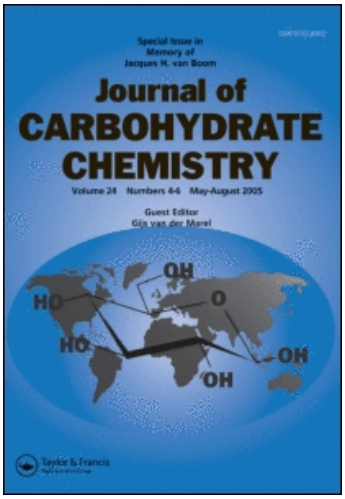

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Micellar Effects on the Oxidation of D-Glucose by Chromic Acid in Perchloric Acidic Medium

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ABSTRACT

Kinetics of the reaction between D-glucose and Cr(VI) in the absence and presence of surfactant micelles have been studied by a spectrophotometric method in aqueous-acidic solutions of perchloric acid. It was observed that the reaction has a non-autocatalytic followed by an autocatalytic pathway. The rate of the initial stage increases with increase in [glucose], [$HClO_4$] and temperature. Due to precipitation, the effect of cationic micelles of cetyltrimethylammonium bromide (CTAB) could not be studied whereas the oxidation is catalyzed by anionic micelles of sodium dodecyl sulfate (SDS) and nonionic micelles of Triton X-100 (TX-100). The results are discussed in terms of the *pseudo*-phase kinetic model. Activation parameters are evaluated and a mechanism consistent with the results is proposed. A rate law for the reaction has also been derived. The redox reaction occurs through a Cr(VI)→ Cr(IV) path.

Key Words: Kinetics; Oxidation; D-Glucose; Chromic acid; Micellar catalysis; Sodium dodecyl sulfate; Triton X-100; Cetyltrimethylammonium bromide.

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INTRODUCTION

Oxidation of sugars by different oxidants has attracted considerable interest. Of special interest is the reaction of glucose and its derivatives with chromium(VI), because it might be involved either in the development or the prevention of chromium(VI)-provoked cell malignancy. The metabolism of chromate, the dominant form of chromium(VI) in neutral aqueous solution, involves the generation of reactive intermediates which ultimately bind to cellular constituents and disrupt their function in the cell.[1,2]

Surfactants are amphipathic molecules having hydrophobic and hydrophilic properties. When these molecules are dissolved in water they can achieve segregation of their hydrophobic portions from the solvent by self-aggregation. The aggregation products, known as micelles, are responsible for altering the rates of organic reactions in aqueous-surfactant solutions. The addition of surfactants to mixtures of chemical reactants are considered in view of the following: first, to further understand factors that influence the rates and course of reactions; second, to gain additional insight into the exceptional catalysis characteristic of enzymatic reactions; third, to explore the utility of micellar systems for the purpose of synthesis.

We are continuing our investigations of micellar effects on the nucleophilic addition-elimination type ninhydrin-amino acid/metal amino acid complexes[3–10] and chromic acid oxidation of different organic reductants.[11–13] In these systems hydrophobic and electrostatic interactions of the reactants with the microenvironment provided by the micelles are exploited to achieve charge separation and storage effects.

Although the chromium(VI)/aldose reactions have been studied in acidic solutions,[14–19] the reactions in the presence of surfactants have attracted little attention.[20–24] Studies in micellar media are useful in understanding the mechanistic aspect and in suggesting the site of the reaction in micellar media; all these are expected to add a new dimension to the chromium(VI)-glucose interaction.

RESULTS AND DISCUSSION

Reaction in Absence of Surfactants

Reaction-Time Curve

The plots between the log(absorbance) versus time (Figure 1) indicate that the oxidative degradation of glucose consists of two separate phases. In the first phase, the reaction follows a nonautocatalytic reaction pathway (oxidation of glucose only). The second phase of the reaction is an autocatalytic pathway which may be due to the oxidation of glucose and of its oxidation product(s). The extent of the first phase depends on the [glucose], [$HClO_4$] and also on temperature; increase in either parameter decreases the nonautocatalytic path.

Determination of Rate Constants

The progress of the reaction was followed by monitoring decay in the [oxidant] at 360 nm. *Pseudo*-first-order rate constants (k_{obs} or k_{ψ}, s^{-1}) for the initial stages of the

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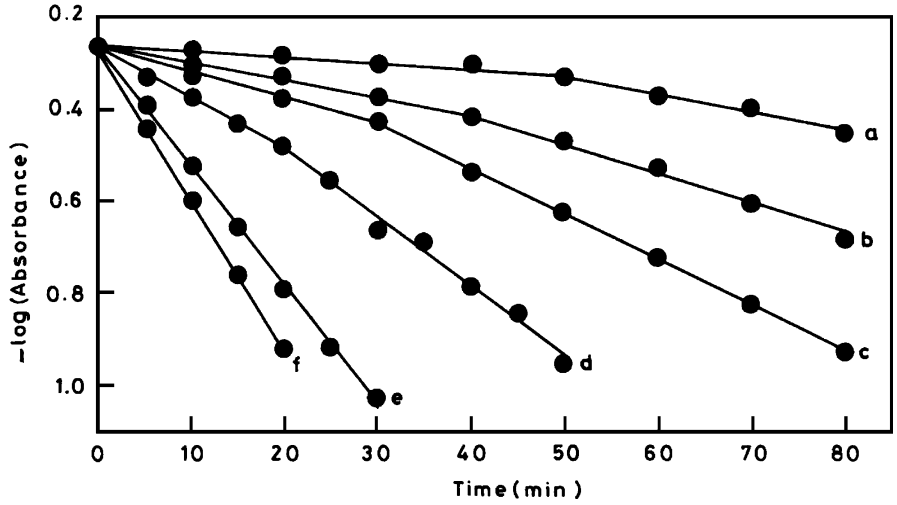

Figure 1. Plots of log(absorbance) versus time for the oxidative degradation of glucose (30.0×10^{-3} mol dm^{-3}) by chromic acid (4.0×10^{-4} mol dm^{-3}) at 60 °C; $[HClO_4] = 0.23$(a), 0.46(b), 0.58(c), 0.69(d), 0.93(e), 1.16 mol dm^{-3}(f).

reaction were obtained from slopes of the plots of log(absorbance) versus time (Figure 1). Reproducible results giving first-order plots (average correlation coefficient, $r \geq 0.992$) were obtained for each reaction run.

