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ORIGINAL CONTRIBUTION

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Kinetics of the oxidative degradation of D-xylose in presence and absence of cationic and anionic surfactants

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Abstract The oxidative degradation of D-xylose by cerium(IV) has been found to be slow in acidic aqueous solution with the evidence of autocatalysis. The reaction is accelerated in the cetyltrimethylammonium bromide (CTAB) micellar medium but sodium dodecyl sulfate (an anionic surfactant) has no effect. The pseudo first-order rate constants have been determined at different [reductant], [oxidant], [H_2SO_4], temperature, and [CTAB]. The reaction rate increased with increasing [D-xylose] and decreased with increase in [H_2SO_4]. The CTAB-micelle-catalyzed kinetic results can be interpreted by the pseudophase model. The kinetic parameters such as association constant (K_s), micellar medium rate constant (k_m), and activation parameters (E_a, $\Delta H^{\#}$ and $\Delta S^{\#}$) are evaluated and the reaction mechanism is proposed. The reaction rate is inhibited by electrolytes and the results provide an evidence for the exclusion of the reactive species from the reaction site.

Keywords Anionic surfactant · Cationic surfactant · D-Xylose · Oxidation · Cerium(IV) · Micelles · Catalysis

Introduction

Despite a large body of information available on the oxidative degradation of organic substrates by cerium(IV) in acidic media [1–12], kinetic studies of the oxidation of monosaccharides by cerium(IV) in the presence of micelle-forming surfactants have been lacking [11, 12]. In this paper, we report a study of the kinetics of the oxidation of D-xylose by cerium(IV) in the absence and presence of cetyltrimethylammonium bromide and sodium dodecyl sulfate. In addition, the effect of inorganic electrolytes (NaCl, $NaNO_3$, and Na_2SO_4) has also been explained in the presence of surfactants.

Experimental

Materials and reagents

D-Xylose (≥99%, s.d. fine, India), ceric ammonium nitrate (99%, Qualigens, India), sulfuric acid (98%, Merck, India), cetyltrimethylammonium bromide (CTAB) (99%, BDH, England), SDS (99%, Sigma, USA), sodium sulfate (98%, Merck, India), sodium nitrate (99%, Merck, India), sodium chloride (99.9%, BDH, India) and acrylonitrile (99%, s.d. fine, India) were used as received. All the solutions were prepared in doubly distilled water (specific conductivity 1.5×10^{-5} Ω^{-1} cm^{-1}).

Kinetic measurements

The reaction was carried out under pseudo first-order conditions ([D-xylose] was always in excess) in a three-necked reaction vessel fitted with a double-surface condenser to prevent evaporation. Both of the reactants were thermostated separately at the desired temperature before mixing. After start, aliquots of the reaction mixture were withdrawn at definite time intervals and the decay in the absorbance of cerium(IV) was measured spectrophotometrically at 385 nm with the help of Bausch & Lomb spectronic-20 spectrophotometer. The pseudo first-order

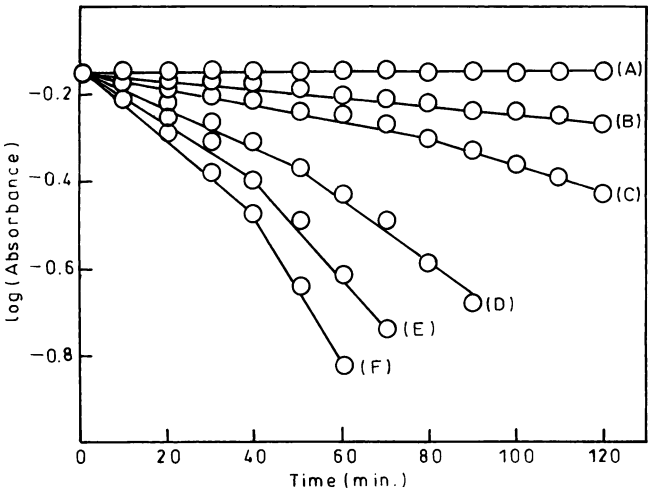


Fig. 1 Plots of log(absorbance) vs time for the Ce(IV)+D-xylose redox reaction. Reaction conditions: [Ce(IV)]=1.0×10^{-3} mol dm^{-3}, [H_2SO_4]=1.83 mol dm^{-3}, [D-xylose]=0.0 (**a**), 1.0 (**b**), 2.0 (**c**), 4.0 (**d**), 6.0 (**e**), and 8.0×10^{-2} mol dm^{-3} (**f**), and temperature=313 K

