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**EFFECT OF CETYLPYRIDINIUM CHLORIDE (CPC) ON D-XYLOSE IN THE
ACIDIC MEDIUM: A KINETIC OXIDATIVE STUDY**

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ABSTRACT

The effect of cationic surfactant (CPC) on the oxidation of D-Xylose by N-bromophthalimide in the presence of acidic medium at 308 K has been studied. The order of reaction with respect to [D-Xylose] was found to be fractional. First and negative fractional order with respect to [oxidant] and $[H^+]$ was found respectively. The presence of inorganic salts (KCl, KBr) exhibits a severe hike in the reaction rate. Retardation effect of phthalimide has also been studied. Mercuric acetate as scavenger in the temperature range of 298-318 K has been reported. The rate of reaction decreased with an increase in dielectric constant of the medium. The effect of cationic surfactant cetylpyridinium chloride (CPC) has been studied. CPC retards the rate of reaction. Thermodynamic and activation parameters have been evaluated. Stoichiometry and Product analysis has been studied. A suitable mechanism in conformity with the kinetic data has been proposed.

Key words: Micellar catalysis; Oxidation; D-Xylose; N-bromophthalimide

INTRODUCTION

Oxidations are key reactions in the synthesis of organic molecules and fine chemicals.¹The kinetics of oxidation of reducing sugars has been the subject of extensive research in recent years.²⁻⁵They is the body's primary source of energy. Energy is stored in the complex molecular structure of the carbohydrates. Carbohydrates must be burned or oxidized if energy is to be released. The study becomes more important from the biological point of view.

An extensive literature survey is available on the kinetics of oxidation of carbohydrates by various organic and inorganic oxidants.⁶⁻⁷ The kinetics of oxidation of arabinose and xylose by iodine in alkaline solution is also studied. The work is also observed in catalyzed and uncatalyzed oxidation of sugars by using N-halo compounds.⁹⁻¹¹ But the Literature survey reveals that the work done in presence of surfactant is very scanty.

In this paper, we report a study of the kinetics of the oxidation of D-xylose by NBP in absence and presence of cetyltrimethylammonium Chloride. Xylose, gives high multiplication function to the bacillus in intestines of human body, improve microbic environment of human body and enhance body immunity ability. It is mainly used for xylitol manufacturing and also extensively used in food processing and pharmaceutical industry. It has been confirmed that two forms of D-xylose, i.e., pyranoid and furanoid, are present in aqueous solutions.¹² Out of these, only the pyranoid form is claimed to be involved in the oxidation reactions.¹³

The application of N-halo compounds in the field of organic synthesis is very wide, such as oxidation reactions, halogenations, acylation and many more applications.¹⁴⁻¹⁵ as they are the sources of positive halogen and the mechanism of these reactions depends on the nature of active oxidising species, which in turn depends on the nature of halogen atom, the groups attached to the nitrogen atom and the reaction conditions. The recent application of NBP has been seen as a brominating and oxidative agents catalyst in pharmaceutical and agrochemicals.¹⁶⁻¹⁷

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NBP is also a very effective and practical halonium ion source for the Hofmann rearrangement.¹⁸

The role of micellar catalysis in recent years has been no need to the introduction. Surfactants are widely used in the field of chemistry, biology, engineering, material science and other areas and find a very large number of applications because of their miracle property.¹⁹⁻²⁰ The cationic surfactant, cetylpyridinium chloride (CPC) with strong bactericidal and resistance to fungi has a cetyl group attached to the nitrogen atom in the aromatic pyridyl group. It is used as an antibacterial agent in toothpaste, mouthwash and also used in hair conditioner.

The present work seeks to study the kinetics of catalytic oxidation of D-Xylose by NBP acidic medium. The main aim of the present study is to: (a) elucidate a plausible mechanism, (b) identify the oxidation products, (c) deduce an appropriate rate law, (d) ascertain the reactive species of oxidant i.e. NBP, (e) calculate activation parameters, and (f) effect of CPC micelle on the rate of oxidation.

