Colloid Polym Sci (2007) 285:745–752
DOI 10.1007/s00396-006-1610-8

ORIGINAL CONTRIBUTION

# Micelle-assisted cerium(IV) oxidation of L-sorbose in aqueous sulfuric acid

**Kabir-ud-Din · Mohd. Sajid Ali · Zaheer Khan**

Received: 23 July 2006 / Accepted: 19 October 2006 / Published online: 24 March 2007

**Abstract** Spectrophotometric kinetic technique has been used to investigate the effect of cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) surfactants on the redox reaction of cerium(IV)+L-sorbose in aqueous sulfuric acid media. The anionic SDS has no effect, whereas the reaction rate increases in the presence of cationic CTAB, which is due to favorable conditions provide by the cationic micelles. The reaction rate decreases with [$H_2SO_4$], and no acid-dependent path has been observed. At constant [$H_2SO_4$], the rate of the reaction is dependent on the first powers of the L-sorbose and cerium(IV) concentrations. The CTAB-assisted reaction is retarded by addition of electrolytes ($Na_2SO_4$, $NaNO_3$, and NaCl), which is attributed to the competition between electrolyte anions and cerium(IV)-sulfato species. Bromide ion (of CTAB or externally added in the form of NaBr) is not oxidized by the cerium(IV) (as a main or side reaction).

**Keywords** Anionic surfactant · Cationic surfactant · L-Sorbose · Oxidation · Cerium(IV) · Micelles · Catalysis

## Introduction

The products of oxidation of aldohexoses/ketohexoses depend on the nature of the oxidant used and other experimental conditions [1]. The oxidative degradation of organic and inorganic compounds with cerium(IV) are potentially interesting, as cerium(IV) is an unusually strong, one-electron oxidant ($E_o$=1.4 V in 1.0 mol dm$^{-3}$ $H_2SO_4$). Due to the specific coordination properties of cerium(IV), unique reactions of this ion can be expected. The kinetics of the oxidation of various monosaccharides by cerium(IV) has been reported on several occasions [2–9]. Surprisingly, no attempt seems to have been made to study the oxidation of simple sugars having ketonic group by cerium(IV) in the presence of surfactants. In continuation to our previous studies [9], L-sorbose is therefore selected to find out if the same mechanism is operative in this case too, as it operates in case of alcohols and ketones [10, 11].

## Experimental

### Materials

L-Sorbose (98%, Fluka, Switzerland), ceric ammonium nitrate (99%, Qualigens, India), sulfuric acid (98%, Merck, India), cetyltrimethylammonium bromide (CTAB, 99%; BDH, England), sodium dodecyl sulfate (SDS, 99%; Sigma, USA), sodium sulfate (98%, Merck), sodium nitrate (99%, Merck), 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, $1.5\times10^{-5}$ $\Omega^{-1}$ cm$^{-1}$).

### Kinetic measurements

Each kinetic run was performed under pseudo first-order conditions using ≥tenfold excess of [L-sorbose] over [Ce (IV)]. A mixture containing appropriate amount of all the

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reactants (except L-sorbose) was thermally equilibrated at the desired temperature in a thermostat (±0.1 °C) and was rapidly added with a measured amount of the L-sorbose solution (pre-equilibrated at the same temperature). 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 a Bausch and Lomb Spectronic-20 spectrophotometer. The first-order rate constants in the absence ($k_{\mathrm{obs}}$, $s^{-1}$) and presence of surfactant ($k_\Psi$, $s^{-1}$) were computed from the initial linear parts of the plots of log(absorbance) versus time (Fig. 1a). Other details of the kinetic measurements were the same as described elsewhere [9, 12, 13].

Product identification and stoichiometry

Paper chromatography was used to identify the oxidation products of L-sorbose. The chromatographic solvent and detection reagent were *n*-butanol–acetic acid–water (4–1–5) and silver nitrate–NaOH–$Na_2S_2O_3$ [14]. The experiments indicated the presence of aldonic acid along with δ- and γ-lactones. The results were compared with the products of L-sorbose from oxidation by bromine and nitric acid. On the other hand, chromotropic acid was used as a specific reagent for the detection of HCHO. Stoichiometry of the L-sorbose oxidation by cerium(IV) was determined by spectroscopic titrations. The reaction was allowed to go to completion at 40 °C. The amount of unreacted cerium(IV) was determined at 385 nm. It was found that 3 mol of cerium(IV) oxidized 1 mol of L-sorbose. Due to the complicated kinetic feature of the reaction (Fig. 1), the exact stoichiometry of the reaction is difficult to predict [15, 16].

