

## Research Article

# Kinetics and Mechanism of Micellar Catalyzed Oxidation of Dextrose by N-Bromosuccinimide in H<sub>2</sub>SO<sub>4</sub> Medium

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Kinetics and mechanism of micellar catalyzed N-bromosuccinimide oxidation of dextrose in H<sub>2</sub>SO<sub>4</sub> medium was investigated under pseudo-first-order condition temperature of 40°C. The results of the reactions studied over a wide range of experimental conditions show that NBS shows a first order dependence, fractional order, on dextrose and negative fractional order dependence on sulfuric acid. The determined stoichiometric ratio was 1:1 (dextrose:N-bromosuccinimide). The variation of Hg(OAc)<sub>2</sub> and succinimide (reaction product) has insignificant effect on reaction rate. Effects of surfactants, added acrylonitrile, added salts, and solvent composition variation have been studied. The Arrhenius activation energy and other thermodynamic activation parameters are evaluated. 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 nonionic micelle was best explained by the Berezin's model.

## 1. Introduction

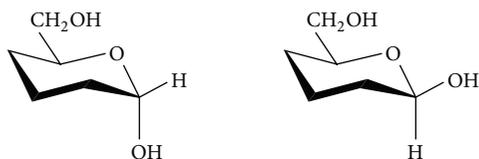
The kinetics of oxidation of sugars has been a subject of extensive research in recent years. The biological as well as the economic importance of carbohydrates is responsible for the great interest in the study of their bio- and physicochemical properties. The versatile nature of N-halomides due to their ability to produce halonium cations, hypohalite species, and nitrogen anion, which act as both bases and nucleophiles [1]. N-haloamides, well known as N-bromosuccinimide, is a very important member of this class of compounds and has received a considerable attention as an oxidizing agent for a wide range of functional groups in both acidic and alkaline media [2–4].

Dextrose is regarded as a representative reducing sugar and is also carbohydrate unit of nucleic acids. These carbohydrate units play important role in mammalian food supply and metabolism. Therefore, interaction of these carbohydrates with metal complexes has been subject of numerous investigations. 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 (Scheme 1).

This study helps to understand the catalytic activity of surfactants along with oxidative capacity of NBS in acidic medium. Kinetic studies of oxidation of different types of organic substrate by NBS have also been investigated by various researchers [5–11] to explore the effect of the substituent on the redox activity of NBS. In the search for more environment-friendly processes, the use of self-assembled surfactant structures opens up a whole range of new possibilities. These organized media, such as vesicles or micelles, can enhance/decrease the reaction rate and selectivity [12]. 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 bio-organic processes. In this regard, micellar effect as a powerful probe has been utilised by various researchers to explore the redox activity of NBS.

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



SCHEME 1: Species of glucose (dextrose).

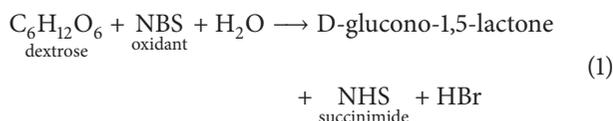
## 2. Experimental

**2.1. Material.** Analytical reagent grade chemicals and triple distilled water were used throughout the investigation. The solution of NBS (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 NBS was standardized by reported method [13]. Solution of dextrose (freshly prepared), sodium dodecyl sulfate, triton X-100, and succinimide (all are S D Fine-Chem Limited, Mumbai, India) was 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 of 40°C.

**2.2. 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 ( $\pm 0.1^\circ\text{C}$ ). 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 NBS by an iodometric determination method. The pseudo first order rate constants ( $k_{\text{obs}}$ ) were calculated as usual. Under the experimental conditions, the possibility of decomposition of the surfactants by NBS 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 nonionic surfactant (TX-100). The pseudo-first-order rate constants ( $k_{\text{obs}}$ ) were reproducible within the experimental error limit.

**2.3. Product Identification and Stoichiometry.** The reaction mixture is as follows: [NBS]  $\gg$  [dextrose] were kept in presence of  $\text{Hg}(\text{OAc})_2$ ,  $\text{H}_2\text{SO}_4$ , surfactants, and acetic acid at room temperature for 72 hours. Determination of unconsumed NBS indicated that one mole of dextrose is oxidized by 1 mole of NBS. This result showed 1:1 stoichiometry according to equation for dextrose which could be formulated as follows.

Stoichiometry of the reaction:



Under the kinetic conditions, [dextrose]  $\gg$  [NBS], 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  $\text{FeCl}_3$ -HCl blue test, paper chromatography, and dinaphthol-sulfuric acid test.