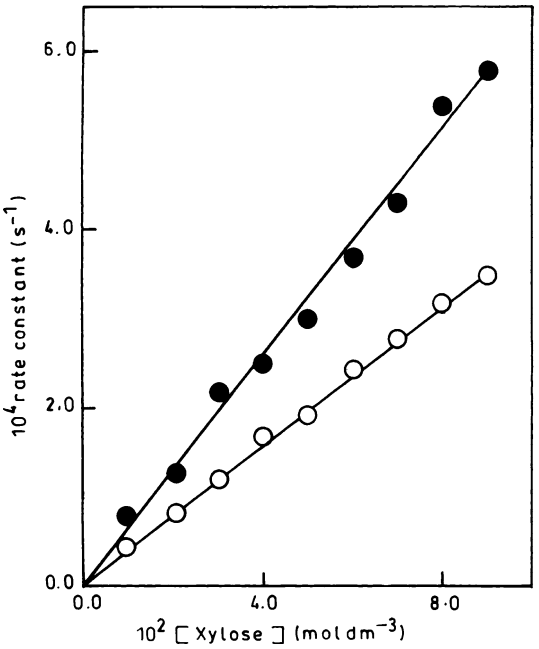


Fig. 2 Effect of [D-xylose] on the rate constants in absence (○) and presence (●) of CTAB. Reaction conditions: [Ce(IV)]=1.0×10^{-3} mol dm^{-3}, [H_2SO_4]=1.83 mol dm^{-3}, [CTAB]=50.0×10^{-4} mol dm^{-3}, and temperature=313 K

rate constants in the absence (k_{obs}, s^{-1}) and presence of surfactants (k_Ψ, s^{-1}) were determined from the linear parts of the plots of log(absorbance) vs time up to the completion of 80% reaction. Other details of the kinetic procedure were the same as described elsewhere [13–15].

Test for free radical

Acrylonitrile (20 cm^3, v/v) was added to the reaction mixture containing [Ce(IV)]=1.0×10^{-3} mol dm^{-3}, [H_2SO_4]=1.83 mol dm^{-3} and [D − xylose]=4.0×10^{-2} mol dm^{-3} at 313 K. The appearance of a white precipitate after some time indicates the formation of free radical.

Critical micelle concentration (cmc) measurement

The critical micelle concentration values of CTAB were determined conductimetrically using a bridge type CM 82 T (Elico Pvt., Hyderabad, India). The values of cmc in different solvents, i.e., water, water+Ce(IV) (=1.0×10^{-5} mol dm^{-3}), water+D-xylose (=4.0×10^{-2} mol dm^{-3}) and water+Ce(IV)+D-xylose at 313 K (obtained from the break point of nearly two straight line portions of the specific conductivity vs [CTAB] plots), are 10.15, 10.0, 10.0 and 8.3×10^{-3} mol dm^{-3}, respectively.

Table 1 Dependence of k_{obs} and k_Ψ([CTAB] =50.0×10^{-2} mol dm^{-3}) on [Ce(IV)] ([D-xylose]=4.0×10^{-2} mol dm^{-3}, [H_2SO_4]=1.83 mol dm^{-3}, T=313 K)

10^3 [Ce(IV)] (mol dm^{-3})	10^4k_{obs} (s^{-1})	10^4k_Ψ (s^{-1})	10^3 [Ce(IV)] (mol dm^{-3})	10^4k_{obs} (s^{-1})	10^4k_Ψ (s^{-1})
0.6	1.9	3.0	1.2	1.3	2.5
0.8	1.9	2.9	1.3	1.3	2.3
0.9	1.8	2.8	1.4	1.2	2.1
1.0	1.7	2.5	1.6	1.1	2.2
1.1	1.4	2.6	1.8	1.1	2.2

Product identification

In a typical set containing a known excess of [D-xylose] over [Ce(IV)] in the presence of H_2SO_4, after the kinetic experiment was over, hydroxylamine solution was added to a part of the reaction mixture. Subsequent additions of $FeCl_3$ and HCl to this mixture gave a blue coloration indicating the presence of lactone in the reaction mixture [16]. Additionally, $FeCl_3$ solution that had been colored violet with phenol when added to the reaction mixture gave

Table 2 Dependence of k_{obs} and k_Ψ([CTAB=50.0×10^{-2} mol dm^{-3}]) on [D-xylose] ([Ce(IV)]=1.0×10^{-3} mol dm^{-3}, [H_2SO_4]=1.83 mol dm^{-3}, T=313 K)