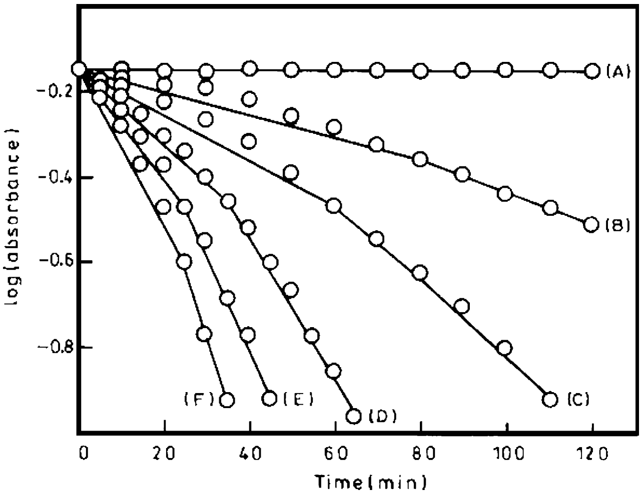


**Fig. 1** Plots of log(Absorbance) vs time for the oxidation of L-sorbose by cerium(IV) Reaction conditions: [Ce(IV)]=$1.0\times10^{-3}$ mol $dm^{-3}$, [$H_2SO_4$]=1.83 mol $dm^{-3}$, [L-sorbose]=0.0 (*A*), 1.0 (*B*), 2.0 (*C*) 4.0 (*D*), 6.0 (*E*) and $8.0\times10^{-2}$ (*F*), temperature=40 °C

Free radical detection

Acrylonitrile (monomer) was used for the identification of free radicals. In a typical experiment, reaction mixture containing [Ce(IV)]=$1.0\times10^{-3}$ mol $dm^{-3}$, [L-sorbose]=$4.0\times10^{-2}$ mol $dm^{-3}$, [$H_2SO_4$]=1.83 mol $dm^{-3}$, and acrylonitrile (=30% v/v) at 40 °C led to the formation of white polymeric product indicating in situ generation of free radicals [17].

Critical micelle concentration

The critical micelle concentration (CMC) of CTAB was determined under the experimental conditions by measuring the surface tension with a S. D. Hardson tensiometer (Kolkata, India) by the ring detachment method. The values under different experimental conditions are summarized in Table 1. It has been established that cationic surfactants show remarkable changes in their aggregation in $H_2SO_4$–water mixed solvent [18]. Our results of CMC decrease are in accord with the earlier observations of micelle formation at relatively low surfactant concentration with the rise of water content [19–21].

## Results and discussion

Reaction-time curve

As the plots deviate from linearity (Fig. 1), it is clear that the oxidation kinetics proceed in two stages, i.e., initial slow stage followed by a relatively faster step. The time at which deviation commenced was found to decrease with increase in [L-sorbose] (Fig. 1) and temperature. The second step is

**Table 1** Values of CMC of CTAB under different experimental conditions determined by surface tension measurements

| Solution[a] | $10^4$ CMC (mol $dm^{-3}$) |
|---|---|
| Water | 9.9 (8.0)[b] |
| Water + cerium(IV) | 2.2 |
| Water + L-sorbose | 9.1 |
| Water + $H_2SO_4$ | 0.21 (0.70)[c] |
| Water + cerium(IV) + $H_2SO_4$ + L-sorbose | 0.15 |

[a] [Ce(IV)]=$1.0\times10^{-3}$ mol $dm^{-3}$, [L-sorbose]=$4.0\times10^{-2}$ mol $dm^{-3}$, [$H_2SO_4$]=1.83 mol $dm^{-3}$, temperature=40 °C

[b] Literature value at 25 °C[d]

[c] Literature value at 25 °C in 1.0 mol $dm^{-3}$ $HNO_3$[d]

[d] Mukerjee P., Mysels K. J. Critical micelle concentration of aqueous surfactant systems, NSRDS-NBS 36. Superintendent of Documents, Washington, DC, 1971, p.107

considered as the autocatalysis, which is due to the catalytic role of one of the oxidation products. One possibility is that the oxidation rate of one of the oxidation products (lactone, whose concentration is small at lower [L-sorbose]) becomes perceptible and shows up at higher [reductant]. Sala et al. [22, 23] studied the oxidation of lactones and reported that the rates of their oxidation are at least tenfold higher in comparison to the corresponding monosaccharides.

### Dependence on [Ce(IV)]

The disappearance of cerium(IV) shows a first-order dependence on [Ce(IV)] under the experimental conditions of [L-sorbose]>>[Ce(IV)] (Table 2).

### Dependence on [L-sorbose]

At constant [Ce(IV)]=$1.0\times10^{-3}$ mol dm$^{-3}$ and [$H_2SO_4$]= 1.83 mol dm$^{-3}$, the effect of [L-sorbose] on $k_{obs}$ has been followed (Table 2). The plot of [L-sorbose] versus rate constant was linear with zero intercept indicating first-order dependence with respect to [L-sorbose] (Fig. 2).

