filled square* SDS, *filled triangle* TX-100

Table 2 Dependence of rate constants (k_{obs}) on [NBP], [dextrose], [H_2SO_4], and acetic acid% (v/v) in the absence and presence of surfactants

10^2 [dextrose] mol dm^{-3}	10^4 [NBP] mol dm^{-3}	10^4 [H_2SO_4]mol dm^{-3}	Acetic acid% (v/v)	$10^{4,a}$ s^{-1}	$10^{4,b}$ s^{-1}	$10^{4,c}$ s^{-1}
1.0	2.0	0.5	30	0.44	0.48	1.50
2.5				0.59	0.65	2.25
5.0				0.72	0.98	3.02
10.0				1.03	1.33	4.60
20.0				1.29	1.61	5.92
2.5 (For a 5.0)	1.0	0.5	30	0.73	0.66	2.27
	2.0			0.72	0.65	2.25
	3.0			0.72	0.65	2.25
	4.0			0.72	0.64	2.24
	5.0			0.71	0.64	2.23
	2.0	0.5	30	0.72	0.65	2.25
		1.0		0.55	0.54	1.63
		2.5		0.40	0.34	0.98
		5.0		0.31	0.22	0.60
		10.0		0.23	0.17	0.42
			20	1.59	0.86	2.58
			25	1.04	0.78	2.39
			30	0.72	0.65	2.25
			40	0.50	0.58	2.05
			50	0.46	0.48	1.52

[a] Without surfactant (aqueous); $[Hg(OAc)_2] = 5.0 \times 10^{-4}$ mol dm^{-3}, acetic acid% (v/v) 30 %, Temp. = 40 °C

[b] [SDS] = 1.0×10^{-2} mol dm^{-3}; $[Hg(OAc)_2] = 5.0 \times 10^{-4}$ mol dm^{-3}, acetic acid% (v/v) 30 %, Temp. = 40 °C

[c] [TX-100] = 1.0×10^{-3} mol dm^{-3}; $[Hg(OAc)_2] = 5.0 \times 10^{-4}$ mol dm^{-3}, acetic acid% (v/v) 30 %, Temp. = 40 °C

Effect of dielectric constant and calculation of the size of the activated complex

In order to find out the effect of the dielectric constant of the medium on the rate of the reaction, the reaction was studied at different dielectric constants (D) of the medium with constant concentrations of all other reactants and at a constant temperature. The dependence of the rate constant on the dielectric constant of the medium is given by the following equation:

$$\log k_{obs} = \log k_0' - \frac{Z_A Z_B e^2 N}{2.303(4\pi\varepsilon_0)d_{AB}RT} \times \frac{1}{\varepsilon} \quad (1)$$

where k_o is the rate constant in a medium of infinite dielectric constant, Z_A and Z_B are the charges of the reacting ion, d_{AB} represents the size of the activated complex, T is the absolute temperature and ε is the dielectric constant of the medium.

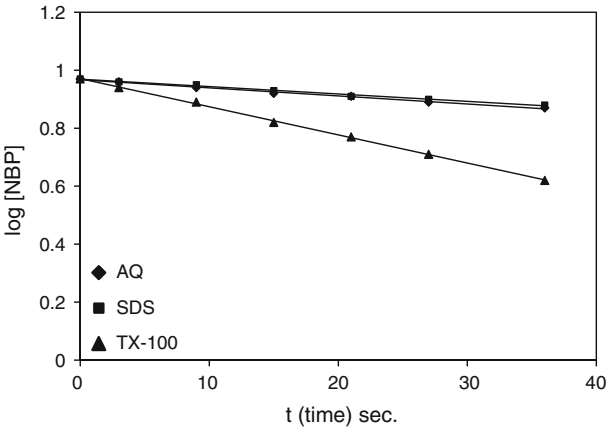


Fig. 2 Plots between t (s) versus log [NBP] at 40 °C: [dextrose] = 2.5×10^{-2} mol dm^{-3} (For *filled diamond* 5.0×10^{-2} mol dm^{-3}), $[Hg(OAc)_2] = 5.0 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.5 \times 10^{-4}$ mol dm^{-3}, acetic acid (30 %) (v/v). *Filled diamond* without surfactant (aqueous), *filled square* SDS, *filled triangle* TX-100