10^2 [D-xylose] (mol dm^{-3})	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0
10^4k_{obs} (s^{-1})	0.4	0.7	1.2	1.7	1.9	2.4	2.8	3.2	3.5
10^3k^{II} (mol^{-1} dm^{3}s^{-1})	4.0	3.5	4.0	4.2	3.8	4.0	4.0	4.0	3.9
10^4k_Ψ (s^{-1})	0.7	1.3	2.2	2.5	3.0	3.7	4.3	5.4	5.8

Table 3 Dependence of k_{obs} and k_ψ([CTAB =50.0x10^{-2} mol dm^{-3}) on [H_2SO_4] and [SO_4^{2-}] ([Ce(IV)]=1.0x10^{-3},[D-xylose] = 4.0x10^{-2}mol dm^{-3}, T= 313K)

[H_2SO_4] (mol dm^{-3})	10^4k_{obs} (s^{-1})	10^4k_ψ (s^{-1})	10^4 [SO_4^{2-}] (mol dm^{-3})	10^4k_{obs} (s^{-1})
0.73	2.0	Turbidity	0.0	1.7
1.10	2.1	Turbidity	1.0	1.7
1.47	1.8	Turbidity	2.0	1.8
1.83	1.7	2.5	4.0	1.8
2.20	1.3	2.5	5.0	1.9
2.57	1.1	2.4	10.0	2.1
2.94	1.1	2.3		
3.30	0.9	2.1		
3.67	0.8	2.0		

a bright yellow coloration [17] indicating the presence of aldonic acid. Seemingly, hydrolysis of lactone (formed in the rate-determining step) to aldonic acid takes place in neutral medium. At higher pH, the proportion of lactone is reduced because of the formation of aldonic acid anions that displace the equilibrium away from the lactones [18].

Results and discussion

Reaction in the absence of surfactants

The plots of log(absorbance) vs time for the oxidation of D-xylose by cerium(IV) deviate from linearity as shown in Fig. 1: this suggests the involvement of two reaction paths, i.e., the initial slow stage followed by a relatively faster step [19, 20]. The time at which the deviation commenced was found to decrease with increase in [D-xylose] (Fig. 1). The pseudo first-order rate constants (k_{obs}) were calculated from the slopes of the initial parts (first stage) of the linear plots. An interesting feature of this reaction is the autocatalysis, due to the catalytic role of one of the oxidation products. Thus, the second-stage oxidation is not a true path of the oxidation of [D-xylose] by cerium(IV): it may be a mixture of the reactions of Ce(IV)+D-xylose and Ce(IV)+oxidation intermediate(s).

Table 4 Dependence of k_{obs} and k_ψ([CTAB]=50.0x10^{-2} mol dm^{-3}) on temperature ([Ce(IV)]=1.0x10^{-3} mol dm^{-3}, [H_2SO_4]=1.83 mol dm^{-3}, [D-xylose]= 4.0 x 10^{-2} mol dm^{-3})

Temperature (K)	303	308	313	318	323
10^4k_{obs} (s^{-1})	0.5	0.9	1.7	3.0	5.6
10^4k_ψ (s^{-1})	0.8	1.4	2.5	4.1	7.5
Parameters	E_a/kJ mol^{-1}	$\Delta H^{\#}$/kJ mol^{-1}	$\Delta S^{\#}$/J K^{-1} mol^{-1}		
Aqueous	99	96	−10		
Micellar	93	90	−27		

The pseudo first-order rate constants (k_{obs}) were calculated at various [Ce(IV)] but at constant [D-xylose], [H_2SO_4], and temperature. The results are recorded in Table 1. This indicates first-order dependence on [Ce(IV)]. The reaction was of first-order with respect to [D-xylose] (the plot of k_{obs} vs [D-xylose] was linear passing through the origin, Fig. 2). This was further confirmed by the constancy of k^{II}, the second-order rate constant (Table 2). The reaction was inhibited by H_2SO_4 (Table 3). The rate constant increased with increase in [SO_4^{2-}] (Table 3) which indicates involvement of Ce(IV)-sulfato species as the reactive species.

The k_{obs} at different temperatures were also obtained and the activation parameters [energy of activation (E_a), enthalpy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$)] were determined from the Arrhenius (Fig. 3) and Eyring equations. The values of E_a, $\Delta H^{\#}$ and $\Delta S^{\#}$ are recorded in Table 4 along with k_{obs}.