### Dependence on [$H_2SO_4$] and $\left[HSO_4^-\right]$

The effect of acid concentration was studied by adding appropriate amounts of $H_2SO_4$. The rate constant decreased with increasing [$H_2SO_4$] (Table 2), indicating removal of the reactive species of cerium(IV). To confirm

**Table 2** Effect of [Ce(IV)], [L-sorbose], [$H_2SO_4$], and $\left[HSO_4^-\right]$ on the oxidation rate of L-sorbose by cerium(IV) in absence ($k_{obs}$) and presence ($k_\Psi$) of CTAB (=$50.0\times10^{-4}$ mol dm$^{-3}$) at 40 °C

| $10^3$ [Ce(IV)] (mol dm$^{-3}$) | [$H_2SO_4$] (mol dm$^{-3}$) | $10^2$[L-sorbose] (mol dm$^{-3}$) | $10^2\left[HSO_4^-\right]$ (mol dm$^{-3}$) | $10^4k_{abs}(s^{-1})$ | $10^4k_\Psi(s^{-1})$ |
|---|---|---|---|---|---|
| 0.6 | 1.83 | 4.0 | | 3.5 | 5.4 |
| 0.8 | | | | 3.7 | 5.1 |
| 0.9 | | | | 3.2 | 4.9 |
| 1.0 | | | | 3.4 | 5.0 |
| 1.1 | | | | 3.0 | 4.4 |
| 1.2 | | | | 2.7 | 4.2 |
| 1.3 | | | | 2.4 | 4.1 |
| 1.4 | | | | 2.4 | 4.0 |
| 1.6 | | | | 2.0 | 3.7 |
| 1.8 | | | | 2.1 | 3.3 |
| 1.0 | 0.73 | 4.0 | | 4.2 | turbidity |
| | 1.10 | | | 4.6 | turbidity |
| | 1.47 | | | 3.5 | turbidity |
| | 1.83 | | | 3.4 | 5.0 |
| | 2.20 | | | 2.9 | 4.1 |
| | 2.57 | | | 2.4 | 3.6 |
| | 2.94 | | | 2.1 | 3.2 |
| | 3.30 | | | 1.9 | 2.7 |
| | 3.67 | | | 1.5 | 2.6 |
| 1.0 | 1.83 | 1.0 | | 1.0 | 1.5 |
| | | 2.0 | | 2.0 | 3.0 |
| | | 3.0 | | 2.5 | 4.2 |
| | | 4.0 | | 3.4 | 5.0 |
| | | 5.0 | | 4.1 | 6.4 |
| | | 6.0 | | 4.9 | 7.1 |
| | | 7.0 | | 6.0 | 8.2 |
| | | 8.0 | | 6.9 | 9.5 |
| | | 9.0 | | 7.7 | 11.1 |
| 1.0 | 1.83 | 4.0 | 5.0 | 3.4 | |
| | | | 10.0 | 3.1 | |
| | | | 15.0 | 3.0 | |
| | | | 20.0 | 2.7 | |
| | | | 25.0 | 2.5 | |
| | | | 30.0 | 2.4 | |
| | | | 35.0 | 2.2 | |
| | | | 40.0 | 2.1 | |

the reactive species of cerium(IV), a series of kinetic runs were also performed at different $\left[HSO_4^-\right]$ (ranges from 0.0 to $40.0\times10^{-2}$ mol dm$^{-3}$) at constant [$H_2SO_4$] (1.83 mol dm$^{-3}$; ignoring the dissociation of $HSO_4^-$). The reaction rate is retarded by an increase in $\left[HSO_4^-\right]$ (Table 2). The retardation in the rate with the increasing $\left[HSO_4^-\right]$ suggests the removal of reactive species of cerium(IV).

### Dependence on $\left[SO_4^{2-}\right]$

It has been established that cerium(IV) forms a variety of complexes with $\left[SO_4^{2-}\right]$ [24–28]. Therefore, a series of kinetic runs was performed in the presence of varying amounts of $\left[SO_4^{2-}\right]$. It was observed that the rate increased with the increasing $\left[SO_4^{2-}\right]$. Under the conditions, [L-sorbose]=$4.0\times10^{-2}$ mol dm$^{-3}$, [Ce(IV)]=$1.0\times10^{-3}$ mol dm$^{-3}$, and [$H_2SO_4$]=1.83 mol dm$^{-3}$ at 40 °C, the values of rate constants were 3.4, 3.4, 3.5, 3.6, 3.7, $3.9\times10^{-4}$ s$^{-1}$ at $\left[SO_4^{2-}\right]$ values of 0.0, 1.0, 2.0, 4.0, 5.0, $10.0\times10^{-4}$ mol dm$^{-3}$, respectively, indicating involvement of Ce(IV)-sulfato species as the reactive species.