This equation suggests that if a plot is made between log k_{obs} vs. $1/\varepsilon$, a straight line can be attained (Table 2; Fig. 3). A negative dielectric effect supports the proposed mechanism. The effect of changing the solvent composition on the rate of reaction has been discussed in detail [37]. For the limiting case of the zero angle approach between two dipoles or an ion–dipole system, it has been shown that a negative slope of a linear line in the plot of log k_{obs} versus $1/\varepsilon$ is a general result for a reaction between a negative ion and a dipole or between two dipoles. A positive slope relates to a positive ion–dipole interaction [38]. The former concept agrees with the observations in the present study.

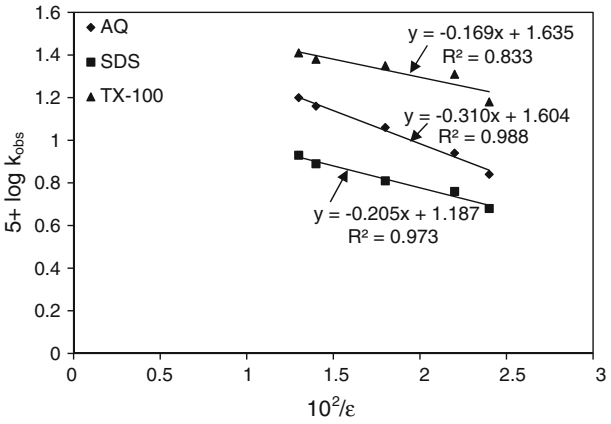


Fig. 3 Plots between $1/\varepsilon$ versus log k_{obs} at 40 °C: [NBP] = 2.0×10^{-4} mol dm^{-3}, [dextrose] = 2.5×10^{-2} mol dm^{-3} (For *filled diamond* 5.0×10^{-2} mol dm^{-3}), $[Hg(OAc)_2] = 5.0 \times 10^{-4}$mol dm^{-3}, $[H_2SO_4] = 0.5 \times 10^{-4}$ mol dm^{-3}. *Filled diamond* without surfactant (aqueous), *filled square* SDS, *filled triangle* TX-100

Effect of $[H_2SO_4]$

To understand the effect of H^+, H_2SO_4 was used. The rate constant decreased with increasing $[H_2SO_4]$. A plot of log k_{obs} vs. log $[H_2SO_4]$ was linear with a slope is negative (Fig. 4; Table 2) and less than unity indicating a negative fractional order dependence of the rate on $[H_2SO_4]$. The findings can be explained by considering the proposed mechanism.

Effect of $[Hg(OAc)_2]$

Mercuric acetate was added to the reaction mixture as scavenger to eliminate Br^- formed in the reaction, which could have produced Br_2 in the reaction. The Br_2 thus formed might cause another parallel oxidation. $Hg(OAc)_2$ thus ensures the oxidation purely through NBP.

Effect of [phthalimide]

The reaction rate is retarded by the addition of phthalimide (NHP) which is one of the products of the reaction. This point to the existence of a pre-equilibrium step as shown below:

$$\mathrm{NBP} + \mathrm{H_2O} \overset{K_1}{\rightleftharpoons} \mathrm{HOBr} + \mathrm{NHP} \tag{2}$$

The positive bromine from NBP can be transferred to the dextrose through the intermediate formation of hypobromous acid (HOBr).