It has been confirmed that two forms of D-xylose, i.e., pyranoid and furanoid, are present in aqueous solutions [21]. Out of these, only the pyranoid form is claimed to be involved in the oxidation reactions [22]. As far as the conformation is concerned, the anomeric –OH in α- and β-

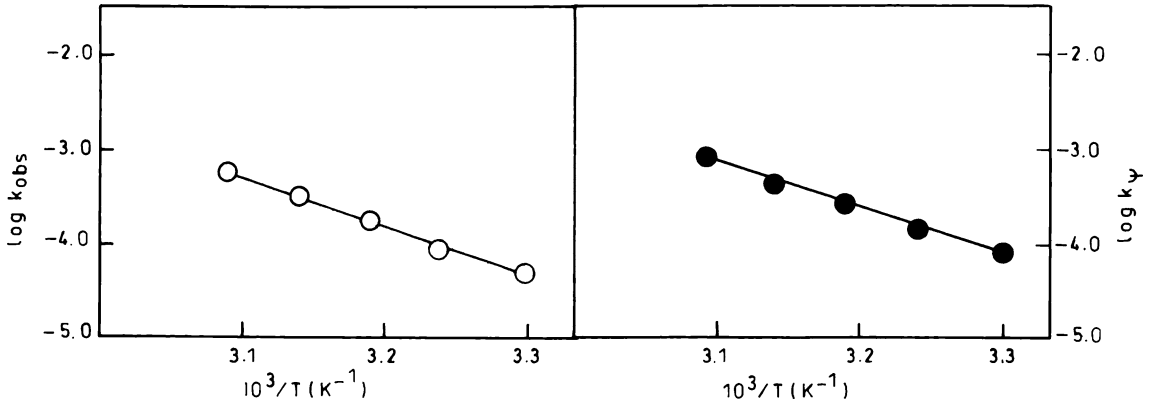
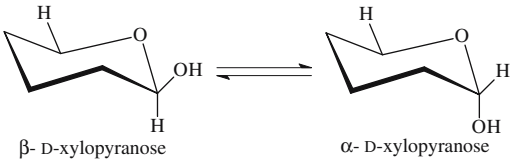


Fig. 3 Arrhenius plots for the Ce(IV)+D-xylose redox reaction in absence (○) and presence (●) of CTAB. Reaction conditions: [Ce(IV)]= 1.0×10^{-3} mol dm^{-3}, [H_2SO_4]=1.83 mol dm^{-3}, [D-xylose]=4.0×10^{-2} mol dm^{-3}, and [CTAB]=50.0×10^{-4} mol dm^{-3}



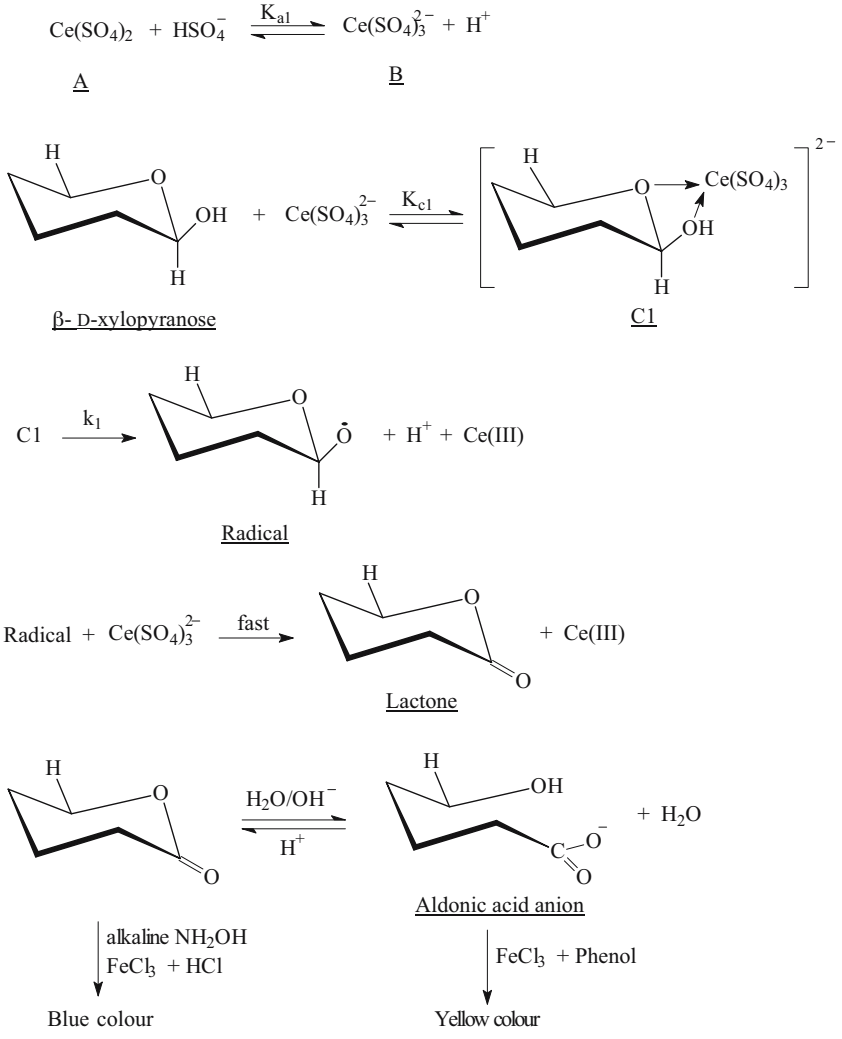
Scheme 1 Anomeric –OH in α- and β-xylose at axial and equatorial positions, respectively