### Dependence on temperature

The effect of temperature on the rate of L-sorbose–cerium (IV) reaction is also seen (Table 3). The values of the energy, enthalpy, and entropy of activation, calculated from the Arrhenius and Eyring equations (Fig. 3), are listed in Table 3. High positive value of enthalpy of activation indicates that transition state is highly solvated. The negative value of $\Delta S^{\#}$ indicates the existence of compact activated state stabilized by a strong hydrogen bonding and large solvation in the electron transfer step. The negative entropy of activation is also a characteristic of rate limiting formation of an intermediate complex. In addition, a lower value of activation energy clearly suggests the catalytic role of CTAB (catalysts lower the activation energy and provide a new reaction path).

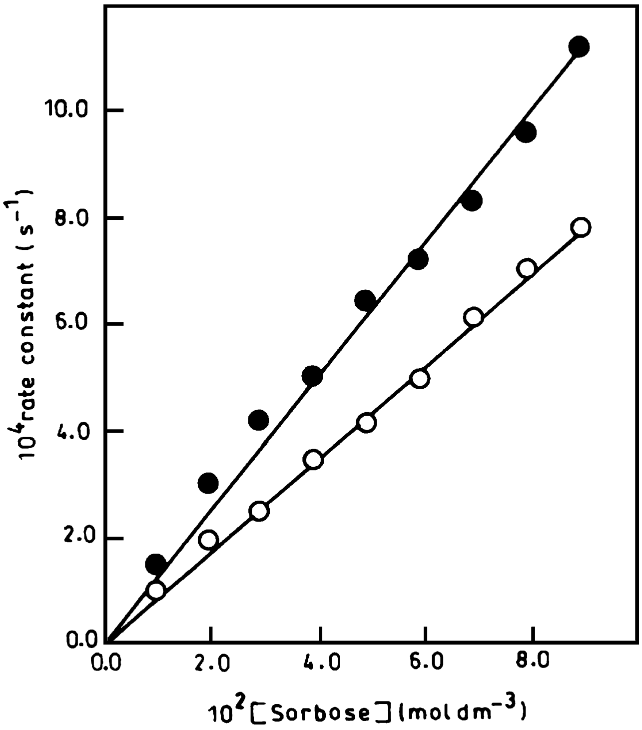


**Fig. 2** Effect of [L-sorbose] on the rate constant. Reaction conditions are [Ce(IV)]=$1.0\times10^{-3}$ mol dm$^{-3}$, [$H_2SO_4$]=1.83 mol dm$^{-3}$, [CTAB]=0.0 (*open circle*), $50.0\times10^{-4}$ mol dm$^{-3}$ (*filled circle*), and temperature=40 °C

### Dependence on [surfactant]

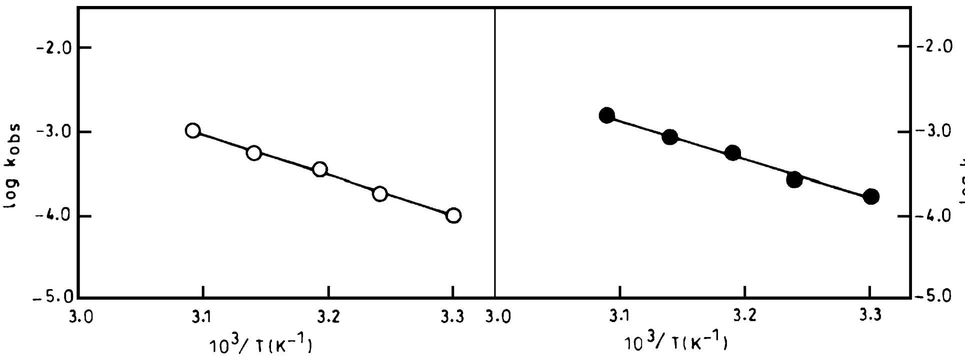
The effect of anionic (SDS) and cationic (CTAB) surfactants on the observed rate constants ($k_\Psi$) were seen by carrying out a series of kinetic runs at different [surfactant] with fixed [Ce(IV)], [L-sorbose], and [$H_2SO_4$] at 40 °C. The values are depicted graphically as $k_\Psi$ -[surfactant] profiles (Fig. 4). It is evident that CTAB produces a rate increasing effect in the entire range of its concentration used, whereas SDS has no effect. The results (Table 4) indicate incorporation/association of the reactants into or at the surface of cationic CTAB micelles. In case of SDS, there is a repulsion between the anionic head-group $\left(-OSO_3^-\right)$ and the reactive Ce(IV) species, whereas the latter may form an ion pair with the positive head group of CTAB micelles, and thus, an increase in the effective concentration of cerium(IV) within a small volume takes place. Furthermore, the partitioning of the L-sorbose in the micellar pseudophase cannot be ruled out because the Stern layer is water-rich (the water activity in the aqueous phase as well as in