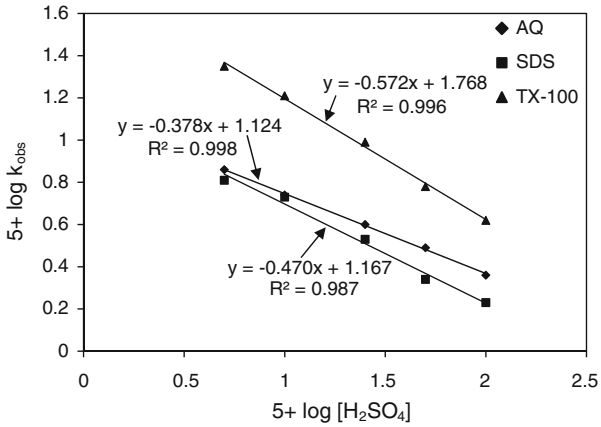


Fig. 4 Plots between log $[H_2SO_4]$ versus log k_{obs} at 40 °C: $[NBP] = 2.0 \times 10^{-4}$ mol dm^{-3}, $[Hg(OAc)_2] = 5.0 \times 10^{-4}$mol dm^{-3}, [dextrose] $= 2.5 \times 10^{-2}$ mol dm^{-3} (For *filled diamond* 5.0×10^{-2} mol dm^{-3}), acetic acid 30 % (v/v). *Filled diamond* without surfactant (aqueous), *filled square* SDS, *filled triangle* TX-100

Effect of salt

Added salts inhibit the micellar catalysis, which is a general phenomenon. The inhibition has been explained by assuming that the counterions compete with an ionic reactant for a site on the micelle. Electrolytes have also been found to increase the aggregation number, decrease the CMC, and cause shape change from spherical to rod-like micelles. The added salts (KCl, KBr, and Na_2SO_4) inhibit the rate of reaction. As the concentration of these electrolytes increases, the concentration of reactants at the reaction site decreases due to salting-out effect of the salts. Addition of electrolytes, in general, is responsible for rate inhibition of micellar-mediated reactions due to the exclusion of the reagent(s) from the micellar pseudo-phase.

Test for free radicals

Addition of acrylonitrile to the reaction mixture does not induce polymerization. Therefore, the reaction does not involve the formation of free radicals. The observations demonstrate that no free radicals are formed in the reaction mechanism.

Temperature effect and activation parameters

The oxidation of dextrose has been studied at 30–50 °C and the data are presented in Table 3. Arrhenius parameters evaluated from linear plots of log k_{obs} versus

Table 3 Effect of temperature and activation parameters

Temperature °C	10^4 k_{obs} s^{-1}		
	a	b	c
30	0.39	0.35	1.20
35	0.54	0.48	1.63
40	0.72	0.65	2.25
45	1.08	0.96	2.89
50	1.52	1.42	3.81
Activation parameters			
E_a (kJ mol^{-1})	53.34	53.86	45.67
log p_Z ($dm^3 mol^{-1}$ s^{-1})	4.76	4.80	3.97
$\Delta H^{\#}$(kJ mol^{-1})	50.74	51.26	43.06
$\Delta S^{\#}$($JK^{-1}mol^{-1}$)	324.54	325.39	315.09
$\Delta G^{\#}$(kJ mol^{-1})	152.32	153.10	141.69

[a] Without surfactant (aqueous); [NBP] = 2.0×10^{-4} mol dm^{-3}, [dextrose] = 5.0×10^{-2} mol dm^{-3}, [$Hg(OAc)_2$] = 5.0×10^{-4} mol dm^{-3}, [H_2SO_4] = 0.5×10^{-4} mol dm^{-3}, acetic acid = 30 % (v/v)

[b] [SDS] = 1.0×10^{-2} mol dm^{-3}; [NBP] = 2.0×10^{-4} mol dm^{-3}, [dextrose] = 2.5×10^{-2} mol dm^{-3}, [$Hg(OAc)_2$] = 5.0×10^{-4} mol dm^{-3}, [H_2SO_4] = 0.5×10^{-4} mol dm^{-3}, acetic acid = 30 % (v/v)