(i) *FeCl<sub>3</sub>-HCl Blue Test* [14, 15]. 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 [16].  $\text{FeCl}_3$  solution that had been colored violet with phenol when added to this reaction mixture gave a bright-yellow coloration [17], 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* [18]. Generally, paper chromatographic technique is used to identify the oxidation products of carbohydrates. Therefore, paper 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) *Dinaphthol-Sulfuric Acid Test* [19]. The test was carried out by treating a little amount of the final reaction mixture with a few drops of  $\beta, \beta'$ -dinaphthol 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.

**2.4. 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 highly structured water layers, which are 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. 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 result in micellar growth and change of shape to ellipsoidal. The critical micelle concentration (CMC) value of surfactants (SDS, TX-100) in the presence and absence of substrate and oxidants were determined from plots of the specific conductivity ( $\kappa$ ) versus surfactant concentration using conductometric determination method and carried out with a digital conductivity meter, model 611E at 40°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

TABLE 1: Critical micelle concentration (CMC) values of SDS and TX-100 in different experimental conditions.

Solution	CMC (mol dm <sup>-3</sup> ), SDS	CMC (mol dm <sup>-3</sup> ), TX-100
Surfactant + water	$9.15 \times 10^{-3}$	$3.20 \times 10^{-4}$
Surfactant + dextrose	$4.29 \times 10^{-3}$	$3.0 \times 10^{-4}$
Surfactant + NBS	$9.45 \times 10^{-3}$	$2.88 \times 10^{-4}$
Surfactant + acetic acid	$2.26 \times 10^{-3}$	$1.66 \times 10^{-5}$
Surfactant + H <sub>2</sub> SO <sub>4</sub>	$1.57 \times 10^{-3}$	$1.27 \times 10^{-5}$
Surfactant + reaction mixture	$3.36 \times 10^{-3}$	$2.90 \times 10^{-5}$

[NBS] =  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup>, [dextrose] =  $2.5 \times 10^{-2}$  mol dm<sup>-3</sup>, and temperature = 40°C.

Literature value at 25°C: (a) SDS =  $8.3 \times 10^{-3}$  mol dm<sup>-3</sup>; (b) TX-100 =  $0.2 \times 10^{-3}$  mol dm<sup>-3</sup>.

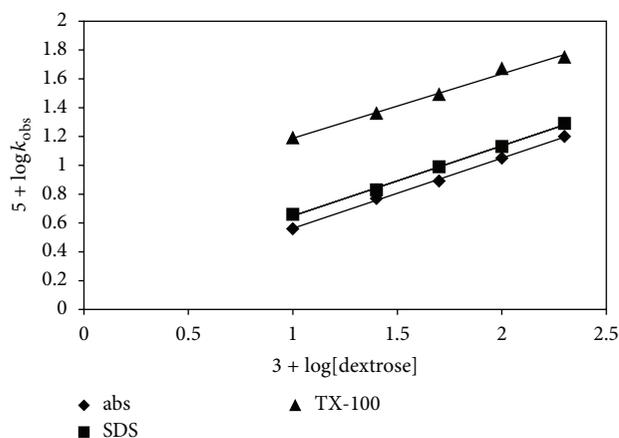


FIGURE 1: Plot of  $\log [\text{dextrose}]$  versus  $\log k_{\text{obs}}$  at 40°C: [NBS] =  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup>, [Hg(OAc)<sub>2</sub>] =  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>] =  $0.5 \times 10^{-4}$  mol dm<sup>-3</sup>, and acetic acid (30%) (v/v). (◆) Without surfactant (aqueous); (■) SDS; (▲) TX-100. abs, SDS, and TX-100 are all defined in the figure.

plot is taken as an indication of micelle formation, and this corresponds to the CMC of surfactant (Table 1).

### 3. Results and Discussion

In order to propose a probable reaction mechanism for micelle catalyzed oxidation of dextrose by NBS, 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<sup>-</sup> ions either as HgBr<sub>2</sub> or as HgBr<sub>4</sub><sup>2-</sup>. Here, mercuric acetate was added as a scavenger.

**3.1. Dependence on [Substrate]<sub>T</sub>, That Is, [Dextrose]<sub>T</sub>.** The effect of varying the concentrations of dextrose on rate in aqueous and micellar media showed that the reaction order is fractional. Further, a plot of  $\log k_{\text{obs}}$  versus  $\log [\text{Dextrose}]$  was linear with a slope less than unity (Figure 1). The results are summarized in Table 2.