Rate Dependence on [Oxidant]

Table 1 summarizes the values of k_{obs} for various concentrations of oxidant at fixed [reductant] (= 30.0×10^{-3} mol dm^{-3}), $[HClO_4]$ (= 0.58 mol dm^{-3}) at constant temperature (= 60°C). The *pseudo*-first-order plots were linear which show that the reaction is first-order with respect to [Cr(VI)], i.e.,

$$v = -d[Cr(VI)]/dt = k_{obs}[Cr(VI)] \quad (1)$$

The Cr(VI) species is postulated to be H_2CrO_4.

Rate Dependence on [Reductant]

The order with respect to [glucose] was determined by studying the reaction at different glucose concentrations (range: $2.0–50.0 \times 10^{-3}$ mol dm^{-3}) and fixed [chromic acid] (= 4.0×10^{-4} mol dm^{-3}), $[HClO_4]$ (= 0.58 mol dm^{-3}) and temperature (= 60 °C). The results (Table 1) are shown graphically in Figure 2(a). A linear variation of log k_{obs} with log[glucose] was found (not shown) with slope = 0.56 ($r = 0.9841$) which indicates that the kinetic order for the [glucose] is fractional.

Rate Dependence on $[HClO_4]$

The effect of $[HClO_4]$ was studied at fixed [oxidant] (= 4.0×10^{-4} mol dm^{-3}) and [reductant] (= 30.0×10^{-3} mol dm^{-3}) at 60 °C. The nonautocatalytic pathway

Table 1. Effect of varying [Cr(VI)], [glucose], [$HClO_4$], [Mn(II)], and temperature on the oxidative degradation of glucose by chromium(VI) in the absence of surfactants.

10^4[Cr(VI)] mol dm^{-3}	10^3[Glucose] mol dm^{-3}	[$HClO_4$] mol dm^{-3}	[Mn(II)] mol dm^{-3}	Temp °C	10^4 k_{obs} s^{-1}
2	30	0.58		60	1.6
3					1.9
4					2.0
5					3.0
6					3.5
4	2	0.58		60	0.6
	5				0.8
	10				1.2
	15				1.5
	20				1.8
	30				2.0
	40				3.1
4	50				3.5
	30	0.58	0	60	2.0
			5		4.3
			10		5.0
			15		5.4
			20		6.0
			25		6.4
			30		8.4
			35		13.4
			40		17.3
			45		24.9
			50		29.0
4	30	0.11		60	0.4
		0.23			0.9
		0.34			1.4
		0.46			1.7
		0.58			2.0
		0.69			3.4
		0.93			not observed
		1.16			not observed
4	30	0.58		40	0.5
				50	0.9
				60	2.0
				70	3.6
				80	4.3

was found to decrease with increasing [$HClO_4$] which disappeared completely at [$HClO_4$] $\geq$ 0.93 mol dm^{-3} (Figure 1). Also, the rate of the autocatalytic path increased gradually with increasing [$HClO_4$]. The results indicate that $HClO_4$ catalyses both the nonauto- and autocatalytic pathways (Table 1). Plot of $logk_{obs}$ versus log[$HClO_4$] was linear with slope = 1.07 (r = 0.9875) indicating first-order dependence in [H^+].

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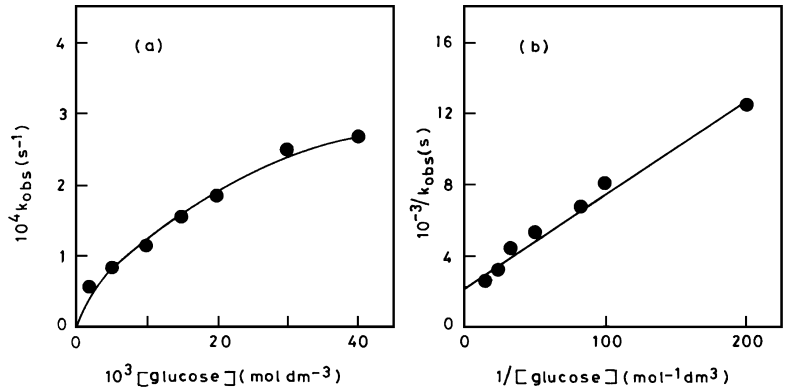

Figure 2. Effect of [glucose] on the rate of oxidative degradation of glucose by chromic acid (4.0×10^{-4} mol dm^{-3}) in $HClO_4$ (0.58 mol dm^{-3}) at 60 °C (a) and double-reciprocal plot between k_{obs} and [glucose] (b).

Rate Dependence on Temperature

A series of kinetic runs were carried out within the temperature range 303–353 K at fixed [oxidant] (= 4.0×10^{-4} mol dm^{-3}), [reductant] (= 30.0×10^{-3} mol dm^{-3}) and [$HClO_4$] (= 0.58 mol dm^{-3}). The values of k_{obs} were found to fit the equations:

$$k_{obs} = A \exp(-E_a/RT) \tag{2}$$

$$k_{obs} = (k_B T/h) \exp(\Delta S^{\#}/R) \exp(-\Delta H^{\#}/RT) \tag{3}$$

where the symbols have their usual meaning.

The Mechanism

Before a mechanism can be proposed, we must consider the species of the reactants that exist under the conditions used herein. Normally, chromic acid is involved in the following acid–base equilibria.[25,26]

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \tag{4}$$

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \tag{5}$$

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \tag{6}$$

$$H_2CrO_4 + H^+ \rightleftharpoons HCrO_3^+ + H_2O \tag{7}$$

The monomeric form ($HCrO_4^-$) predominates in dilute solution. It does not lose a proton until the pH is raised to ca. 7 but gains a second proton into a H_0 (Hammet acidity function) range of − 1 to − 3. Equilibria (6) and (7) are important, respectively, only at higher concentrations of chromic acid and in the presence of an acid in the

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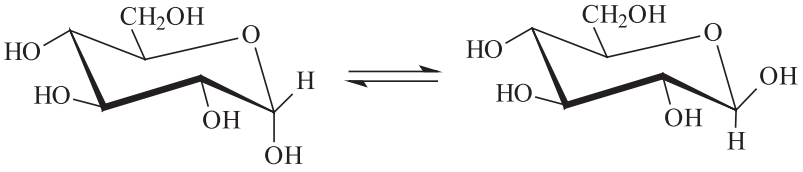
system. Thus, under our experimental conditions H_2CrO_4 seems to be the reactive species. Also, the aqueous solution of sugar is an equilibrium mixture of α- and β-anomers. Glucose is a polyhydroxyaldehyde and, in equilibrium, it mainly consists of α- and β-pyranose forms. The ratio of the α- and β-pyranose forms has been estimated from NMR studies at 30°C to be 36: 64 for D(+)-glucose.[27]