xylose are present in axial and equatorial positions, respectively (Scheme 1).

It has also been established [23] that β-isomer should be more reactive than the α-isomer. On the other hand, different types of cerium(IV)-sulfato complexes such as $CeSO_4^{2+}$, $Ce(SO_4)_2$, $Ce(SO_4)_2HSO_4^-$, $CeH_3(SO_4)_4^-$, and $Ce(SO_4)_3^{2-}$, all present in sulfuric acid, have been proposed as the reactive species during the oxidation of organic substrates in this medium. To confirm the participation of different species, the effect of SO_4^{2-} ion was studied. The observed increase in k_{obs} with increase in $[SO_4^{2-}]$ (Table 3) indicates a sulfato complex of cerium(IV) to be the reactive species. Hardwick and Robertson [24] has observed that ca. 93% of cerium(IV) is present as $Ce(SO_4)_3^{2-}$ in 1 N H_2SO_4 and this species has been considered as the reactive species [6, 11, 12]. As addition of H_2SO_4 has produced a decreasing effect on k_{obs}, the inhibition may be explained as due to the removal of the reactive species either by shifting equilibrium (reaction (1)) to the left-hand side or by protonation of the reactive species. Based on the observations recorded above, a probable mechanism may be proposed for the low-acidity region, that is, $[H_2SO_4]$= 1.83 mol dm^{-3} (Scheme 2).

In Scheme 2, reaction (1) represents the conversion of the neutral Ce(IV) species into the anionic species in the presence of H_2SO_4. The second step is the complex formation between the reactive species of cerium(IV) and β-D-xylopyranose. The redox decomposition of this complex C1 in the subsequent rate-determining step gives rise to a free radical and Ce(III) (reaction (3)). The lactone will

Scheme 2 Probable mechanism for the low acidity region



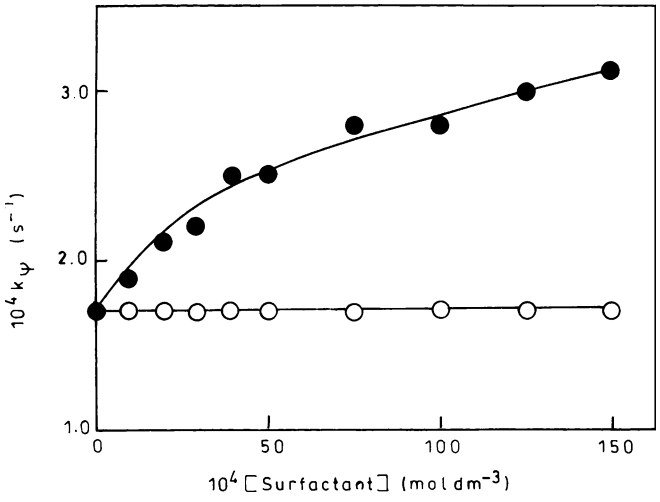


Fig. 4 Effect of [surfactant] (CTAB (●) and SDS (○)) on rate constant (k_ψ). Reaction conditions: [Ce(IV)]=1.0×10^{-3} mol dm^{-3}, [H_2SO_4]=1.83 mol dm^{-3}, [D-xylose]=4.0×10^{-2} mol dm^{-3}, and temperature=313 K

be the oxidation product of D-xylose in accordance with reaction (4). The reactivity of lactone towards the oxidant is higher in comparison to the corresponding monosaccharides. This was the main reason for the complex kinetic behavior of the reaction (*vide supra*).