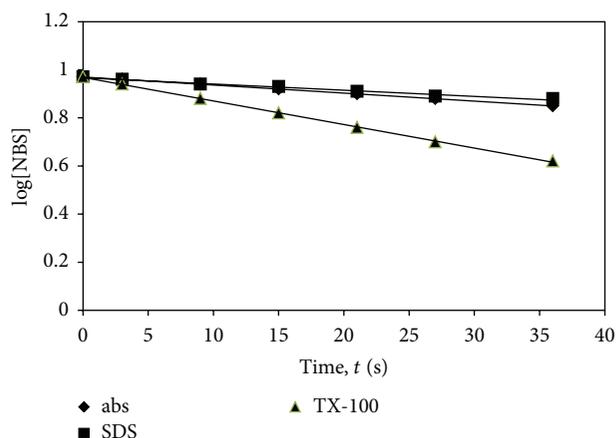


FIGURE 2: Plot of  $t$  (s) versus  $\log [\text{NBS}]$  at 40°C: [dextrose] =  $2.5 \times 10^{-2}$  mol dm<sup>-3</sup>, [Hg(OAc)<sub>2</sub>] =  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>] =  $0.5 \times 10^{-4}$  mol dm<sup>-3</sup>, and acetic acid (30%) (v/v). (◆) Without surfactant (aqueous); (■) SDS; (▲) TX-100.

**3.2. Dependence on [NBS]<sub>T</sub>.** The reaction is of first order in [NBS] both in absence and in presence of surfactant as indicated by the linearity of a plot of  $\log [\text{NBS}]$  versus time (Figure 2). This was further confirmed by the fact that the first order rate constant is invariant with different initial concentrations of NBS (Table 2).

**3.3. 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 [20]:

$$\log k_{\text{obs}} = \log k'_0 - \frac{Z_A Z_B e^2 N}{2.303 (4\pi\epsilon_0) d_{AB} RT} \times \frac{1}{\epsilon}, \quad (2)$$

where  $k'_0$  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  $\epsilon$  is the dielectric constant of the medium. This equation suggests that if a plot is made of  $\log k_{\text{obs}}$  versus  $1/\epsilon$ , a linear relationship can be obtained (Table 2 and Figure 3).

**3.4. Effect of [H<sub>2</sub>SO<sub>4</sub>].** The reaction was carried out by using different concentrations of H<sub>2</sub>SO<sub>4</sub> with keeping other parameters constant. It was found that the value of rate constant decreases with increasing concentration of H<sub>2</sub>SO<sub>4</sub> acid as it is shown in Figure 4, Table 2.

**3.5. Effect of [Hg(OAc)<sub>2</sub>].** Mercuric acetate was added to the reaction mixture as scavenger to eliminate Br<sup>-</sup> formed in the reaction which could have produced Br<sub>2</sub> in the reaction. The Br<sub>2</sub> thus formed might cause another parallel oxidation. Hg(OAc)<sub>2</sub> thus ensures the oxidation purely through NBS.

TABLE 2: Dependence of first-order rate constants  $k_{\text{obs}}$  on [NBS], [dextrose], and  $[\text{H}_2\text{SO}_4]$  for the oxidation of dextrose by N-bromosuccinimide in the absence and presence of SDS and TX-100 at 40°C.

$10^2$ , [dextrose] mol dm <sup>-3</sup>	$10^4$ , [NBS] mol dm <sup>-3</sup>	$10^4$ , $[\text{H}_2\text{SO}_4]$ mol dm <sup>-3</sup>	Acetic acid (%) (v/v)	$10^4, k_{\text{obs}} \text{ s}^{-1}$		
				Aqueous <sup>a</sup>	SDS <sup>b</sup>	TX-100 <sup>c</sup>
1.0	2.0	0.5	30	0.36	0.46	1.54
2.5				0.59	0.68	2.30
5.0				0.78	0.98	3.07
10				1.13	1.35	4.63
20				1.6	1.95	5.59
2.5	1.0	0.5	30	0.78	0.69	2.34
	2.0			0.78	0.68	2.30
	3.0			0.78	0.68	2.29
	4.0			0.76	0.68	2.28
	5.0			0.74	0.67	2.25
2.5	2.0	0.5	30	0.78	0.68	2.30
		1.0		0.64	0.54	1.74
		2.5		0.48	0.38	1.0
		5.0		0.38	0.30	0.65
		10		0.31	0.24	0.46
2.5	2.0	0.5	20	0.39	0.94	2.64
			30	0.42	0.86	2.47
			35	0.57	0.68	2.30
			40	0.78	0.57	2.10
			50	0.88	0.48	1.55

<sup>a</sup> $[\text{Hg}(\text{OAc})_2] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ .

<sup>b</sup> $[\text{SDS}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[\text{Hg}(\text{OAc})_2] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ .

<sup>c</sup> $[\text{TX-100}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{Hg}(\text{OAc})_2] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ .

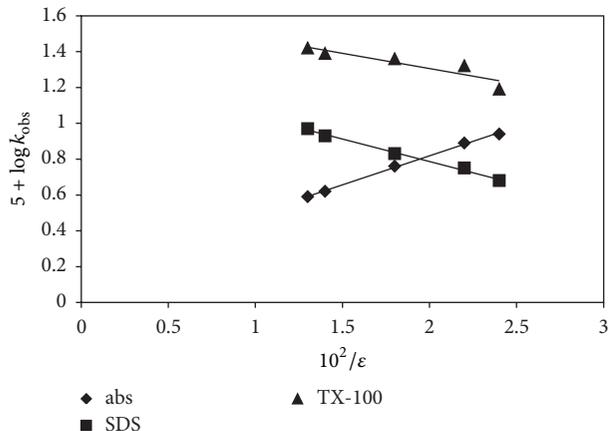


FIGURE 3: Plot of  $1/\epsilon$  versus  $\log k_{\text{obs}}$  at 40°C:  $[\text{NBS}] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{dextrose}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{Hg}(\text{OAc})_2] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ , and  $[\text{H}_2\text{SO}_4] = 0.5 \times 10^{-4} \text{ mol dm}^{-3}$ . (◆) Without surfactant (aqueous); (■) SDS; (▲) TX-100. abs, SDS, and TX-100 are all defined in the figure.

3.6. *Effect of [Succinimide]*. Different concentrations of succinimide were added to the reaction cell with keeping other parameters constant. It was found that the value of rate constant decreases with increasing concentration of succinimide. This points to the existence of a preequilibrium step as shown below:

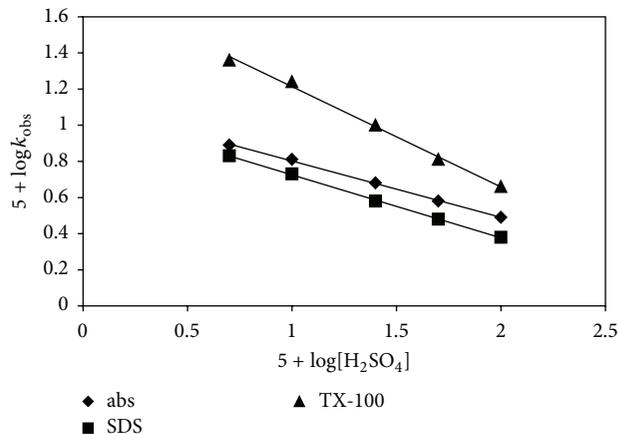
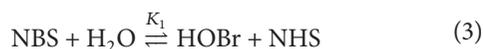


FIGURE 4: Plot of  $\log [\text{H}_2\text{SO}_4]$  versus  $\log k_{\text{obs}}$  at 40°C:  $[\text{NBS}] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{Hg}(\text{OAc})_2] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{dextrose}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$ , and acetic acid 30%(v/v). (◆) Without surfactant (aqueous); (■) SDS; (▲) TX-100.

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

3.7. *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

TABLE 3: Dependence on temperature and activation parameters.

	<sup>a</sup> 10 <sup>4</sup> <i>k</i> <sub>obs</sub> s <sup>-1</sup>	<sup>b</sup> 10 <sup>4</sup> <i>k</i> <sub>obs</sub> s <sup>-1</sup>	<sup>c</sup> 10 <sup>4</sup> <i>k</i> <sub>obs</sub> s <sup>-1</sup>
Temperature (°C)			
30	0.40	0.37	1.26
35	0.51	0.51	1.66
40	0.78	0.68	2.30
45	1.0	1.08	3.02
50	1.32	1.49	4.10
Activation parameters			
<i>E</i> <sub>a</sub>	48.81	53.42	45.21
log <i>p</i> <sub>Z</sub>	4.05	4.75	3.90
Δ <i>H</i> <sup>#</sup>	46.20	50.82	42.60
-Δ <i>S</i> <sup>#</sup>	323.68	325.01	314.90
Δ <i>G</i> <sup>#</sup>	147.51	152.55	141.17

<sup>a</sup>[NBS] = 2.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>; [dextrose] = 2.5 × 10<sup>-2</sup> mol dm<sup>-3</sup>; [H<sub>2</sub>SO<sub>4</sub>] = 0.5 × 10<sup>-4</sup> mol dm<sup>-3</sup>; [Hg(OAc)<sub>2</sub>] = 5.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>; acetic acid (30%) (v/v).

<sup>b</sup>[NBS] = 2.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>; [dextrose] = 2.5 × 10<sup>-2</sup> mol dm<sup>-3</sup>; [H<sub>2</sub>SO<sub>4</sub>] = 0.5 × 10<sup>-4</sup> mol dm<sup>-3</sup>; [Hg(OAc)<sub>2</sub>] = 5.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>; [SDS] = 1.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>; acetic acid (30%) (v/v).