(8)

α–D-glucose β–D-glucose

The results mentioned above allow us to propose the following mechanism under the kinetic conditions used herein:

$$HCrO_4^- + H^+ \overset{K_p}{\rightleftharpoons} H_2CrO_4 \tag{9}$$

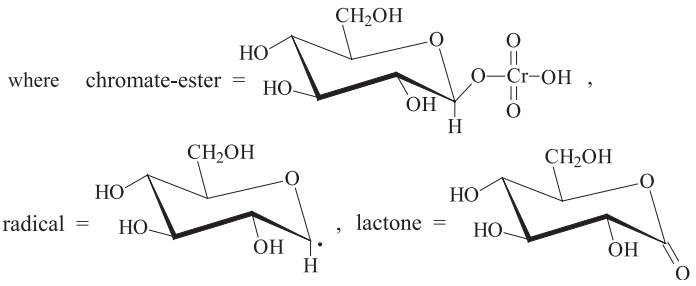
$$H_2CrO_4 + \underset{\underline{A}}{\text{glucose}} \overset{K_{csl}}{\rightleftharpoons} \underset{\underline{A1}}{\text{chromate} - \text{ester}} \tag{10}$$

$$A1 \overset{k_1}{\rightarrow} Cr(IV) + \text{lactone} \tag{11}$$

$$Cr(IV) + A \overset{\text{fast}}{\rightarrow} Cr(III) + \text{radical} \tag{12}$$

$$\text{radical} + H_2CrO_4 \overset{\text{fast}}{\rightarrow} Cr(V) + \text{lactone} \tag{13}$$

$$Cr(V) + A \overset{\text{fast}}{\rightarrow} Cr(III) + \text{lactone} \tag{14}$$



Scheme 1. Mechanism of the oxidative degradation of glucose by chromium(VI) in acidic medium.

It has been established in the oxidation of aldoses by metal ions that the anomer having OH-1 equatorial undergoes faster oxidation than the corresponding anomer

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having OH-1 axial.[28] Therefore, the reaction is presumed to follow the '*chromate-ester*' formation between the chromium(VI) and equatorial anomeric OH-1 of β-pyranose. The chromate-ester formation is similar to the oxidation of alcohols/α-hydroxy acids/carboxylic acids by chromium(VI).[11–13,29–31] In the rate-determining step, the 'chromate-ester' breaks leading to the formation of chromium(IV) and lactone. After the slow two-electron step (11), reactions (12–14) may follow (Scheme 1).

Sala et al.[32,33] studied the oxidation of lactones by chromium(VI) and reported that the rate of oxidation is at least 10-fold higher in comparison to the corresponding monosaccharides. They also suggested that, with excess chromium(VI), further oxidation of the lactone (formed in the rate determining step) occurs by abstraction of the α–H to yield the α–keto acid, preceding the decarboxylation process (Scheme 2).

$$\text{lactone} + Cr^{VI} \longrightarrow \text{-----} \longrightarrow Cr^{III} + \text{keto acid} \quad (15)$$

$$\text{keto acid} + Cr^{VI} \longrightarrow \text{-----} \longrightarrow Cr^{III} + CO_2 + \text{other products} \quad (16)$$

Scheme 2. Mechanism of oxidation of intermediates (lactone or keto acid) formed during the oxidative degradation of glucose by chromium(VI).

Thus, it is concluded that under the present kinetic conditions (non-autocatalytic/autocatalytic), the exact stoichiometry and product analysis cannot be predicted. The autocatalytic part may include oxidation of lactone and its oxidation product (keto acid, Eqs. 15 and 16). The rate law derived on the basis of Scheme 1 mechanism is written as:

$$\nu = \frac{-d[Cr(VI)]}{dt} = \frac{k_1 K_{es1} K_p [H^+][Cr(VI)]_T[\text{glucose}]}{1 + K_p[H^+] + K_{es1}K_p[H^+][\text{glucose}]} \quad (17)$$

which, on comparison with Eq. 1, gives Eq. 18

$$k_{obs} = \frac{k_1 K_{es1} K_p [H^+][\text{glucose}]}{1 + K_p[H^+] + K_{es1}K_p[H^+][\text{glucose}]} \quad (18)$$

On rearrangement, Eq. 18 can be written as Eq. 19

$$1/k_{obs} = B_1/[\text{glucose}] + B_2 \quad (19)$$

with $B_1 = (1 + K_p [H^+])/(k_1 K_{es1} K_p [H^+])$ and $B_2 = 1/k_1$. According to Eq. 19, a double-reciprocal plot between k_{obs} and [glucose] should be linear at constant $[H^+]$ with intercept = $1/k_1$ and slope = $(1 + K_p[H^+])/k_1 K_{es1}\ K_p[H^+]$. This has been found to be the case (Figure 2(b)). Another point of interest is that the mechanism satisfies the Michaelis–Menten reciprocal relationship and thus provides kinetic proof for complex formation. The values of k_1 and K_{es1} have been calculated as $5.0 \times 10^{-4}\ s^{-1}$ and 348 $mol^{-1}\ dm^3$, respectively, from the intercept and slope of the Figure 2(b) plot. Substituting the values of k_1, K_{es1}, K_p, $[H^+]$ and [glucose] in Eq. 18, k_{cal} have been obtained for various kinetic runs and compared with the experimentally determined values (k_{obs}) (Table 2). Agreement between most of the observed and calculated rate constant values provides supporting evidence to the proposed mechanism.

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Table 2. Comparison of k_{obs} and k_{cal} values for the oxidative degradation of glucose by chromium(VI).[a]

10^3 [Glucose] mol dm^{-3}	10^4 k_{obs} s^{-1}	10^4 k_{cal}[b] s^{-1}	$(k_{obs} - k_{cal})/k_{obs}$
2	0.6	0.3	+ 0.50
5	0.8	0.8	+ 0.00
10	1.2	1.3	− 0.08
15	1.5	1.7	− 0.13
20	1.8	2.1	− 0.16
30	2.0	2.5	− 0.25
40	3.1	2.9	+ 0.06
50	3.5	3.3	+ 0.06

[a]Conditions were the same as in Table 1.
[b]Calcd. using Eq. 18.