[c] [TX-100] = 1.0×10^{-3} mol dm^{-3}; [NBP] = 2.0×10^{-4} mol dm^{-3}, [dextrose] = 2.5×10^{-2} mol dm^{-3}, [$Hg(OAc)_2$] = 5.0×10^{-4} mol dm^{-3}, [H_2SO_4] = 0.5×10^{-4} mol dm^{-3}, acetic acid = 30 % (v/v)

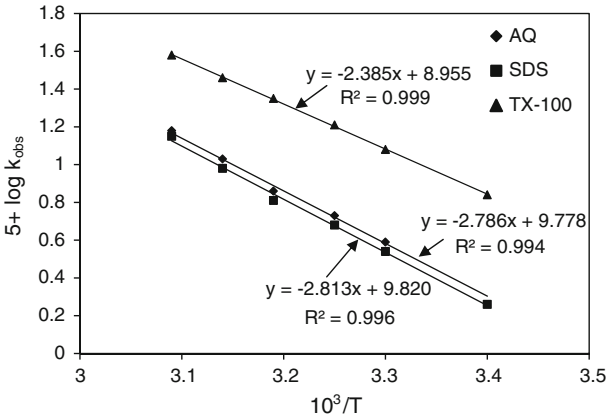


Fig. 5 Plots between 1/T versus log k_{obs}, [NBP] = 2.0×10^{-4} mol dm^{-3}, [dextrose] = 2.5×10^{-2} mol dm^{-3} (For *filled diamond* 5.0×10^{-2} mol dm^{-3}), $[Hg(OAc)_2] = 5.0 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.5 \times 10^{-4}$ mol dm^{-3}, acetic acid 30 % (v/v). *Filled diamond* without surfactant (aqueous), *filled square* SDS, *filled triangle* TX-100

1/*T* are presented (Fig. 5) in Table 3. The large negative value of $\Delta S^{\#}$ in the presence of TX-100 indicates that more ordered activated complex is formed. The fairly high positive values of $\Delta H^{\#}$ and $\Delta G^{\#}$ indicate that the transition state is highly solvated. Here, E_a is the energy of activation, $\Delta H^{\#}$ is the enthalpy of activation, $\Delta S^{\#}$ is the entropy of activation, $\Delta G^{\#}$ is the free energy of activation.

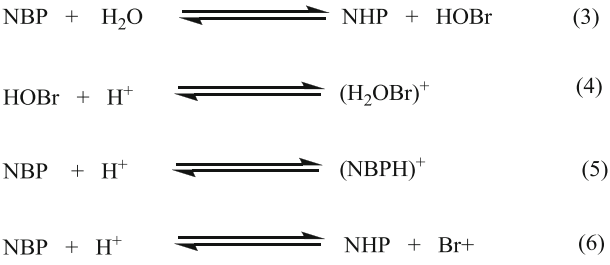
Mechanism

The monosaccharides are considered as a polyol and the reactivities of –OH groups can be influenced by the presence of the carbonyl group. Monosaccharides exist mainly as pyranoid and furanoid forms, the former being more stable [39] (Scheme 2).

On the other hand, NBP exists in the following equilibria [40] as in Scheme 3.