<sup>c</sup>[NBS] = 2.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>; [dextrose] = 2.5 × 10<sup>-2</sup> mol dm<sup>-3</sup>; [H<sub>2</sub>SO<sub>4</sub>] = 0.5 × 10<sup>-4</sup> mol dm<sup>-3</sup>; [Hg(OAc)<sub>2</sub>] = 5.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>; [TX-100] = 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>; acetic acid (30%) (v/v).

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<sub>2</sub>SO<sub>4</sub>) 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 pseudophase.

**3.8. 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.

**3.9. 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*<sub>obs</sub> versus 1/*T* are presented (Figure 5) in Table 3. The large negative value of Δ*S*<sup>#</sup> in the presence of TX-100 indicates that more ordered activated complex is formed. The fairly high positive values of Δ*H*<sup>#</sup> and Δ*G*<sup>#</sup> indicate that the transition state is highly solvated. Here, *E*<sub>a</sub> = energy of activation, Δ*H*<sup>#</sup> = enthalpy of activation, Δ*S*<sup>#</sup> = entropy of activation, and Δ*G*<sup>#</sup> = free energy of activation.

**3.10. Mechanism.** The monosaccharides are considered 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 [21].

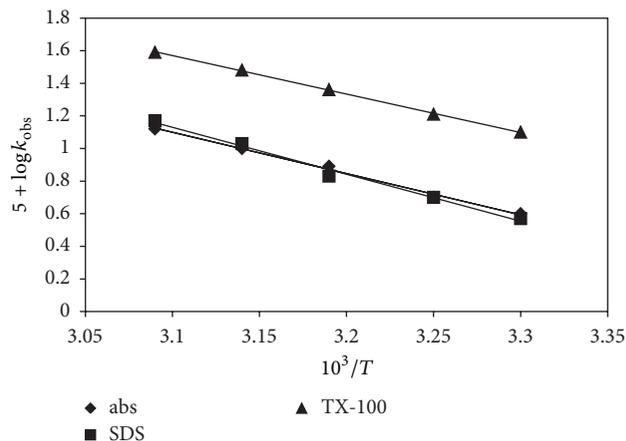
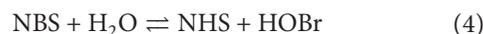


FIGURE 5: Plot of 1/*T* versus log *k*<sub>obs</sub>, [NBS] = 2.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>, [dextrose] = 2.5 × 10<sup>-2</sup> mol dm<sup>-3</sup>, [Hg(OAc)<sub>2</sub>] = 5.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>] = 0.5 × 10<sup>-4</sup> mol dm<sup>-3</sup>, and acetic acid 30%(v/v). (◆) Without surfactant (aqueous); (■) SDS; (▲) TX-100.

On the other hand, NBS exists in the following equilibria [22].

Reactive species of NBS in aqueous medium;



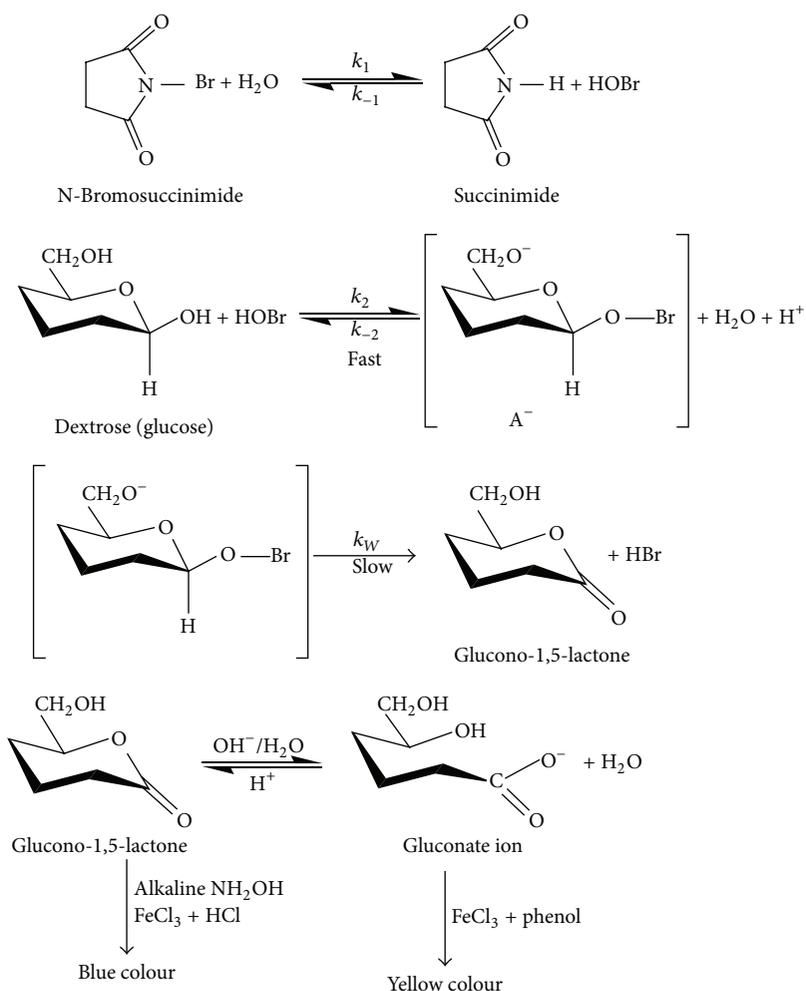
Since, assumption of NBS or (NBSH)<sup>+</sup> as the reactive species, the rate law fails to explain the negative effect of succinimide. Hence, neither of these species, NBS and (NBSH)<sup>+</sup>, can be taken as the reactive species. When HOBr is taken as the reactive species, the rate law explains the negative effect of [H<sup>+</sup>] and [NHS]. Thus, HOBr is taken as the most reactive species, which gave the rate law capable of explaining all the kinetic observations and other effects.