Rate Dependence on Mn(II)

Mn(II) is known to act as a trap for Cr(IV), if formed, in the rate determining step of the oxidation of organic compounds by Cr(VI).[34,35] In such a case, the oxidation rate is known to decrease by half. The rate data for the effect of Mn(II) are summarized in Table 1. It can be seen that the rate increases by increasing the [Mn(II)]. This rules out the possibility of formation of Cr(IV) in the rate determining step in the presence of Mn(II). Scheme 1 is, therefore, modified as Scheme 3, which is an example of a one-step three-electron reduction of Cr(VI) to Cr(III) without involvement of Cr(IV) as an intermediate.

$$\underset{\underline{A}}{\text{D-glucose}} + \text{Mn}^{II} \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \underset{\underline{A2}}{\text{D-glucose---Mn(II)}^{-+}} \quad (20)$$

$$\underset{\underline{A2}}{A2} + \underset{}{H_2CrO_4} \overset{K'_{es}}{\rightleftharpoons} \underset{\underline{A3}}{A2\text{—chromium(VI)}} \quad (21)$$

$$\underset{}{A3} \xrightarrow{k'} \underset{}{Cr^{III}} + \underset{}{Mn^{III}} + \underset{}{\text{lactone}} \quad (22)$$

Scheme 3. Mechanism of the oxidative degradation of glucose by chromium(VI) in presence of Mn(II).

After the slow step, following reactions may take place (Scheme 4).

In Scheme 3, the first step represents formation of a complex (A2) between glucose and Mn(II) because polyhydroxylated compounds are known to interact strongly with metal ions. The formation of a complex between D-gluconic acid and Mn(II) has been reported.[36] Complex A2 then forms chromate-ester (A3) with chromium(VI). The equilibrium between β-anomer and Mn(II) is fast. In the presence of chromium(VI), the equilibrium shifts towards the right-hand side because A2 is consumed and gets converted to A3. As the reaction proceeds, the equilibrium involving K'_{es} also

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$$Mn^{III} + A \longrightarrow Mn^{II} + \text{lactone} \quad (23)$$

or

$$2Mn^{III} + 2H_2O \longrightarrow Mn^{II} + MnO_2 + 4H^+ \quad (24)$$

$$Mn^{IV} + A \longrightarrow Mn^{II} + \text{lactone} \quad (25)$$

or

$$2Mn^{III} \longrightarrow Mn^{II} + Mn^{IV} \quad (26)$$

Scheme 4. Probable participation of Mn(III) in the glucose oxidation by chromium(VI).

shifts in the forward direction. In analogy to our previous studies,[12,13] we assume that A3 decomposes by a one-step, three-electron oxidation-reduction mechanism directly to chromium(III); one of the electrons transferred is given by the manganese atom and the other two by the glucose.

Reaction in the Presence of Cationic CTAB Micelles

Attempts were first made to see the role of cationic micelles on the oxidation of glucose by chromium(VI). Addition of cationic CTAB (= 10.0×10^{-4} mol dm^{-3}) to a solution of the reaction mixture containing [glucose] = 30.0×10^{-3} mol dm^{-3} and [$HClO_4$] = 0.58 mol dm^{-3} resulted in a white precipitate at room temperature ($\sim$ 25°C); this indicated that the effect of cationic CTAB micelles cannot be studied.

Reaction in the Presence of Anionic SDS and Non-ionic TX-100 Micelles

The effect of varying the surfactant concentrations upon the oxidation rate of glucose (= 30.0×10^{-3} mol dm^{-3}) by chromium(VI) (= 4.0×10^{-4} mol dm^{-3}) in presence of $HClO_4$ (= 0.58 mol dm^{-3}) was studied at a fixed temperature (60 °C).

Reaction–Time Curve

Figure 3 shows examples of the kinetic curves from which the k_ψ (s^{-1}) for the oxidation were evaluated. Once again it is clear that the oxidation kinetics proceed in two steps and that seemingly the same mechanism is being followed both in aqueous (vide supra) and in aqueous-surfactant media. Also, the time at which the deviation from linearity in the plots of log (absorbance) versus time (two-step reaction) commenced was found to decrease with increase in [surfactant] (Figure 3). Seemingly, the nonautocatalytic step oxidation becomes fast at higher [surfactant]. Therefore, the effect of [surfactant] (Table 3) was seen up to concentrations where both steps could be seen because at this stage we are interested only in the initial stage oxidation (the first step) of glucose.

Rate Dependence on Variables

To see the effects of [oxidant], [reductant], [$HClO_4$], temperature, and to further confirm the mechanism, a series of kinetic runs were performed at constant [surfactant].

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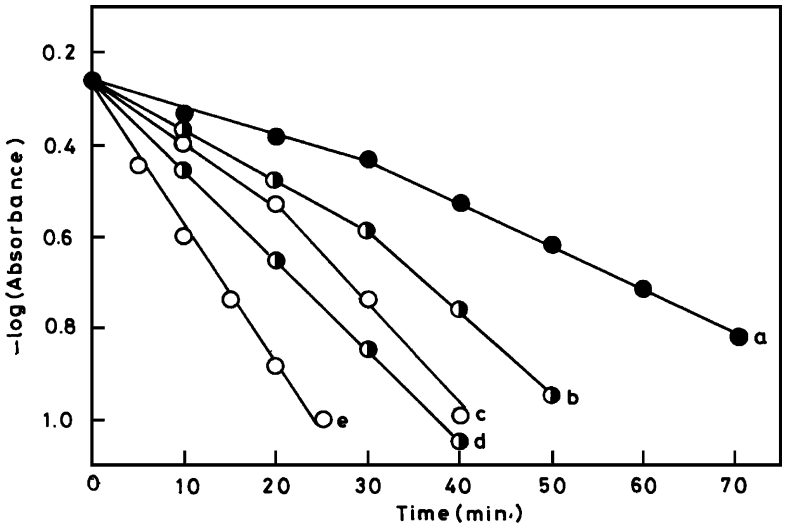

Figure 3. Effect of [surfactant] on the plot of log(absorbance) versus time for the oxidative degradation of glucose by chromic acid; [SDS] = 0.0 (a), 26×10^{-3} (b), 208×10^{-3} mol dm^{-3} (d); [TX-100] = 67×10^{-3} (c), 201×10^{-3} mol dm^{-3} (e). Conditions were the same as in Figure 1(c).