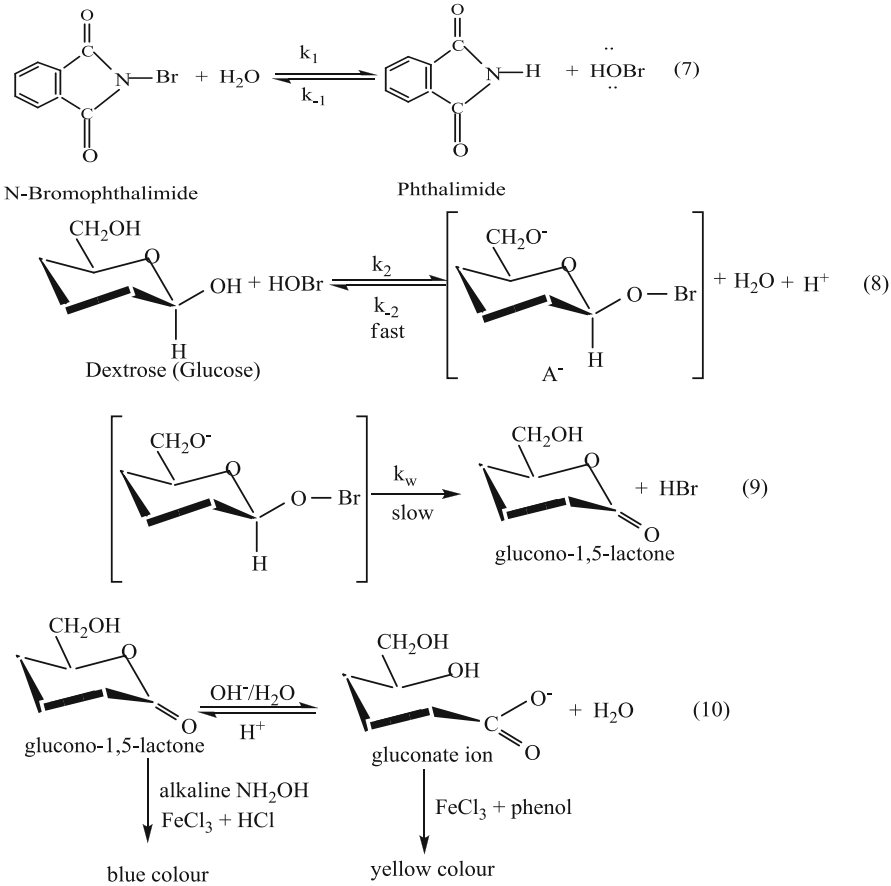
Since on assumption of NBP or $(NBPH)^+$ as the reactive species, the rate law fails to explain the negative effect of phthalimide. Hence, neither of these species, NBP and $(NBPH)^+$ can be taken as the reactive species. When HOBr is taken as the reactive species, the rate law explains the negative effect of $[H^+]$ and [NHP]. Thus, HOBr is taken as the most reactive species, which gave the rate law capable of explaining all the kinetic observations and other effects.

Scheme 2 Species of glucose (dextrose)



Scheme 3 Reactive species of NBP in aqueous medium

According to the experimental conditions above, HOBr is the most reactive species of NBP and considering the fact that one mole of dextrose is oxidized by one mole of NBP in Scheme 4.



Scheme 4 Mechanism of the reaction

In Scheme 4 (Eq. 7–10), S stands for dextrose, K_1, K_2 are the equilibrium constant for the step 1 and 2, k is the rate constant, A^- is intermediate species. The Eq. (11) is in good agreement with the experimental results. The rate of disappearance of [NBP] can be expressed in Eq. (12). Eq. (13) and (14) satisfactorily explains the kinetic results with respect to [NBP], [dextrose], [H_2SO_4] and [NHP].

$$-\frac{d[NBP]}{dt} = \frac{kK_1K_2[dextrose][NBP]_T}{[NHP][H^+] + K_1K_2[dextrose] + K_1[H^+]} \tag{11}$$

where

$$[NBP]_T = [NBP] + [HOBr] + [A^-]$$
$$rate = k_{obs}[NBP]_T \tag{12}$$

$$K_{obs} = \frac{rate}{[NBP]_T} = \frac{kK_1K_2[dextrose][NBP]_T}{[NHP][H^+] + K_1K_2[dextrose] + K_1[H^+]} \tag{13}$$

$$\frac{1}{k_{obs}} = \frac{[H^+][NHP]}{kK_1K_2[dextrose]}\frac{[H^+]}{kK_2[dextrose]} + \frac{1}{k} \tag{14}$$