According to Scheme 2, the overall reaction rate is given by Eq. (1):

$$k_{obs1} = \frac{k_1 K_{c1}[\mathrm{D-xylose}]}{\left([\mathrm{H^+}]/K_{a1}\left[\mathrm{HSO_4^-}\right] + 1\right)} \quad (1)$$

Eq. (1) is reduced to Eq. (2) because the equilibrium in reaction (1) lies well to right due to which $1 >> [\mathrm{H^+}]/K_{a1}\left[\mathrm{HSO_4^-}\right]$,

$$k_{obs1} = k_1 K_{c1}[\mathrm{D-xylose}] \quad (2)$$

Eq. (2) may well explain the observed first-order dependence on [D-xylose].

Reaction in the presence of surfactants

The influence of both anionic (SDS) and cationic (CTAB) micelles on the reaction rate was studied. The effect of adding different amounts of SDS to a solution containing constant [Ce(IV)]=1.0×10^3 mol dm^3, [H_2SO_4]=1.83 mol dm^{-3} and [D − xylose]=4.0×10^2 mol dm^3 was seen at 313 K (Fig. 4). The observation of anionic SDS micelles producing no effect on the reaction rate is understandable in view of the electrostatic repulsion between the anionic head group of SDS micelles and the negatively charged reactive species of cerium(IV).

Rate constant increase with increase in [CTAB] (Table 5, Fig. 4) indicates incorporation/association of the reactants into or on the surface of the CTAB micelles. The negatively charged reactive species of cerium(IV) may form ion pairs with the positively charged CTAB micelles resulting in an increase in the effective concentration of cerium(IV) within a small volume. It has also been established that micelles can cause change of mechanism of reactions. Therefore, to confirm the mechanism in micellar medium, several kinetic experiments were also performed at constant [CTAB] (=50.0×10^{-4} mol dm^{-3}) with varying [Ce(IV)] (Table 1), [D-xylose] (Table 2, Fig. 2), [H_2SO_4] (Table 3), and temperature (Table 4). The results indicate that the dependence on each variable in the presence of CTAB micelles is the same as in aqueous medium. Thus, the reaction proceeds through the same mechanism in aqueous as well as in CTAB medium. A lower value of activation energy (Table 4) clearly suggests the catalytic behavior of CTAB micelles by providing a new reaction path.

Several models have been proposed to explain the catalysis of rate in the presence of micelles [25–29]. The variation of rate constant with surfactant is treated on the assumption that the substrate (Ce(IV)) is distributed between the aqueous and micellar pseudophases as given in Scheme 3 (where $(Ce(IV))_m$ is the micellized cerium(IV), $[D_n]$=[surfactant]$_T$−cmc, k_w and k_m are first-order rate constants in aqueous and micellar pseudophases, respectively, and K_s is micelle-cerium(IV) binding constant).

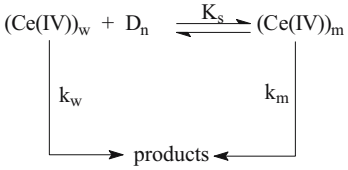
According to Scheme 3, the rate law may be expressed as

$$k_\psi = \frac{k_w + k_m K_s[D_n]}{1 + K_s[D_n]} \quad (3)$$

Table 5 Effect of [CTAB] on the pseudo first-order rate constant for the oxidation of [D-xylose] (=4.0×10^{-2} mol dm^{-3}) by cerium(IV) (=1.0×10^{-3} mol dm^{-3}) in H_2SO_4 (=1.83 mol dm^{-3}) at 313 K

10^4 [CTAB] (mol dm^{-3})	0	10	20	30	40	50	75	100	125	150
$10^4 k_\psi$ (s^{-1})	1.7[a]	1.9	2.1	2.2	2.5	2.5	2.8	2.8	3.0	3.1
$10^4 k_{\psi cal}$ (s^{-1})		1.8	2.1	2.3	2.5	2.6	2.8	2.9	3.0	3.0
$\frac{k_\psi - k_{\psi cal}}{k_\psi}$		+0.05	0.00	−0.05	0.00	−0.04	0.00	−0.04	0.00	+0.03

[a]Taken as k_w [25–29]



Scheme 3 Distribution of cerium (IV) in aqueous and micellar pseudophases

which, on rearrangement, gives Eq. (4)

$$\frac{1}{(k_w - k_\psi)} = \frac{1}{(k_w - k_m)} + \frac{1}{(k_w - k_m)K_s[D_n]} \quad (4)$$

According to Eq. (4), the plot of $1/(k_w - k_\psi)$ vs $1/[D_n]$ should be linear. In our study, the plot is linear (Fig. 5), suggesting validity of this model. The values of K_s and k_m (calculated from the slope and intercept) were found to be 257 mol^{-1} dm^3 and 3.4×10^{-4} s^{-1}, respectively. From the values of K_s, k_m and $[D_n]$, $k_{\psi\,cal}$ was obtained using Eq. (3) and this was in good agreement with the observed k_ψ .