The k_ψ-values, obtained as a function of different variables, are summarized in Tables 4 and 5. The behavior upon variation of [Cr(VI)], [glucose], [$HClO_4$], and [Mn(II)] at constant [surfactant] was identical to the aqueous medium results which shows that the reaction mechanism in the presence of anionic and non-ionic micelles remains the same as that of the aqueous medium.

Table 3. Effect of varying [SDS] and [TX-100] on the oxidative degradation of glucose (30.0×10^{-3} mol dm^{-3}) by chromium(VI) (4.0×10^{-4} mol dm^{-3}) in $HClO_4$ (0.58 mol dm^{-3}) at 60 °C.

10^3 [SDS] mol dm^{-3}	10^4 k_ψ s^{-1}	10^4 $k_{\psi cal}$ s^{-1}	10^3[TX-100] mol dm^{-3}	10^4 k_ψ s^{-1}	10^4 $k_{\psi cal}$ s^{-1}
4.3	2.2	–	1.0	2.1	–
8.0	2.4	–	2.2	2.3	–
10.0	2.5	–	4.4	2.7	2.9
13.0	2.6	2.4	8.8	2.8	3.4
17.0	2.7	2.7	12.0	3.2	3.7
22.0	2.8	2.8	16.8	3.4	3.9
26.0	2.8	3.2	23.0	3.6	4.3
34.0	2.9	3.2	33.6	3.8	3.6
40.0	3.0	3.1	40.0	4.0	4.0
			50.0	4.2	–
			58.0	4.4	–
			67.0	5.1	–

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Table 4. Effect of varying [Cr(VI)], [Glucose], [$HClO_4$], [Mn(II)], and temperature on the oxidative degradation of glucose by chromium(VI) in the presence of anionic SDS micelles (26.0×10^{-3} mol dm^{-3}).

10^4 [Cr(VI)] mol dm^{-3}	10^3 [Glucose] mol dm^{-3}	[$HClO_4$] mol dm^{-3}	[Mn(II)] mol dm^{-3}	Temp °C	10^4 k_{obs} s^{-1}
2	30	0.58		60	2.0
3					2.7
4					2.8
5					3.5
6					4.3
4	2	0.58		60	1.1
	5				1.7
	10				2.1
	15				2.5
	20				2.6
	30				2.8
	40				4.1
	50				4.5
4	30	0.58	0		2.8
			5		3.5
			10		3.8
			15		4.3
			20		4.7
			25		5.6
			30		6.8
			35		8.2
			40		15.3
			45		17.5
			50		19.9
4	30	0.11		60	0.8
		0.23			1.1
		0.34			1.9
		0.46			2.3
		0.58			2.8
		0.69			4.1
		0.93			not observed
		1.16			not observed
4	30	0.58		30	0.3
				40	1.5
				50	1.9
				60	2.8
				70	4.1
				80	7.7

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Table 5. Effect of varying [Cr(VI)], [Glucose], [$HClO_4$], [Mn(II)], and temperature on the oxidative degradation of glucose by chromium(VI) in the presence of non-ionic TX-100 micelles (67.0×10^{-3} mol dm^{-3}).

10^4 [Cr(VI)] mol dm^{-3}	10^3 [Glucose] mol dm^{-3}	[$HClO_4$] mol dm^{-3}	[Mn(II)] mol dm^{-3}	Temp °C	10^4 k_{obs} s^{-1}
2	30	0.58	0	60	3.5
3					3.8
4					5.1
5					5.6
6					6.0
4	2	0.58		60	2.2
	5				2.9
	10				4.0
	15				4.2
	20				4.6
	30				5.1
	40				5.6
	50				5.8
4	30	0.58	0		5.1
			5		5.5
			10		6.0
			15		6.7
			20		13.8
			25		14.4
			30		14.6
			35		18.9
			40		21.5
			45		25.6
			50		26.3
4	30	0.11		60	1.1
		0.23			2.3
		0.34			3.2
		0.46			4.2
		0.58			5.1
		0.69			7.2
		0.93			not observed
		1.16			not observed
4	30	0.58		30	0.7
				40	1.3
				50	2.4
				60	5.1

Analysis of the k_ψ—[Surfactant] Profiles

The observed *pseudo*-first order rate constants, k_ψ are also shown graphically in Figure 4 as the rate constant–[surfactant] profiles. Interestingly, we see that the anionic SDS micelles produce a moderate catalytic effect in the entire concentration range used while the same micelles show no effect on the oxidation of oxalic and glycolic acids by chromic acid.[12,13] The observed data reveal a nearly one-fold increase in k_ψ with the

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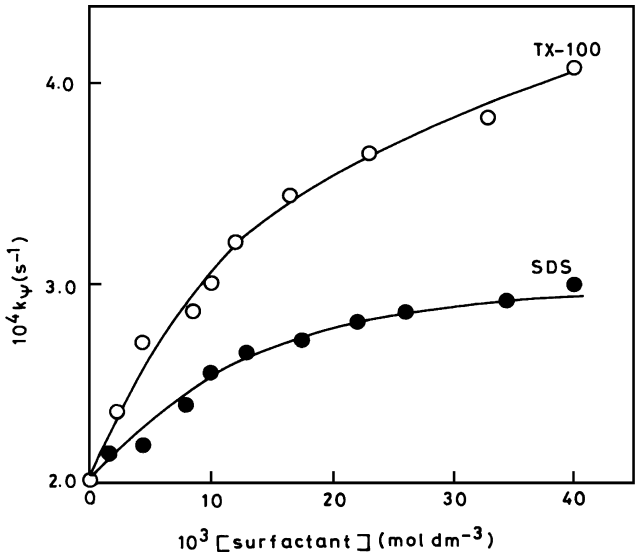

Figure 4. Rate constant–[surfactant] profiles for the oxidative degradation of glucose by chromic acid. Conditions were the same as in Figure 1(c).

increase in [SDS] from 0.0 to 40.0×10^{-3} mol dm^{-3}. Similar observations were obtained in the presence of TX-100, with about a two-fold increase in k_ψ.