Effect of varying [surfactants]

Plot of k_{obs} versus [TX-100] indicate the rate enhancement at lower concentrations of TX-100. The rate acceleration is due to preferential partitioning of the negatively charged dextrose-NBP complex (by hydrogen bonding) and neutral substrate in the micellar surface (Stern layer). Thus, TX-100 allows the reaction to proceed in both aqueous and micellar interphases. The partitioning mode leads to higher local concentration of both the reactants at the micelle-water interphase compared to their stoichiometric concentrations. TX-100 permits the reaction in both the phases with a preferential rate enhancement in the micellar phase. At higher concentration, the value of k_{obs} finally tends to attain a limiting value (Fig. 6; Table 4).

Plot of k_{obs} versus [SDS] shows a continuous decrease in the reaction rate. In fact, this type of rate retarding effect by the surfactants is due to the accumulated substrate in the micellar phase (Stern layer) cannot participate in the reaction and consequently the reaction rate is retarded (Fig. 7; Table 4).

The kinetic model to explain the micellar effects

Micellar catalysis critically depends on the interactions of the micelle with the substrate(s) and the activated complex. This is an extremely complicated problem because a number of different interactions are involved including those associated with the headgroup of the surfactant, different segments of the alkyl chain and the counterions. In Berezin's model [41], a solution above the CMC may be considered as a two-phase system, consisting of an aqueous phase and a micellar pseudo-phase. The reactants (S and O) may be distributed as shown in Scheme 5. A quantitative rate expression for a bimolecular reaction occurring only in aqueous (k_W path) and micellar (k_M path) phase for the pseudo-first order rate constant is given below:

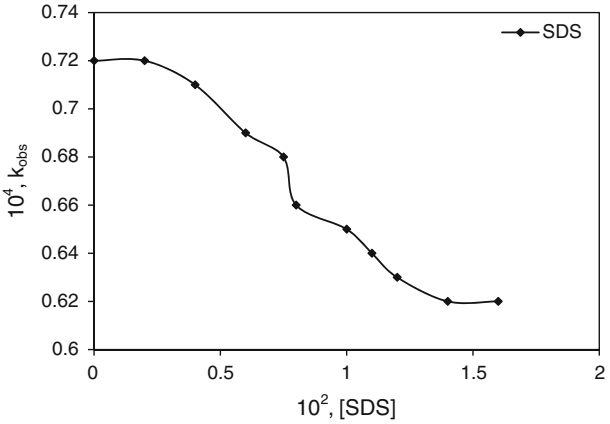


Fig. 6 Plot of [SDS] versus k_{obs}, [NBP] = 2.0×10^{-4} mol dm^{-3}, [dextrose] = 2.5×10^{-2} mol dm^{-3}, $[Hg(OAc)_2] = 5.0 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.5 \times 10^{-4}$ mol dm^{-3}, acetic acid 30 % (v/v)

Table 4 Effect of surfactants on the pseudo-first-order rate constants (k_{obs}) for the reaction of dextrose with NBP at 40 °C

[NBP] = 2.0×10^{-4} mol dm^{-3}, [dextrose] = 2.5×10^{-2} mol dm^{-3}, $[Hg(OAc)_2] = 5.0 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.50 \times 10^{-4}$ mol dm^{-3}, acetic acid = 30 % (v/v)