According to the above experimental conditions HOBr is the most reactive species of NBS, considering the fact that one mole of dextrose is oxidized by one mole of NBS in Scheme 2.

In the scheme, S stands for dextrose, *K*<sub>1</sub>, *K*<sub>2</sub> are the equilibrium constant for the step 1 and 2, *k* is the rate constant, and A<sup>-</sup> is intermediate species. Equation (8) is in good agreement with the experimental results. The rate of disappearance of [NBS] can be expressed in (9). Equation (10) satisfactorily explains the kinetic results with respect to [NBS], [dextrose], [H<sub>2</sub>SO<sub>4</sub>], and [NHS]. consider

$$\text{rate} = \frac{kK_1K_2 [\text{dextrose}] [\text{NBS}]_T}{[\text{H}^+] [\text{NHS}] + K_1 [\text{H}^+] K_1K_2 [\text{dextrose}]}, \quad (8)$$

$$\text{rate} = k_{\text{obs}} [\text{NBS}]_T, \quad (9)$$



SCHEME 2: Mechanism of the reaction.

$$k_{\text{obs}} = \frac{\text{rate}}{[\text{NBS}]_T}$$

$$= \frac{kK_1K_2 [\text{dextrose}]}{[\text{NHS}] [\text{H}^+] + K_1K_2 [\text{dextrose}] + K_1 [\text{H}^+]}, \quad (10)$$

$$\frac{1}{k_{\text{obs}}} = \frac{[\text{H}^+] [\text{NHS}]}{kK_1K_2 [\text{dextrose}]} + \frac{[\text{H}^+]}{kK_2 [\text{dextrose}]} + \frac{1}{k}.$$

3.11. *Effect of Varying [Surfactants]*. Plot of  $k_{\text{obs}}$  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-NBS 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 reactants at the micelle-water interphase compared to their stoichiometric concentrations. TX-100 permits the reaction in both phases with a preferential rate enhancement in the micellar phase. At higher concentration, the value of  $k_{\text{obs}}$  finally tends to attain a limiting value (Figures 6 and 7, Table 4).

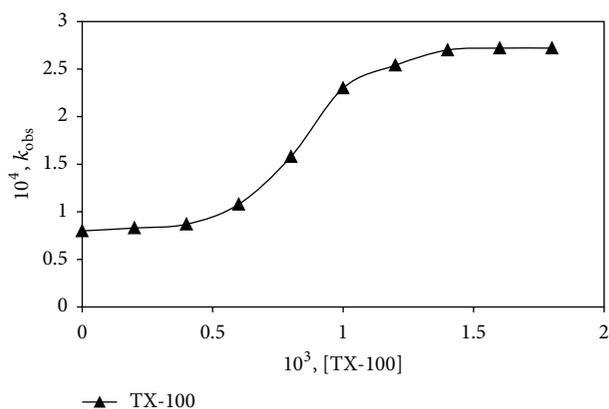


FIGURE 6: Plot of [TX-100] versus  $k_{\text{obs}}$ ,  $[\text{NBS}] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{dextrose}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{Hg}(\text{OAc})_2] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{H}_2\text{SO}_4] = 0.5 \times 10^{-4} \text{ mol dm}^{-3}$ , and acetic acid 30%(v/v).

Plot of  $k_{\text{obs}}$  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 fact that the accumulated substrate in the micellar phase (Stern layer) cannot participate

TABLE 4: Effect of [SDS] and [TX-100] on the  $k_{\text{obs}}$  for the reaction of dextrose with NBS at 40°C.