To explain the catalytic/inhibitory effect of surfactants on k_ψ many models have been advanced. First of all we attempted to use the micellar *pseudo*-phase model proposed by Menger and Portnoy[37] for which the reaction scheme may be given as

$$\begin{array}{ccc} (Cr(VI))_w & \xrightarrow{k'_w} & P \\ D_n \rightleftharpoons K_{Cr} & & \\ (Cr(VI))_m & \xrightarrow{k'_m} & P \end{array}$$

Scheme 5. Partitioning of one reactant (chromium(VI)) in aqueous and micellar phases.

where the subscripts w and m represent the aqueous and micellar phases, respectively, D_n the micellized surfactant, k_w' and k_m' the *pseudo*-first-order rate constants in the respective phases, P the product (s), and K_{Cr}, the micelle-oxidant association constant ($K_{Cr} = [Cr(VI)_m]/[Cr(VI)_w][D_n]$; in relating reactant partitioning to reactivity it is customary to define an association constant.[37]). The observed rate law, $v = k_\psi [Cr(VI)]$, and Scheme 5 give rise to Eq. 27[38]

$$k_\psi = \frac{k'_w + k'_m K_{Cr}[D_n]}{1 + K_{Cr}[D_n]} \tag{27}$$

(k_ψ is the *pseudo*-first order rate constant for the overall reaction).

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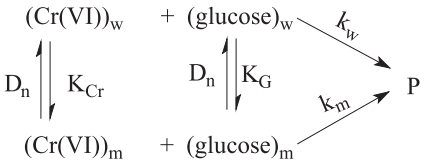
Eq. 27 may be rearranged to Eq. 28 which can be used to calculate K_{Cr} and cmc provided k'_m is known

$$\frac{(k'_w - k_\psi)}{(k_\psi - k'_m)} = K_{Cr}[\text{surfactant}]_T - K_{Cr} \times \text{cmc} \tag{28}$$

On several occasions, Bunton et al.[39] determined the values of rate constants (k'_m) from the plateau region of the rate constant—[surfactant] profiles. Unfortunately, we have not observed the rate maximum during the variation of [surfactant]. Therefore, Eq. 28 is inadequate for the present case. Alternatively, Eq. 27 can be modified to Eq. 29 according to which the plot of $1/(k'_w - k_\psi)$ versus $1/[D_n]$ should be linear. Eq. 29 was found to be inadequate too as no linearity was observed in

$$\frac{1}{(k'_w - k_\psi)} = \frac{1}{(k'_w - k'_m)} + \frac{1}{(k'_w - k'_m)K_{Cr}[D_n]} \tag{29}$$

the plot of $(k'_w - k_\psi)^{-1}$ vs. $[D_n]^{-1}$. On the basis of these observations we conclude that both reactants, i.e., chromic acid and glucose, are incorporated into/or at the micelle headgroup's layer. Therefore, Scheme 5 is modified as Scheme 6.



Scheme 6. Partitioning of two reactants (chromium(VI) and glucose) in aqueous and micellar phases.

The *pseudo*-first-order rate constants are related to second-order rate constants as

$$k'_w = k_w[(\text{glucose})_w], \text{ and} \tag{30}$$

$$\begin{aligned} k'_m &= k_m[(\text{glucose})_m]/[D_n] \\ &= k_m M_G^S \end{aligned} \tag{31}$$

Here the concentration of micellar bound reactive glucose in the micellar reaction region is expressed as the mole ratio (M_G^S) of micellar bound glucose, $(\text{glucose})_m$, to micellized surfactant, D_n. (In fact, k_m is second-order rate constant in the micellar *pseudo*-phase and therefore the availability of reagents is conditioned by preliminary partition equilibria; and this constrained space is delimited by the volume of solution occupied by aggregated surfactant). Eq. 27 now takes the form of Eq. 32[40] when

values of k'_w and k'_m are substituted from Eqs. 30 and 31. In order to determine k_m and K_{Cr} kinetically we need the cmc under kinetic conditions because the presence of alcohols[41] (mono-, di-, tri-, and polyhydric) and carbohydrates[42] in aqueous micellar solutions are known to affect a number of micellar parameters.[43] On the other hand, addition of H^+ ions also decreases both cmc and micellar effective dielectric constant but increases micellar aggregation number.[44,45] Therefore, the value of cmc of SDS at constant contents of glucose (= 30.0×10^{-3} mol dm^{-3}) and H^+ ions (= 0.58 mol dm^{-3}) at 60 °C was determined conductimetrically under different experimental conditions. These values are summarized in Table 6. In order to confirm the observed value of cmc, a graphical kinetic method developed by Broxton et al.[46] under typical kinetic reaction conditions was also used. In this method the cmc value was obtained from the point of intersection of two linear plots of k_ψ versus [surfactant] drawn through the observed points below and just above the cmc. The application of this method is shown in Figure 5. The result, given in Table 6, shows no significant difference from that obtained by the conductimetric technique.

$$k_\psi = \frac{k_w[\text{glucose}]_T + (K_{Cr}k_m - k_w)M_G^S[D_n]}{1 + K_{Cr}[D_n]} \tag{32}$$

For a given value of cmc, the constants k_m and K_{Cr} were calculated from Eq. 32 using the non-linear least squares technique detailed elsewhere.[7] The best fit values so

Table 6. Values of activation parameters (E_a, $\Delta H^{\#}$, and $\Delta S^{\#}$), rate constants (k_ψ, k_m, and k_2^m) and binding constants (K_{Cr} and K_G) for the oxidation of glucose (30.0×10^{-3} mol dm^{-3}) by chromium(VI) (4.0×10^{-4} mol dm^{-3}) in [$HClO_4$] (0.58 mol dm^{-3}) at 60 °C.

Parameters	Aqueous	SDS[a]	TX-100[b]
E_a (kJ mol^{-1})	57	53	59
$\Delta H^{\#}$ (kJ mol^{-1})	54	50	57
$\Delta S^{\#}$ (JK^{-1} mol^{-1})	−154	−162	−131
10^4 k_{obs} or k_ψ (s^{-1})	2.0	2.8	5.1
10^3cmc (mol dm^{-3})		10.8 10.9[c]	0.3
10^4 k_m (s^{-1})		7.8	32.7
10^4 k_2^m (mol dm^{-3} s^{-1})[d]		1.1	22.2
10^3 k_w (mol dm^{-3} s^{-1})	6.6	–	–
K_{Cr} (mol^{-1} dm^3)		98	54
K_G (mol^{-1} dm^3)		44	70
k_w/k_2^m		61	3
η_r	1.01	1.02 1.01[e]	1.08

[a][SDS] = 26.0×10^{-3} mol dm^{-3}.
[b][TX-100] = 67.0×10^{-3} mol dm^{-3}.
[c]Obtained from Broxton method.[46]
[d]Second-order rate constants, k_2^m, are based on the relation $k_2^m = V_m \cdot k_m$, where V_m is the volume element in dm^3 per mol of micellized surfactant.
[e]Solution (a) + NaBr (= 50.0×10^{-2} mol dm^{-3}).