**Table 3** Pseudo first-order rate constants, activation, and other parameters for the oxidation of L-sorbose by cerium(IV) in the absence and presence of CTAB ($50.0\times10^{-3}$ mol dm$^{-3}$)[a]

| Temperature (°C) | $10^4k_{\mathrm{obs}}(s^{-1})$ | $10^4k_{\psi}(s^{-1})$ |
|---|---|---|
| 30 | 1.0 | 1.7 |
| 35 | 1.8 | 2.4 |
| 40 | 3.4 | 5.0 |
| 45 | 5.6 | 8.4 |
| 50 | 9.8 | 13.4 |
| Parameters | | |
| $Ea$, kJ mol$^{-1}$ | 94.0 | 88.0 |
| $\Delta H^{\#}$, kJ mol$^{-1}$ | 91.0 | 86.0 |
| $\Delta S^{\#}$, J K$^{-1}$ mol$^{-1}$ | −22.0 | −37.0 |
| $K_s$, mol$^{-1}$ dm$^3$ | | 62.5 |
| $k_m$, s$^{-1}$ | | 8.4 |

[a] [Ce(IV)]=$1.0\times10^{-3}$ mol dm$^{-3}$,[$H_2SO_4$]=1.83 mol dm$^{-3}$, [L-sorbose]=$4.0\times10^{-2}$ mol dm$^{-3}$

**Fig. 3** Arrhenius plots for the oxidation of L-sorbose by cerium(IV). Reaction conditions are [Ce(IV)]=1.0×$10^{-3}$ mol $dm^{-3}$, [$H_2SO_4$]=1.83 mol $dm^{-3}$, [L-sorbose]=4.0×$10^{-2}$ mol $dm^{-3}$, [CTAB]=0.0 (*open circle*), 50.0×$10^{-4}$ mol $dm^{-3}$ (*filled circle*)



the micellar pseudophase is same) [29]. In the present case, the [$H_2SO_4$] is high but, keeping in mind the well-known fact that in presence of SDS micelles the effective local pH in the vicinity of the micellar surface is lower (about 2 units) [30], chances of $H^+$ inclusion in the Stern layer is high due to purely electrostatic interaction between $-OSO_3^-$ and $H^+$. As a result, partitioning of cerium(IV) into the micellar pseudophase is not possible.

The first-order rate constants ($k_\Psi$) for the cerium(IV) oxidation of L-sorbose were obtained over a range of concentrations of oxidant, L-sorbose, $H_2SO_4$, and temperature in the presence of CTAB (=50.0×$10^{-4}$ mol $dm^{-3}$) also. The results are given in Tables 2 and 3 and Figs. 2 and 3. First-order dependence was observed both for the oxidant and reductant with $H_2SO_4$ having the same effect (inhibition) as in the absence of surfactant. These observations undoubtedly show that the reaction mechanism in the presence of cationic surfactant remains the same as that in the homogeneous aqueous medium.

## Dependence on [electrolytes] in the presence of CTAB

The effect of added electrolytes on the rate were also explored because electrolytes, as additives, in micellar systems acquire a special place due to their ability to induce structural changes which may, in turn, modify substrate–surfactant interactions [31]. The observed data in presence of inorganic salts ($Na_2SO_4$, $NaNO_3$, and NaCl) are shown graphically in Fig. 5.

## Mechanism

In our study of micellar rate effects, CTAB is found to increase, whereas anionic SDS has no effect. This clearly indicates the involvement of a negatively charged species of cerium(IV) [attraction and repulsion, respectively, between the negatively charged Ce(IV) species and the head groups of the two types of surfactant micelles seemingly play important role in the present case].

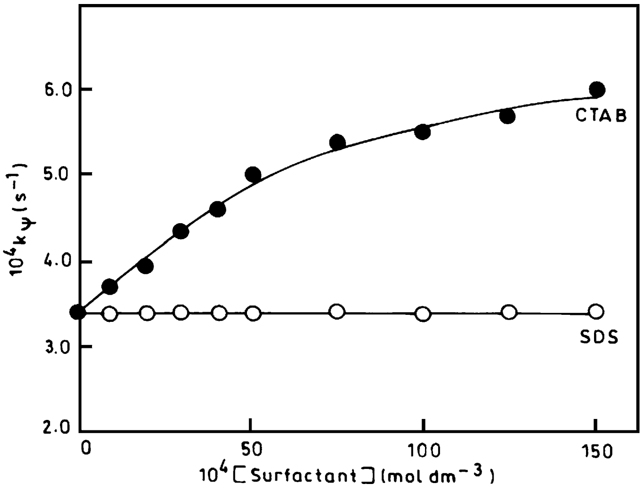


**Fig. 4** Effect of surfactants (SDS [*open circle*], CTAB [*filled circle*]) on $k_\Psi$. Reaction conditions are [Ce(IV)]=1.0×$10^{-3}$, [$H_2SO_4$]=1.83 mol $dm^{-3}$, [L-sorbose]=4.0 × $10^{-2}$ mol $dm^{-3}$, and temperature=40 °C