Probable reaction site

Micellar pseudophases has different properties (varying degree of water activity, the microenvironment, hydrophobicity and polarity of the micellar pseudophase). Therefore, the exact reaction site for a micelle-mediated reaction cannot be proposed. Only the localization of the reactant(s) can be considered. Though hydrophobicity of D-xylose is diminished (due to the presence of four hydrophilic –OH groups), its incorporation into the micellar pseudophase cannot be ruled out because the Stern layer is water-rich. The positive catalytic effect of CTAB micelles indicates that the anionic species of cerium(IV) may get associated into the Stern layer through electrostatic interaction with the positive head group of the CTAB micelles. ($Ce(SO_4)_3^{2-}$ may form an ion pair with $-N^+(CH_3)_3$). Thus, we assume that the catalytic behavior of CTAB micelles is caused by the inclusion of the reactants into the Stern layer. As the reaction proceeds through the formation of a complex (Scheme 2, reaction (2)), the associated $Ce(SO_4)_3^{2-}$ forms an intermediate with the anomeric –OH of D-xylose. The micelles thus

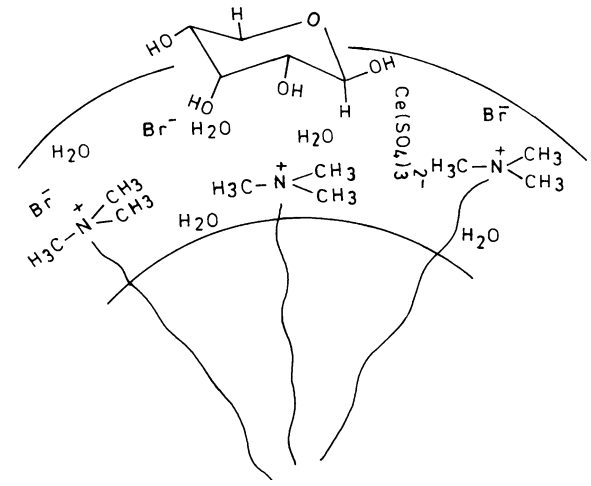


Fig. 6 Probable reaction site for the oxidation of D-xylose by cerium(IV) in the presence of CTAB

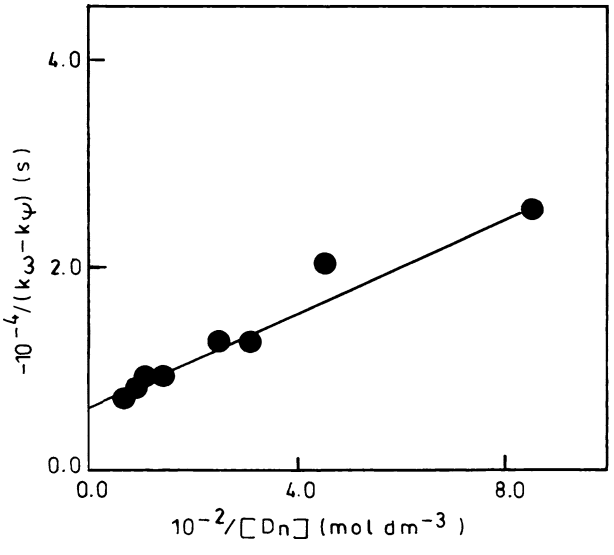


Fig. 5 Plot of $1/(k_w - k_\psi)$ vs $1/[D_n]$ for the Ce(IV)+D-xylose redox reaction in CTAB. Reaction conditions were the same as in Fig. 4