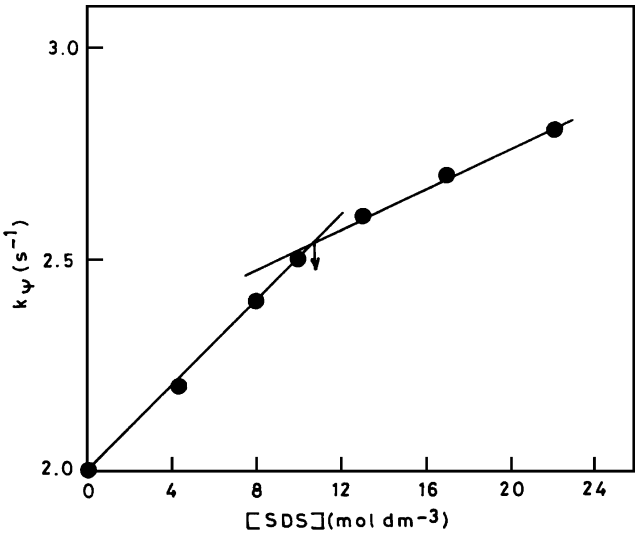


Figure 5. Broxton plot for the determination of cmc of SDS under the kinetic conditions. Conditions were the same as in Figure 1(c).

obtained are summarized in Table 6. In order to confirm the validity of rate Eq. 32, values of k_w, K_{Cr}, k_m, cmc and [glucose] were used to find $k_{\psi cal}$ (Table 3) which is in excellent agreement with the experimental k_ψ; this provides supporting evidence for the proposed mechanism (Scheme 6) and to Eq. 32. Moreover, the fitting of the observed data to Eq. 32 is evident from the plots of Figure 4 where solid lines are drawn through the calculated k_ψ points.

Probable Source of Catalytic Effects of SDS and TX-100 on the Rate of Oxidation of Glucose by Chromium(VI)

Most of the micellar-mediated organic/inorganic reactions are believed to occur either inside the Stern layer or at the interfacial junctural region of Stern and Gouy-Chapman layers.[38,47] The activity of water at the surface of ionic micelles is not very different from that of the bulk solvent.[48] The electrostatic surface potential at the micellar surface can attract or repel reaction species and strong hydrophobic interaction can bring about incorporation into micelles even of the reagents that bear the same charge/or neutral as the ionic micelles. The exact site of reaction /location of the reactants in the micellar structure and degree of association /incorporation/penetration of reactants into the micellar structure have a major influence on the reactivity. Let us now take into account the kinetic results obtained in the micellar systems. As discussed above, both the reactants may be expected to partition/associate between the aqueous and micellar phases.

The micelles are very effective at incorporating hydrophobic and hydrophilic substrates into the Stern layer (water-rich region). The most obvious source of micellar catalysis of the oxidation of glucose by chromic acid in presence of anionic and

non-ionic micelles may be the dissociation of chromic acid. The micelles affect the pH of solutions by changing the acid-dissociation constants as well as changing the protonation equilibrium $H_2CrO_4 + H^+ \rightleftharpoons HCrO_3^+ + H_2O$. When we take the following into account: 1) increase in the $[H^+]$ increases the micellar catalysis (Table 4), 2) H_2CrO_4 is not distributed in the SDS micellar phase,[30] and 3) the effective local pH is lower by ca. 2 units in the vicinity of anionic micellar surface,[49] the species $HCrO_3^+$ seems to be the reactive one in SDS micellar media. From purely electrostatic considerations, $HCrO_3^+$ can be assumed to reside predominantly in the Stern-layer. Most probably, ion-pair formation takes place between the anionic headgroups of micelle and cationic $HCrO_3^+$, hence the equilibrium is shifted towards the right hand side. In analogy to the well known fact of distribution of alcohols between aqueous and SDS micelles,[50,51] the distribution of glucose between aqueous and SDS micelles cannot be ruled out (because the catalysis of the rate in the surfactant solution is indicative of availability of glucose at the reaction site). We see that the micelles thus help in bringing the reactants together which may then orient them in a manner suitable for ester formation.

In case of TX-100, both H_2CrO_4 and glucose get associated with the micelles through hydrogen-bonding. These associated reactants facilitate formation of the chromate ester.

Perusal of Figure 4 reveals that not only is the overall rate enhancement higher in TX-100 in comparison to SDS, but the former is more effective even at low concentration which suggests that hydrogen bonding is more important than coulombic attraction. There are no electrostatic interactions with the polar head groups of TX-100, but this nonionic surfactant should stabilize an undissociated H_2CrO_4 (relative to the more hydrophilic $HCrO_3^+$) and glucose through hydrogen-bonding. Thus, we may safely conclude that incorporation of uncharged chromic acid takes place into the TX-100 micelles.

Effect of Inorganic Electrolytes

The overall catalysis or inhibition factor is highly sensitive toward the concentration of added counter-ions. Micellar catalysis of bimolecular reactions is generally reduced by adding salts and the effects depend largely on the nature of counter-ion to the micelle. In general, the effect of anion and cation is unimportant for anionic and cationic surfactants, respectively. The salt effect upon the reaction of glucose with chromic acid in anionic micelles of SDS follows the expected pattern (Figure 6). NaBr, LiBr and NH_4Br are effective inhibitors whereas $HClO_4$ is a catalyst. The effect of potassium salts (KCl, KBr, KNO_3, and K_2SO_4), tetramethylammonium bromide and tetra-*n*-butylammonium bromide could not be studied due to the solubility problem. The reaction mixture ($[K_2Cr_2O_7] = 4.0 \times 10^{-4}$ mol dm^{-3}, $[HClO_4] = 0.58$ mol dm^{-3}, [glucose] = 30×10^{-3} mol dm^{-3}, and [SDS]=26×10^{-3} mol dm^{-3}) became turbid after the addition of 5.0×10^{-2} mol dm^{-3} of the above mentioned salts.