**Table 4** Effect of [CTAB] on the pseudo first-order rate constant for the oxidation of L-sorbose by cerium(IV) at 40 °C ([Ce(IV)]=1.0×$10^{-3}$ mol $dm^{-3}$, [L-sorbose]=4.0×$10^{-2}$ mol $dm^{-3}$, [$H_2SO_4$]=1.83 mol $dm^{-3}$)

| $10^4$ [CTAB] (mol $dm^{-3}$) | $10^4\,k_\psi(s^{-1})$ | $10^4\,k_{\psi cal}(s^{-1})$ | $\frac{(k_\psi - k_{\psi cal})}{k_\psi}$ |
|---|---|---|---|
| 0.0 | 3.4 | | |
| 10.0 | 3.7 | 3.7 | 0.00 |
| 20.0 | 3.9 | 3.9 | 0.00 |
| 30.0 | 4.3 | 4.2 | 0.02 |
| 40.0 | 4.6 | 4.4 | 0.04 |
| 50.0 | 5.0 | 4.6 | 0.08 |
| 75.0 | 5.6 | 5.0 | 0.07 |
| 100.0 | 5.5 | 5.3 | 0.04 |
| 125.0 | 5.7 | 5.6 | 0.02 |
| 150.0 | 6.0 | 5.8 | 0.03 |

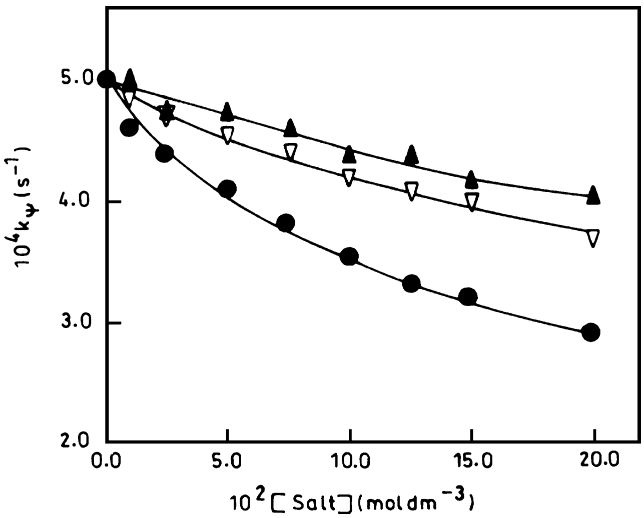


**Fig. 5** Effect of $Na_2SO_4$ (*filled circle*), $NaNO_3$ (*open inverted triangle*), and NaCI (*filled triangle*) on $k_\Psi$. Reaction conditions are the same as in Fig. 4 with [CTAB]=$50.0\times10^{-4}$ mol dm$^{-3}$

In aqueous solutions, L-sorbose mainly exists as cyclic hemiacetal, which is in dynamic equilibrium with acyclic form. It has been established that the pyranoid form is more reactive than the furanoid [32]. The rate of mutarotation ($\alpha-\text{sorbose} \rightleftharpoons \beta-\text{sorbose}$) is known to be acid-catalyzed, and under the experimental conditions, the mutarotation equilibrium is immediately attained. The β-form, having −OH group at C-1 at the equatorial position, is more reactive than the α-form (−OH axial) [33]. Intermolecular conversion of a monosaccharide into another through the ene–diol rearrangement in acidic medium does not interfere.

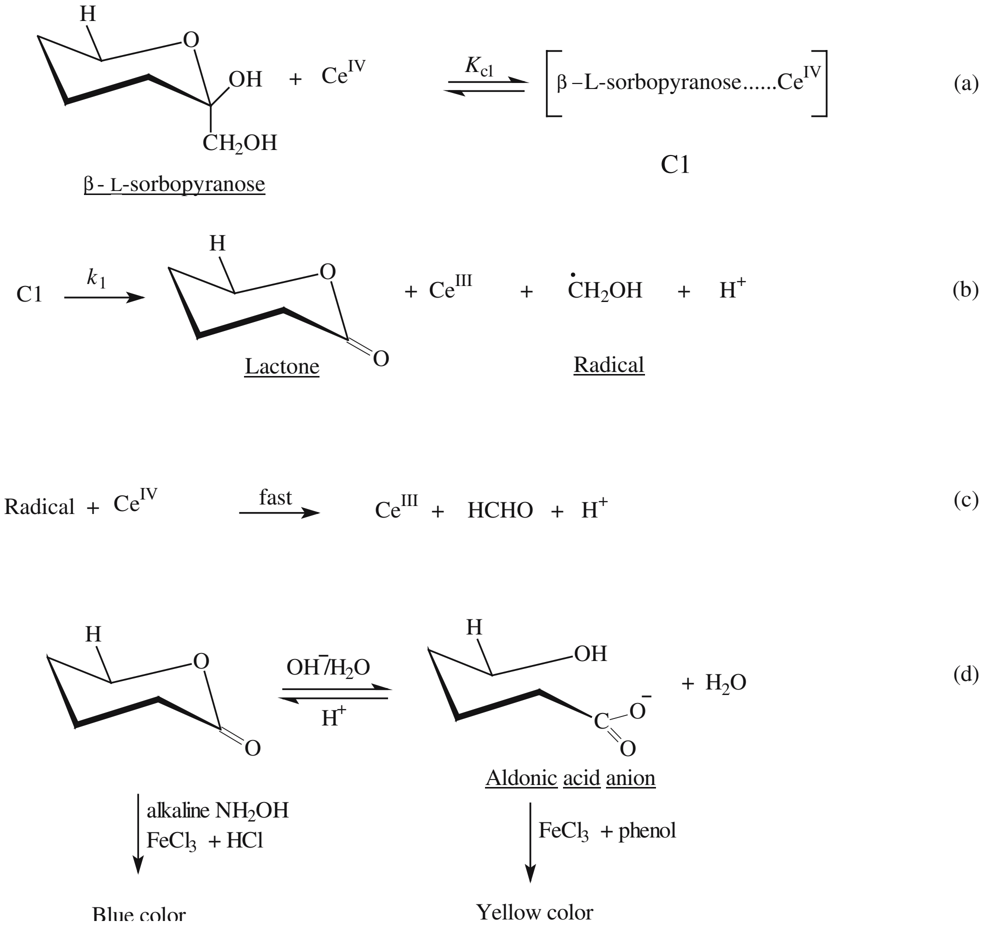
Reactions a to d in Scheme 1 are thus proposed to account for the oxidation of L-sorbose by cerium(IV) in $H_2SO_4$.