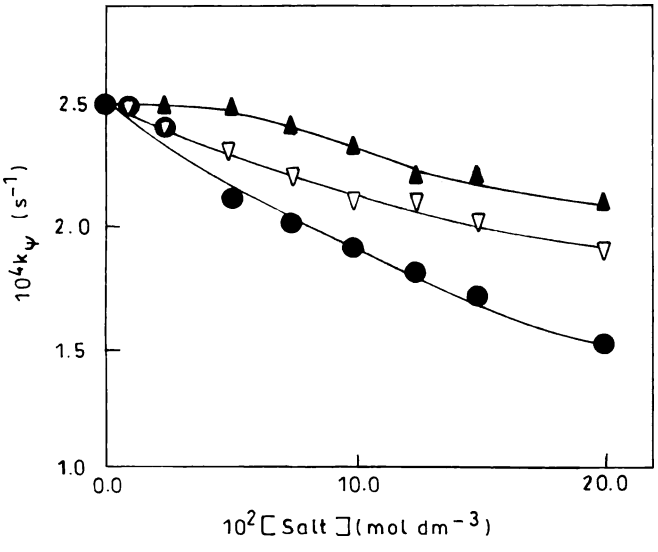


Fig. 7 Effect of inorganic electrolytes [Na_2SO_4 (●), $NaNO_3$ (▽), and NaCl (▲)] on rate constant (k_ψ). Reaction conditions were the same as in Fig. 4 with [CTAB]=50.0×10^{-4} mol dm^{-3}

help in bringing the reactants together which may now orient in a manner suitable for complex formation (see Fig. 6, which shows the probable reaction site to be the Stern and Gouy–Chapman layers' junctural region).

Salt effect

A series of kinetic runs were carried out to see the role of inorganic electrolytes (Na_2SO_4, $NaNO_3$, and NaCl) in the CTAB-catalyzed oxidation of D-xylose by cerium(IV). It was observed that the added salts inhibit the rate of reaction (Fig. 7). Each anion is an inhibitor and the inhibitory power increases in the order: $SO_4^{2-} > NO_3^- > Cl^-$. As the concentration of these electrolytes increases, the concentration of cerium(IV) at the reaction site (Fig. 6) decreases due to the salting out nature of these salts (the counterions of the added salts compete with $Ce(SO_4)_3^{2-}$ for the CTAB head group region). Our kinetic salt effect thus suggests that some additional factors than changes in micellar size and shape will be involved in the present system.

References

1. Richardson W (1965) In: Wiberg KB (ed) Oxidation in organic chemistry. Academic, New York, p 244
2. Wiberg KB, Ford PC (1969) J Am Chem Soc 91:124
3. Young LB, Trahanovsky WS (1969) J Am Chem Soc 91:5060
4. Pottenger CR, Johnson DC (1970) J Polym Sci A-1 8:301
5. Butterworth RF, Hanessian S (1971) Synthesis 70
6. Mehrotra RN, Amis ES (1974) J Org Chem 39:1788
7. Krupenskii VI (1978) Zh Obsch Khim 48:2228
8. Virtanen POI, Lindroos R, Oikarinen E, Vaskuri J (1987) Carbohydr Res 167:29
9. Sen Gupta KK, Sen Gupta S, Mahapatra A (1989) J Carbohydr Chem 8:713
10. Sen Gupta KK, Sen Gupta S, Mandal SK, Mahapatra A (1990) J Chem Res (S):60
11. Kabir-ud-Din, Ali MS, Khan Z (2005) Colloid Polym Sci 284:10
12. Kabir-ud-Din, Ali MS, Khan Z (2006) Int J Chem Kinet 38:18
13. Khan Z, Kabir-ud-Din (1999) Int J Chem Kinet 31:409
14. Khan Z, Kabir-ud-Din (2000) Indian J Chem 39A:522
15. Kabir-ud-Din, Morshed AMA, Khan Z (2003) J Carbohydr Chem 22:835
16. Sen Gupta KK, Begum BA, Pal BB (1998) Carbohydr Res 309:303
17. Khan Z, Babu PSS, Kabir-ud-Din (2004) Carbohydr Res 339:133
18. Capon B (1969) Chem Rev 69:407
19. Pare B, Pipada M, Choube A, Bhagwat VW (2003) Oxid Commun 26:95
20. Khan Z, Raju, Akram M, Kabir-ud-Din (2004) Int J Chem Kinet 36:359
21. Mathlouthi M, Luu DV (1980) Carbohydr Res 78:225
22. Rudrum M, Shaw DF (1965) J Chem Soc 52
23. Perlin AS (1964) Can J Chem 42:2365
24. Hardwick TJ, Robertson E (1951) Can J Chem 29:818
25. Menger FM, Portnoy CE (1967) J Am Chem Soc 89:4698
26. Bunton CA, Fendler EJ, Sepulveda L, Yang K-U (1968) J Am Chem Soc 90:5512
27. Fendler JH, Fendler EJ (1975) Catalysis in micellar and macromolecular systems. Academic, New York
28. Bunton CA (1979) Cat Rev Sci Eng 20:1
29. Bunton CA (1997) J Mol Liq 72:231