EXPERIMENTAL

Materials

N-bromophthalimide (NBP) as oxidant was used as obtained (Sigma-Aldrich, Germany, 99% pure). The melting point of the oxidant was found to be 481 K. Solution of NBP was prepared in 80% distilled acetic acid and stored in a black-coated flask to prevent photochemical deterioration.²¹ And standardized iodometrically against the standard solution of sodium thiosulphate (Qualigens). The surfactant N-cetylpyridinium chloride (CPC) (AR, SRL India), D-Xylose (Loba Chem, Mumbai, India), potassium iodide (KI), potassium chloride (KCl), potassium bromide (KBr), phthalimide (NHP) (all S.d. fine), mercuric acetate (Hg(OAc)₂) (Loba Chem, Mumbai, India). Perchloric acid (S.d. fine) it maintains the hydrogen ion concentration constant. Distilled glacial acetic acid (s.d. fine) was used as solvent. Freshly prepared starch solution used as an indicator. Double distilled water was used in preparation of solution and throughout the course of reaction. All the kinetic measurements were carried out at constant temperature of 308K.

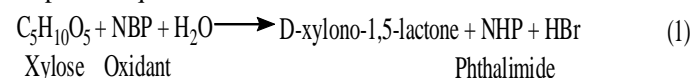
Kinetic measurements

The reactions were carried out in glass-stopper Pyrex vessel whose outer surface was black coated to eliminate photochemical effects. These vessels were kept in an electrically operated thermostatic water bath maintained at a constant temperature. The requisite volume of reactants D-Xylose, CPC, Hg(OAc)₂, HClO₄, CH₃COOH, Hg(OAc)₂ and water were placed in a vessel and thermo-stated at 308 K for thermal equilibrium. A pre-equilibrated amount of

the oxidant solution i.e. NBP which was also thermo stated at the same temperature was rapidly added to the reaction. The progress of the reaction was followed by estimating the amount of unconsumed NBP iodometrically at regular time intervals using freshly prepared starch as indicator. The course of the reaction was studied for two half-lives.

Stoichiometry of the reaction

To determine the stoichiometry of the reaction various sets of experiments were performed with different [NBP]: [Xylose] ratios, under the condition of [NBP] >> [Xylose]. The stoichiometry of the reaction was established by equilibrating the mixture consisting of NBP, Xylose, CPC, HClO₄, Hg(OAc)₂ and acetic acid for 72 h. The stoichiometric results indicated consumption of 1 mol of Xylose consumes 1 mol of NBP as represented by the following empirical equation:



After completion of the reaction, the unconsumed NBP was estimated. It was found that one mole of Xylose is oxidized by one mole of NBP. Thus, the ratio of consumption of reductant to oxidant is 1:1.

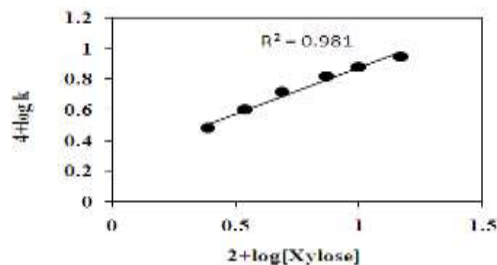
Product analysis

After the kinetic experiment, hydroxylamine solution was added to a part of the reaction mixture. Subsequent addition of FeCl₃ and HCl to this mixture gave a blue color indicates the presence of lactone in the reaction mixture.²² Additionally, FeCl₃ solution that had been colored violet with phenol when added to the reaction mixture gave a bright yellow color indicates the presence of aldonic acid.²³

RESULTS AND DISCUSSION

Effect of variation of reactant [d-xylose]

The rate of reaction increased from 3.01x 10⁻⁴ to 8.88 x 10⁻⁴ s⁻¹ with increase in concentration of Xylose from 2.5 x 10⁻² to 15 x 10⁻² mol l⁻¹ at constant concentration of other reactants at 308 K. The plot of log k versus log [Xylose] was linear with a fractional slope (0.981), indicating fractional order with respect to [Xylose]. The results are presented in Table 1 and Figure 1.