$10^2$ , [SDS] mol dm <sup>-3</sup>	$10^4$ , $k_{\text{obs}}$ s <sup>-1</sup>	$10^3$ , [TX-100] mol dm <sup>-3</sup>	$10^4$ , $k_{\text{obs}}$ s <sup>-1</sup>
0	0.80	0	0.80
0.2	0.78	0.2	0.83
0.4	0.77	0.4	0.87
0.6	0.74	0.6	1.08
0.75	0.72	0.8	1.58
0.8	0.71	1.0	2.30
1.0	0.68	1.2	2.54
1.1	0.65	1.4	2.70
1.2	0.62	1.6	2.72
1.4	0.58	1.8	2.72
1.6	0.54		
$k_w$ , s <sup>-1</sup> ( $10^{-4}$ )	1.09	$k_w$ , s <sup>-1</sup> ( $10^{-4}$ )	0.55
$(K_S + K_O)$ , dm <sup>3</sup> mol <sup>-1</sup> ( $10^{-5}$ )	3.91	$(K_S + K_O)$ , dm <sup>3</sup> mol <sup>-1</sup> ( $10^{-6}$ )	3.20

[NBS] =  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup>; [dextrose] =  $2.5 \times 10^{-2}$  mol dm<sup>-3</sup>; [Hg(OAc)<sub>2</sub>] =  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>; [H<sub>2</sub>SO<sub>4</sub>] =  $0.5 \times 10^{-4}$  mol dm<sup>-3</sup>; acetic acid (30%) (v/v).

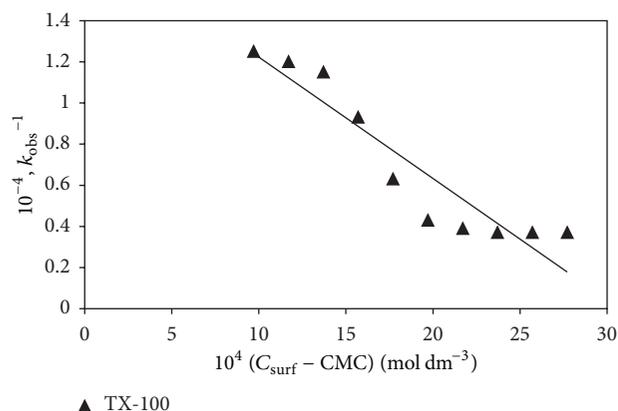


FIGURE 7: Plot of  $k_{\text{obs}}^{-1}$  versus  $(C_{\text{surf}} - \text{CMC})$  at 40°C: [NBS] =  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup>, [dextrose] =  $2.5 \times 10^{-2}$  mol dm<sup>-3</sup>, [Hg(OAc)<sub>2</sub>] =  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>] =  $0.5 \times 10^{-4}$  mol dm<sup>-3</sup>, and acetic acid (30%) (v/v); (▲) TX-100.

in the reaction and consequently the reaction rate is retarded (Figures 8 and 9, Table 4).

**3.12. 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 [23], a solution above the CMC may be considered a two-phase system, consisting of an aqueous phase and a micellar pseudophase. The reactants (S and O) may be distributed as

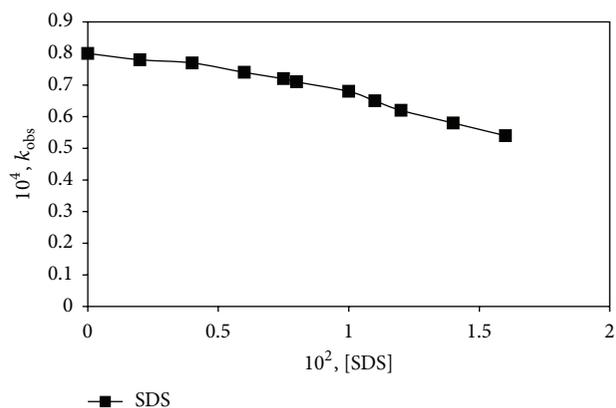


FIGURE 8: Plot of [SDS] versus  $k_{\text{obs}}$ , [NBS] =  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup>, [dextrose] =  $2.5 \times 10^{-2}$  mol dm<sup>-3</sup>, [Hg(OAc)<sub>2</sub>] =  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>] =  $0.5 \times 10^{-4}$  mol dm<sup>-3</sup>, and acetic acid 30%(v/v).