10^2 [SDS] mol dm^{-3}	10^4, k_{obs} s^{-1}	10^3 [TX-100] mol dm^{-3}	10^4, k_{obs} s^{-1}
0	0.72	0	0.72
0.2	0.72	0.2	0.75
0.4	0.71	0.4	0.85
0.6	0.69	0.6	1.02
0.75	0.68	0.8	1.53
0.8	0.66	1.0	2.25
1.0	0.65	1.2	2.50
1.1	0.64	1.4	2.67
1.2	0.63	1.6	2.69
1.4	0.62	1.8	2.70
1.6	0.62		

$$k_{obs} = \frac{k_w + k'_m K_S K_0 (C_{Surf} - CMC)}{[1 + K_S (C_{Surf} - CMC)][1 + K_0 (C_{Surf} - CMC)]} \quad (15)$$

where, K_S and K_o are the association constants of dextrose and NBP, respectively with surfactants, C_{Surf} is the analytical concentration of surfactants, $k'_M = (k_M/V)$, V being molar volume of the micelle and k_W and k_M are the pseudo-first order rate constant in absence and presence of micelles, respectively. Since the oxidant will be uncharged species and the substrate is large molecules, the hydrophobic and electrostatic interactions will be large and hence it may be expected that K_S and K_0 will be high. Since C_{Surf} is small it may be possible that $k_W \gg k'_M K_S K_o (C_{surf}–CMC)$ so that the Eq. (15) takes the form

$$k_{obs} = \frac{k_w}{1 + [(K_S + K_0)(C_{Surf} - CMC)]1 + K_S K_0 (C_{Surf} - CMC)^2} \quad (16)$$

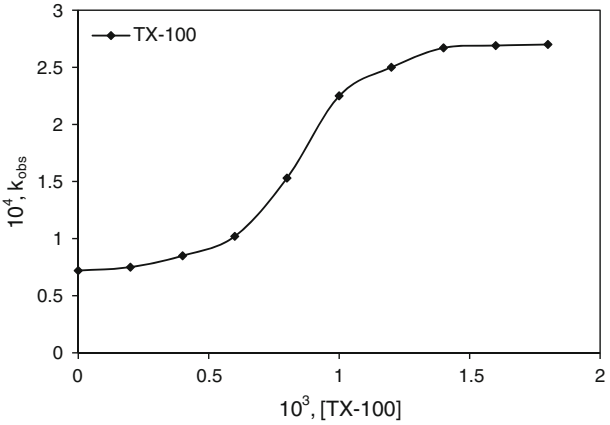
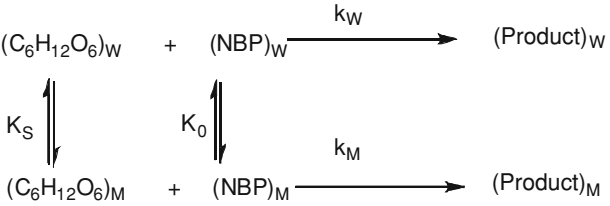


Fig. 7 Plot of [TX-100] versus k_{obs}, [NBP] = 2.0×10^{-4} mol dm^{-3}, [dextrose] = 2.5×10^{-2} mol dm^{-3}, $[Hg(OAc)_2] = 5.0 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.5 \times 10^{-4}$ mol dm^{-3}, acetic acid 30 % (v/v)



Scheme 5 Berezin's model

Again, since (C_{surf}−CMC) is very small, the terms containing $(C_{surf}-CMC)^2$ may be neglected, and the Eq. (16) may be rearranged to:

$$\frac{1}{k_{obs}} = \frac{1}{k_W} + \frac{K_S + K_0}{k_W}(C_{Surf} - CMC) \tag{17}$$

Plot of k_{obs}^{-1} versus (C_{surf}−CMC) for dextrose is linear (Figs. 8, 9; Table 5).