The rate law for this reaction scheme is

$$\frac{-d[\mathrm{Ce(IV)}]}{dt} = k_1 K_{c1}[\mathrm{L-sorbose}][\mathrm{Ce(IV)}] \tag{1}$$

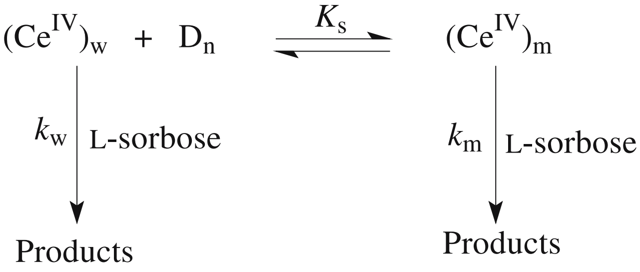
which very well accounts for the observed order in [Ce(IV)] and [L-sorbose]. As explained above, exact equation for observing the inverse-order kinetics each in [$H_2SO_4$] and $\left[HSO_4^-\right]$ cannot be derived due to the uncertainty of the involved protonic equilibrium producing the active Ce(IV) species.

**Scheme 1** Proposed mechanism of [Ce(IV)] and [L-sorbose] reaction



## Analysis of $k_\Psi$-[surfactant] profile

Let us now take into account the kinetic results obtained in the micellar system. For the analysis of observed micellar effects, the pseudophase model [34] can be considered as:



**Scheme 2** Pseudophase model of observed micellar effects

Here, $[Ce(IV)]_w$ and $[Ce(IV)]_m$ are the oxidants in aqueous and micellar pseudophase, respectively; $K_s$ is the binding constant with micellized surfactant ($D_n$), and $k_w$ and $k_m$ are the rate constants in aqueous and micellar medium. According to Scheme 2, the relevant expression for the observed rate constant is

$$k_\Psi = \frac{k_w + k_m K_s[D_n]}{1 + K_s[D_n]} \tag{2}$$

which can be modified to

$$\frac{1}{(k_w - k_\Psi)} = \frac{1}{(k_w - k_m)} + \frac{1}{(k_w - k_m)K_s[D_n]} \tag{3}$$

According to Eq. 3, a plot of the left-hand side versus $1/[D_n]$ should give a straight line with an intercept $[=1/(k_w-k_m)]$ and slope $[=1/(k_w-k_m)\,K_s]$, which can be used to obtain the values of $k_m$ and $K_s$ (Table 3). Interestingly, linearity in the plot of $1/(k_w-k_\Psi)$ versus $1/[D_n]$ was observed (Fig. 6), implying that Scheme 2 model is adequate for the oxidation of L-sorbose by cerium(IV) ($k_w=k_{obs}$, the first-order rate constant obtained in the absence of surfactant under similar experimental conditions; its value is $3.4\times10^{-4}$ s$^{-1}$; see Table 2).

Micelle mediated reactions occur either inside the Stern layer or at the interface between micellar and bulk water solvent. However, micellar mediated reactions are also found to occur at the interfacial junctural region of Stern and Gouy–Chapman layers. Micellar surfaces are water-rich [35]. Due to different properties of micellar pseudophase, it is not possible to precisely locate the exact site of reaction but, at least, localization of reactants can be considered. The main factor involved in the kinetic micellar effect is the increased concentration of reactants into a small volume through electrostatic and hydrophobic interactions. The chemically active species of cerium(IV) may associate through electrostatic interaction with the positive head group of CTAB micelles. The other reactant, L-sorbose, has no hydrophobicity due to the presence of 5-OH groups. As the reaction proceeds through the formation of a complex (Reaction a), associated Ce(IV) may form complex C1 at the junctural region [15, 16]. The complex may now orient in a manner suitable for continuing the reaction.