Effect of variation of oxidant [NBP]

To find out the order with respect to [NBP], the k_{obs} values were determined at different NBP concentrations at constant concentrations of other reactants at 308 K. The plots of $\log [NBP]$ versus time were found to be straight lines, indicating that the order with respect to oxidant was one. The results are presented in Table 1

Effect of variation of acid [HClO₄]

The rate of reaction decreased from 5.51×10^{-4} to $3.56 \times 10^{-4} s^{-1}$ with increase in concentration of $[H^+]$ from $1.5 \times 10^{-4} mol .L^{-1}$ to $4.0 \times 10^{-4} mol .L^{-1}$. The plot of $\log k$ versus $\log [H^+]$ produced a straight line with a negative slope and less than unity indicating that

order with respect to $[H^+]$ ion was negative fractional value. The results are presented in Table 1 and Figure 2.

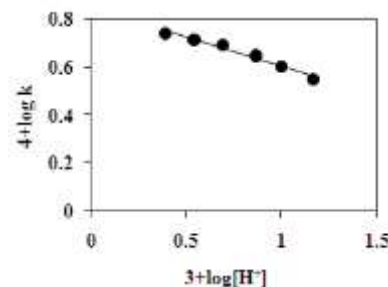


Table 1: Effect of [D-Xylose], [NBP], [H⁺], [Hg⁺⁺], [CPC] and acetic acid % on the rate of oxidation reactions

10 ² [D-Xylose] (mol l ⁻¹)	10 ⁴ [NBP] (mol l ⁻¹)	10 ³ [H ⁺] (mol l ⁻¹)	10 ⁴ [Hg ⁺⁺] (mol l ⁻¹)	[CH ₃ COOH] %	10 ³ [CPC] (mol l ⁻¹)	10 ⁴ k _{obs} s ⁻¹
2.5	1.0	2.0	2.0	50	5.0	3.01
3.5	1.0	2.0	2.0	50	5.0	4.01
5.0	1.0	2.0	2.0	50	5.0	5.21
7.5	1.0	2.0	2.0	50	5.0	6.56
10.0	1.0	2.0	2.0	50	5.0	7.55
15.0	1.0	2.0	2.0	50	5.0	8.88
5.0	1.0	2.0	2.0	50	5.0	5.21
5.0	2.0	2.0	2.0	50	5.0	5.20
5.0	3.0	2.0	2.0	50	5.0	5.20
5.0	4.0	2.0	2.0	50	5.0	5.20
5.0	1.0	1.5	2.0	50	5.0	5.51
5.0	1.0	2.0	2.0	50	5.0	5.21
5.0	1.0	2.5	2.0	50	5.0	4.96
5.0	1.0	3.0	2.0	50	5.0	4.46
5.0	1.0	3.5	2.0	50	5.0	4.03
5.0	1.0	4.0	2.0	50	5.0	3.56
5.0	1.0	2.0	2.0	50	5.0	5.21
5.0	1.0	2.0	4.0	50	5.0	5.21
5.0	1.0	2.0	6.0	50	5.0	5.22
5.0	1.0	2.0	8.0	50	5.0	5.21
5.0	1.0	2.0	2.0	30	5.0	6.71
5.0	1.0	2.0	2.0	40	5.0	6.12
5.0	1.0	2.0	2.0	50	5.0	5.21
5.0	1.0	2.0	2.0	60	5.0	4.66
5.0	1.0	2.0	2.0	70	5.0	3.91
5.0	1.0	2.0	2.0	50	2.0	7.21
5.0	1.0	2.0	2.0	50	3.0	6.81
5.0	1.0	2.0	2.0	50	4.0	5.99
5.0	1.0	2.0	2.0	50	5.0	5.21
5.0	1.0	2.0	2.0	50	6.0	4.45
5.0	1.0	2.0	2.0	50	7.0	3.98
5.0	1.0	2.0	2.0	50	8.0	3.21

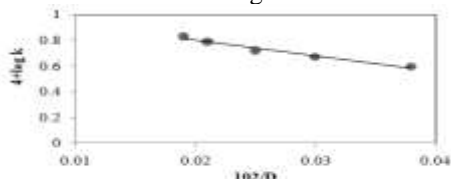
Effect of variation of acetic acid [CH₃COOH]

The rate of the reaction decreased from 6.71×10^{-4} to $3.91 \times 10^{-4} \text{ s}^{-1}$ with increase in acetic acid percentage from 30 to 70%. The rate of oxidation was found to depend on the dielectric constant (polarity) of the medium. To study the effect of dielectric constant of the medium on the rate of reaction, the micellar catalyzed oxidation of Xylose by NBP was studied in various compositions of acetic acid. The data clearly reveal that the rate decreases with an increase in the percentage of acetic acid.