Conclusions

The oxidation of dextrose by NBP experienced a slow reaction rate in both absence of surfactants and presence of SDS, but increased in rate in the presence of the TX-100 surfactant. The reactive species of NBP for the oxidation in an acidic medium was HOBr. In our body, HOBr formed by the eosinophils in the presence of H_2O_2, and eosinophil peroxidase provides a potent mechanism by which eosinophils kill multicellular parasites and certain bacteria such as tuberculosis bacteria. Aldonic acid is the main product of the reaction, which is a very important compound. Under the comparable experimental conditions, the catalytic ability of SDS and TX-100

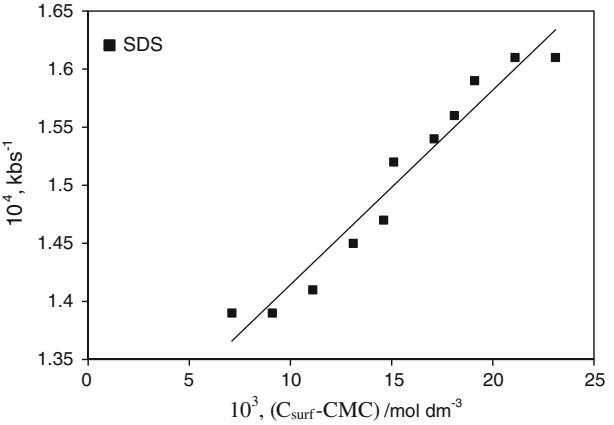


Fig. 8 Plots between k_{obs}^{-1} versus (C_{surf}−CMC) at 40 °C: [NBP] = 2.0×10^{-4} mol dm^{-3}, [dextrose] = 2.5×10^{-2} mol dm^{-3}, [$Hg(OAc)_2$] = 5.0×10^{-4} mol dm^{-3}, [H_2SO_4] = 0.5×10^{-4} mol dm^{-3}, acetic acid (30 %) (v/v), *filled square* SDS

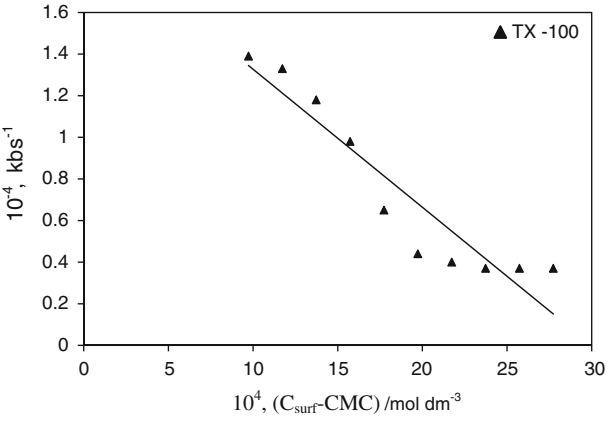


Fig. 9 Plots between k_{obs}^{-1} *versus* (C_{surf}−CMC) at 40 °C: [NBP] = 2.0×10^{-4} mol dm^{-3}, [dextrose] = 2.5×10^{-2} mol dm^{-3}, [$Hg(OAc)_2$] = 5.0×10^{-4} mol dm^{-3}, [H_2SO_4] = 0.5×10^{-4} mol dm^{-3}, acetic acid (30 %) (v/v), *filled triangle* TX-100

Table 5 Other parameters obtained from Berezin's model

Other parameters obtained from Berezin's model		
	k_W (s^{-1})	($K_s + K_o$) (dm^3 mol^{-1})
SDS	0.80×10^{-4}	1.28×10^{-5}
TX-100	0.50×10^{-4}	3.31×10^{-6}

[NBP] = 2.0×10^{-4} mol dm^{-3}, [dextrose] = 2.5×10^{-2} mol dm^{-3}, [$Hg(OAc)_2$] = 5.0×10^{-4} mol dm^{-3}, [H_2SO_4] = 0.50×10^{-4} mol dm^{-3}, acetic acid 30 % (v/v)

towards the oxidation of dextrose by NBP was in the order: (TX-100) > (SDS). The observed results were explained by plausible mechanisms and the related rate laws were deduced. It can be stated that TX-100 accelerates and SDS decreases the rate for the oxidation of dextrose by NBP in an acidic medium.

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