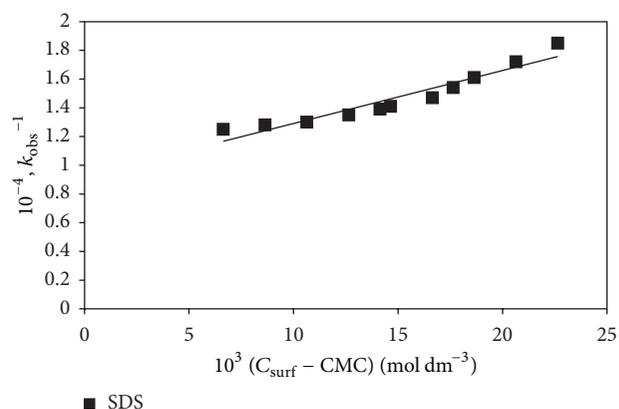
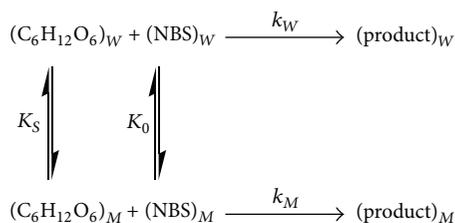


FIGURE 9: Plot of  $k_{\text{obs}}^{-1}$  versus  $(C_{\text{surf}} - \text{CMC})$  at 40°C: [NBS] =  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup>, [dextrose] =  $2.5 \times 10^{-2}$  mol dm<sup>-3</sup>, [Hg(OAc)<sub>2</sub>] =  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>] =  $0.5 \times 10^{-4}$  mol dm<sup>-3</sup>, and acetic acid (30%) (v/v); (■) SDS.

shown in Scheme 3. 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 in the scheme and

$$k_{\text{obs}} = \frac{k_w + k'_M K_S K_O (C_{\text{Surf}} - \text{CMC})}{[1 + K_S (C_{\text{Surf}} - \text{CMC})][1 + K_O (C_{\text{Surf}} - \text{CMC})]} \quad (11)$$

where  $K_S$  and  $K_O$  are the association constants of dextrose and NBS, respectively, with surfactants,  $C_{\text{Surf}}$  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  $K_O$  will be high. Since  $C_{\text{Surf}}$  is small it



SCHEME 3: Berezin's model.

may be possible that  $k_W \gg k'_M K_S K_0 (C_{\text{surf}} - \text{CMC})$  so that (11) takes the form

$$k_{\text{obs}} = \frac{k_W}{1 + (K_S + K_0)(C_{\text{surf}} - \text{CMC}) + K_S K_0 (C_{\text{surf}} - \text{CMC})^2}. \quad (12)$$

Again, since  $(C_{\text{surf}} - \text{CMC})$  is very small, the terms containing  $(C_{\text{surf}} - \text{CMC})^2$  may be neglected, and (12) may be rearranged to

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_W} + \frac{K_S + K_0}{k_W} (C_{\text{surf}} - \text{CMC}). \quad (13)$$

Plot of  $k_{\text{obs}}^{-1}$  versus  $(C_{\text{surf}} - \text{CMC})$  for dextrose is linear (Figures 7 and 9, Table 4).

#### 4. Conclusion

The oxidation of dextrose by NBS 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 NBS for the oxidation in an acidic medium was HOBr. In our body HOBr formed by the eosinophils in the presence of  $\text{H}_2\text{O}_2$ , and eosinophil peroxidase provides a potent mechanism by which eosinophils kill multicellular parasites, certain bacteria such as tuberculosis bacteria. Aldonic acid is the main product of the reaction, which is very important compound. Under the comparable experimental conditions, the catalytic ability of SDS and TX-100 towards the oxidation of dextrose by NBS was in the following 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 NBS in an acidic medium.

#### Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

#### Acknowledgments

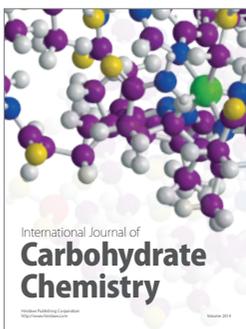
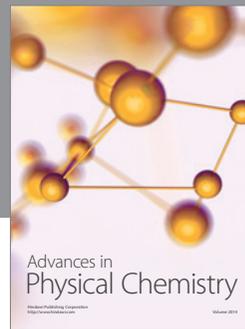
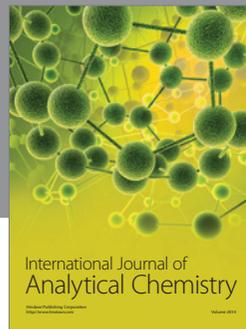
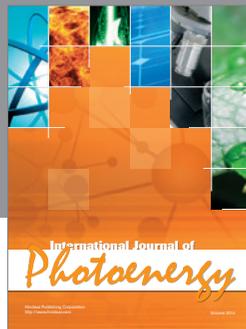
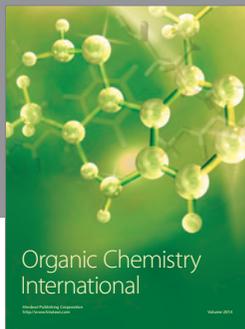
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