The effect of dielectric constant of the medium on the rate constant of a reaction between two ions has been described by the well-known equation given.²⁴

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

where k_{obs} is the rate constant in a medium of infinite dielectric constant, Z_A and Z_B are the charges of reacting ions, d_{AB} refers to the size of activated complex and T is absolute temperature and D is the dielectric constant of the medium. A plot has been made between $4 + \log k$ and $1/D$, which gave a straight line having a slope equal to $\{-Z_A Z_B e^2 N\} / 2.303(4\pi\epsilon_0) d_{AB} RT$. The results are presented in Table 1 and Figure 3.

**Effect of variation of mercuric acetate [Hg (OAc)₂]**

The effect of [Hg (OAc)₂] observed in the range from 2.0×10^{-4} to $8.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ was found to be an insignificant effect on the rate of oxidation. An insignificant effect of mercuric acetate excludes the possibility of its involvement either as a catalyst, co-catalyst or as an oxidant because it does not help the reaction proceed without NBP. Thus in view of such kinetic observations, Hg (OAc)₂ acts only as a scavenger for any Br⁻ formed and inhibits the formation of free bromine. According to Bailar (1956), mercuric acetate reacts with Br⁻ and exists as HgBr₂⁴⁻ or unionized HgBr₂. Therefore; all the experiments have been carried out in presence of Hg (OAc)₂. The results are presented in Table 1.

Effect of variation of initially added product [NHP]

The effect of added phthalimide was studied, which was found to decrease the rate of oxidation reaction. Thus, the retardation of reaction rate on the addition of phthalimide suggests a pre equilibrium step

involving a process in which phthalimide is one of the products.



If this equilibrium is involved in the oxidation process, the rate should be an inverse function of phthalimide concentration because additions of phthalimide increase the aggregation number, due to that these reduce the catalytic efficiency of surfactants and decrease the number of micelles.

Test for free radical

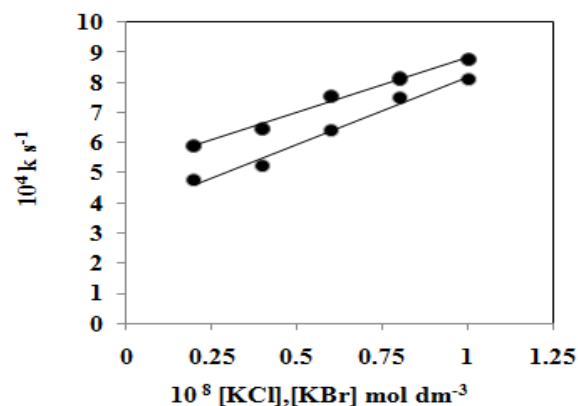
To test the presence of free radicals in the reaction, a known amount of acrylonitrile was added in a reaction mixture. The reaction neither induces polymerization nor retards the reaction rate which may be attributed to the inertness shown by free radicals.

Effect of variation of salts

The rate of reaction increased with increase in concentration of [Br⁻] and [Cl⁻]. The salt effect on micellar catalyzed reactions has been rationalized by assuming a competition between the reactant and the counter ion for a "binding site" on or in the micelle. The salt effect on micellar catalysis should be considered in the light of its competition with the substrate molecule, which interacts with the micelles electrostatically and hydrophobically, and structural changes, which occur on salt addition. The results are presented in Table 2 and Figure 4.

Table 2: The effect of varying concentration of inorganic salts on the rate of reaction at 308k

$10^8 \text{ mol}\cdot\text{L}^{-1}$	$\frac{[\text{KCl}]}{4 \cdot 10^4 \text{ s}}$	$\frac{[\text{KBr}]}{4 \cdot 10^4 \text{ s}}$
0.2	5.92	4.76
0.4	6.48	5.21
0.6	7.56	6.41
0.8	8.13	7.47
1.0	8.76	8.09