Table 5 summarizes the values of second order rate constants ($k^{II}$, mol$^{-1}$ dm$^3$ s$^{-1}$) for the reactivity of different monosaccharides with cerium(IV). These results indicate that the presence of −OH, −CHO, and ketonic groups increases the reducing power in the order aldohexoses<aldopentoses<ketohexoses. The trend shows that the oxidation by cerium(IV) seemingly depends on the number of −OH groups, stereochemistry, and the chelating ability of the monosaccharides. D-Fructose has greater tendency to reduce cerium(IV) in comparison to L-sorbose and other monosaccharides (L-sorbose>L-arabinose>D-xylose>D-mannose>D-glucose). It is interesting to note that the oxidation rate of various monosaccharides studied is of the same order. This means that these sugars are oxidized by a common mechanism; that is, cerium forms a complex with C-1 hydroxyl group of the sugar before its rate-limiting disproportionation to a free radical.

## Salt effect

It has been established that catalysis or inhibition factor is highly sensitive towards the concentration of added counterions. Figure 5 clearly indicates that all the added inorganic anions $\left(SO_4^{2-},\ NO_3^-, Cl^-\right)$ inhibit the CTAB-catalyzed

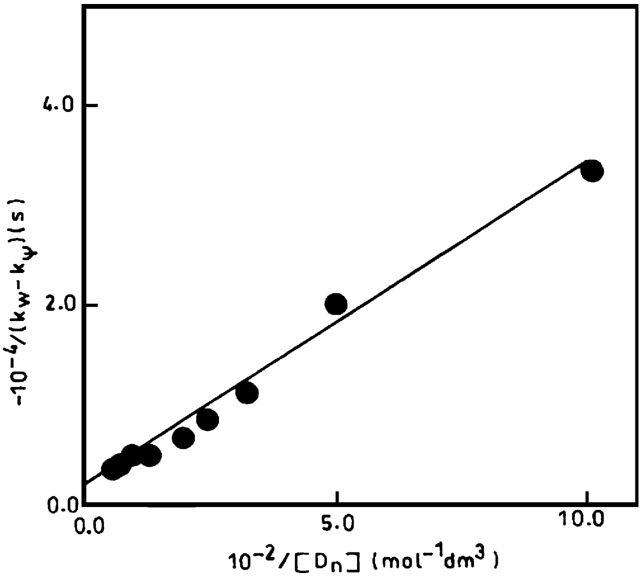


**Fig. 6** Plot of $1/(k_w-k_\Psi)$ versus $1/[D_n]$ for the reaction in CTAB. Reaction conditions are $[Ce(IV)]=1.0\times10^{-3}$ mol dm$^{-3}$, $[H_2SO_4]=1.83$ mol dm$^{-3}$, [L-sorbose]$=4.0\times10^{-2}$ mol dm$^{-3}$, and temperature=40 °C

**Table 5** Second-order rate constants for the oxidation of monosaccharides by cerium(IV) in the absence ($k^{\mathrm{II}}$) and presence $\left(k_{\Psi}^{\mathrm{II}}\right)$ of CTAB (=$50.0\times10^{-4}$ mol dm$^{-3}$)

| Monosaccharide[a] | $10^3\,k^{\mathrm{II}}\left(\mathrm{mol^{-1}\,dm^3\,s^{-1}}\right)$ | $10^3\,k_{\Psi}^{\mathrm{II}}\left(\mathrm{mol^{-2}\,dm^3\,s^{-1}}\right)$ | References |
|---|---|---|---|
| D-glucose | 2.8 | 4.3 | [36] |
| D-mannose | 3.8 | 6.0 | unpublished work |
| D-xylose | 4.2 | 6.3 | [37] |
| L-arabinose | 5.5 | 9.5 | [38] |
| L-sorbose | 8.5 | 12.5 | present work |
| D-fructose | 9.5 | 13.0 | [9] |

[a] [Monosaccharide]=$4.0\times10^{-2}$ mol dm$^{-3}$, [$H_2SO_4$]=1.83 mol dm$^{-3}$, [Ce(IV)]=$1.0\times10^{-3}$ mol dm$^{-3}$, temperature=40 °C

reaction, which may be due to the exclusion of reactive species from the reaction site. The added salts follow the expected retardation trend $k_{\Psi}\left(\mathrm{SO_4^{2-}}\right) < k_{\Psi}\left(\mathrm{NO_3^-}\right) < k_{\Psi}\left(\mathrm{Cl^-}\right)$.

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