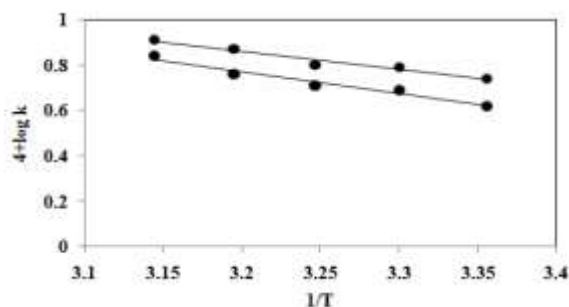


Effect of variation of temperature and activation parameters

Activation parameters are believed to provide useful information regarding the environment in which chemical reactions take place. The effect of temperature on rate constant was studied in the temperature range of 298-318 K. From Arrhenius plots, the value of activation energy (Ea) was calculated and the values of entropy of activation (ΔS) and free energy of activation (ΔG) were computed from Eyring equation. The values of negative ΔS and positive (ΔH) suggest the formation of more ordered activated complexes and transition state is highly solvated. The value of energy of activation shows that the reaction is slow and enthalpy is controlled. The results are presented in Table 3 and Figure 5.

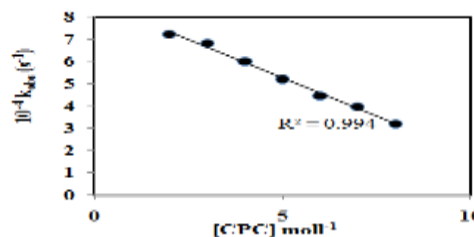
Table 3: Activation parameters for CPC catalyzed reactions of oxidation of D-xylose by NBP

Parameters	Without CPC k.10 ⁴ s ⁻¹	With CPC k.10 ⁴ s ⁻¹	
298K	5.54	4.21	
303K	6.11	4.98	
308K	6.26	5.21	
313K	7.44	5.88	
318K	8.08	6.95	
ΔEa (kJ.mol ⁻¹)	18.98	20.20	
ΔH(kJ.mol ⁻¹)	16.42	17.64	
ΔS(Jk.mol ⁻¹)	-59.42	-58.80	
ΔG(kJ.mol ⁻¹)	34.72	35.75	
log Pz	0.016	0.143	



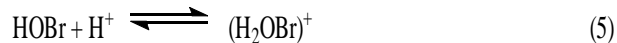
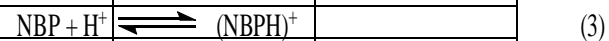
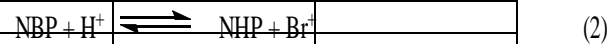
Effect of variation of surfactant [CPC]

CPC, a representative cationic surfactant is found to retard the rate of reaction. The plot of k_{obs} versus [CPC] indicates that the rate decreases in a continuous fashion and it tends to level off at a higher concentration of CPC. Bunton and Cerichelli noted a similar observation in the oxidation of ferrocene by Fe (III) salts in the presence of cationic cetyl trimethylammonium bromide (CTAB). Similar micellar effects have been noted in the oxidation of D-sorbitol by pentavalent vanadium ion. The results are presented in Table 1 and Figure 6.



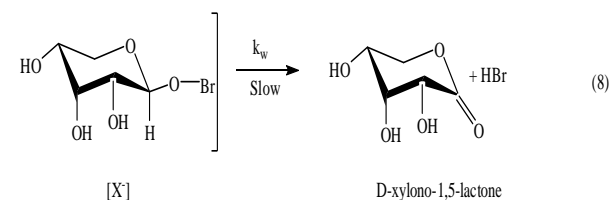
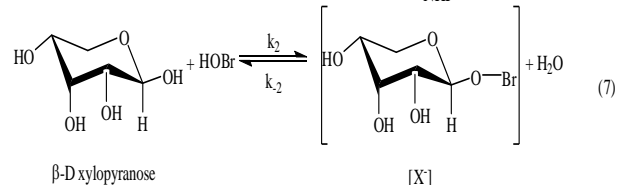
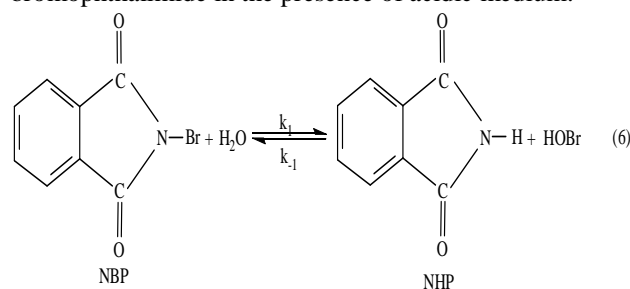
Reaction mechanism and rate law

On the basis of the results, the following mechanism may be proposed in order to explain the mechanistic path of the molecular reaction of D-Xylose. It has been reported that NBP is good oxidizing and brominating agent that because of large polarity. NBP, like other similar N-halo imides, may exist in various forms in acidic medium, i.e., free NBP, protonated NBP, Br⁺, HOBr, (H₂OBr)⁺. The monosaccharides are considered as a polyol and the reactivities of -OH groups can be influenced by the presence of the carbonyl group. Aldohexoses exist mainly as pyranoid and furanoid forms, the former being more stable. The pyranoid form mainly exists in a chair conformation. On the contrary, various species of NBP in aqueous media are given in reactions (2-5).



Addition of phthalimide in the reaction mixture decreases the rate of oxidation in acidic media. This suggests that the pre equilibrium step involves a process in which phthalimide is one of the products. When NBP or (NBPH)⁺ is assumed as the reactive species, the derived rate laws fail to explain the negative effect of phthalimide. Hence neither of these species can be considered as the reactive species. When (H₂OBr)⁺ is taken as the reactive species, the rate law obtained shows first order kinetics with respect to hydrogen ion concentrations, contrary to our observed negative fractional order with respect to HClO₄. Although equilibrium (4) fully explains the negative effect of phthalimide, but the contrary findings of HClO₄ dependence rules out the possibility of cationic bromine (Br⁺) as reactive species. Thus, the only choice left is HOBr, which,

when considered as the reactive species of NBP, leads to a rate law capable of explaining all the kinetic observations and other effects in the light of kinetic observations, HOBr can safely assumed to be the main reactive species of NBP for the present reaction. On the basis of above experimental findings Scheme -1 can be proposed for effect of cationic surfactant on the oxidation of D-Xylose by N-bromophthalimide in the presence of acidic medium.



Scheme-1

On the basis of scheme 1, it is evident that equation (8) is the rate determining step. Let $[\text{X}^-]$ be the intermediate formed out of the equation (7) which acts a reactant in equation (8) of scheme 1.

Then rate shall be:

$$\text{rate} = k [\text{X}] \quad (9)$$

The below rate law is in good agreement with our experimental findings i.e. addition of $[\text{H}^+]$ decreases the rate, addition of $[\text{NHP}]$ decreases the rate and increasing $[\text{D-Xylose}]$ increases the rate. This confirms the validity of the proposed mechanism.

$$K_1 = \frac{[\text{NHP}][\text{HOBr}]}{[\text{NBP}]} \quad (10)$$

$$K_2 = \frac{[\text{X}^-][\text{H}^+]}{[\text{xylose}][\text{HOBr}]} \quad (11)$$

$$\text{rate} = \frac{kK_1K_2[\text{xylose}][\text{NBP}]}{[\text{H}^+][\text{NHP}]} \quad (12)$$

$$\text{rate} = \frac{kK_1K_2[\text{xylose}][\text{NBP}]_T}{[\text{H}^+][\text{NHP}] + K_1[\text{H}^+] + K_1K_2[\text{xylose}]} \quad (13)$$

CONCLUSION

The kinetic studies for the micellar effect on the oxidation of D-Xylose by N-bromophthalimide in the presence of acidic medium demonstrate the following conclusions, the reactive species of oxidant NBP is HOBr not NBP itself. Oxidation products were identified and activation parameters were evaluated for the catalyzed and uncatalyzed reaction. A plausible mechanism and a related rate law have been worked out. CPC has been found to retard the rate of reaction. In this paper the entropy of activation for the catalyzed and uncatalyzed reaction was found as -58.80 $\text{Jk}^{-1}\text{mol}^{-1}$ and -59.42 $\text{Jk}^{-1}\text{mol}^{-1}$ respectively. The observed negative entropy of activation clearly supports the interaction between the species leading to the formation of an activated complex. In conclusion, it can be said that cationic micelle of CPC is an efficient catalyst for the oxidation of the D-Xylose by NBP in acidic medium.

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