In discussing the way in which salts inhibit the SDS catalysed reaction, we assume/speculate that the cation of the salt (H^+, NH_4^+, Li^+, and Na^+) tends to exclude glucose from the neighborhood of the anionic micelles. However, an alternative explanation is that these cations (except H^+) also exclude the hydrogen ion from the reaction site (Stern layer). In the present situation, exclusion of reactive species by added salts follow the retardation trend k_ψ (Na^+) < k_ψ (Li^+) < k_ψ (NH_4^+) (Figure 6). The observed

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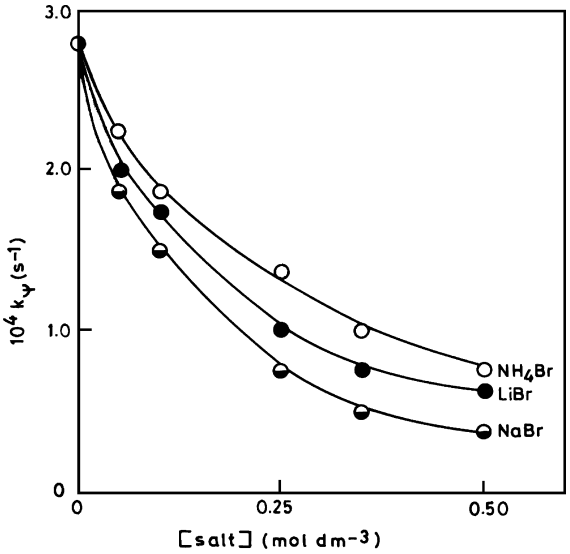

Figure 6. Effect of inorganic salts on the reaction rate of the oxidative degradation of glucose (30.0×10^{-3} mol dm^{-3}) by chromic acid (4.0×10^{-4} mol dm^{-3}) in $HClO_4$ (0.58 mol dm^{-3}) at 60 °C in presence of SDS (26.0×10^{-3} mol dm^{-3}).

behavior is due to the higher polarization power of the cation. In terms of their concentrations, hydrogen ions produce a catalytic effect, which is consistent with the evidence that [$HCrO_3^+$] increases with [$HClO_4$] which, in turn, increases the k_ψ value. These results confirm that both reactants ($HCrO_3^+$ and glucose) are associated/incorporated to micelles of SDS, because only in relatively high concentrations do competing cations drive them out of the micelle. Further, addition of salts are known to bring changes in micellar size and shape that may affect the rate values but, in view of the relative viscosity values (η_r) of solutions left at the end of kinetic runs, this possibility is ruled out (the η_r values are recorded in Table 6; changes in micellar size and shape are known to alter flow behavior with concomitant rise in viscosity[52]).

General

The second-order rate constant, k_m (unit in s^{-1}), is calculated by taking concentration as a mole ratio. This constant cannot be compared directly with the second-order rate constant, k_w, in water for which the concentration is specified as molarity (unit of k_w in mol^{-1} dm^3 s^{-1}—the two have different dimensions!). In order to circumvent the difficulty, Bunton[47] assumed that the comparison can be made by considering a volume element of reaction in the micellar *pseudo*-phase and then estimating the molarity of the reactant in that volume element. An apparent second-order rate constant, k_2^m, was then defined as

$$k_2^m = k_m \cdot V_m \tag{33}$$

where V_m is the molar volume of the micellar reaction region. The values of V_m for anionic SDS[38,47] and non-ionic TX-100 micelles[7] have been found as 0.14 and 0.68 $dm^3\ mol^{-1}$, respectively (the quoted values are of the Stern layer in the case of SDS and of the outer-shell reaction region for TX-100). As a result, the values of the second-order rate constants for the glucose oxidation reaction in SDS and TX-100 micelles are 61 and 3 times less than the second-order rate constant in water (k_w/k_2^m, see Table 6).

Glucose is hydrophilic and highly soluble in water. The value of its binding/association constant (K_G) with TX-100 is higher in comparison to SDS (Table 6) which clearly indicates that hydrogen bonding between –OH groups of glucose and polar head groups of TX-100 micelles is an important factor. On the other hand, this type of bonding is not possible with anionic head groups of SDS micelles.

Values of thermodynamic parameters calculated using Eq. 2 are given in Table 6. A useful/meaningful mechanistic explanation of the $\Delta H^{\#}$ and $\Delta S^{\#}$ values is not possible because the k_ψ does not represent a single elementary kinetic step; it is a complex function of true rate, binding, and ionization constants.

EXPERIMENTAL

Materials and method. D(+)-Glucose, reductant (Merck, India, 99%), potassium dichromate, oxidant (Merck, India, 99%), perchloric acid (Merck, India, 70% solution), manganese(II) sulfate-1-hydrate (Merck, India, 99%), Triton X-100, TX-100 (Fluka, Germany, 99%), cetyltrimethylammonium bromide, CTAB (Fluka, Germany, 99%), and sodium dodecyl sulfate, SDS (Fluka, Germany, > 98%) were used without further purification. Stock solutions of the reagents of desired concentrations were prepared in double distilled water.

Kinetic measurements. Kinetic experiments were carried out in a vessel immersed in a constant temperature-controlled (± 0.1°C) oil bath. The reaction was initiated by adding to an equilibrated mixture of chromium(VI) and perchloric acid the requisite quantity of pre-equilibrated glucose solution. The progress of the reaction was followed by measuring the absorbance of the remaining chromium(VI) at known time intervals at 360 nm on a Spectronic-20 Bausch & Lomb Spectrophotometer. At this wavelength, neither chromium(III) nor the oxidized products has any appreciable absorbance. The *pseudo*-first-order conditions were maintained with a large excess of reductant over oxidant concentration. Other details are described elsewhere.[11–13,19,22–24]

Stoichiometry. Several reaction mixtures with [chromium(IV)] > [carbohydrate] ([oxidant] = 5.0×10^{-4} mol dm^{-3}:[reductant]=0.5 to 4.5×10^{-4} mol dm^{-3}) at fixed [H^+] (= 0.58 mol dm^{-3}) were prepared and kept for several days at room temperature. After completion of the reactions, the unconsumed oxidant was determined spectrophotometrically. The consumption ratio, by assuming that glucose was totally consumed under these conditions, was found to be 4:1 (Cr(IV):glucose). Due to the auto-acceleration nature of the reaction, exact stoichiometry equation and products formed are difficult to predict. However, the carbohydrate has been used in sufficient excess throughout the kinetic investigations to ensure that the rate of reduction of the chromium(VI) is proportional to the rate of oxidation of the organic substrates themselves, but not the rate of destruction of any reactive organic intermediates.[53] Moreover, since

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the initial rate of consumption of chromium(VI) under these conditions was always first-order, the rate of oxidation of the intermediate products cannot be kinetically significant.[53]

Free radical detection. A solution of glucose (17.8×10^{-3} mol dm^{-3}) was added to a mixture of chromium(VI) (1.4×10^{-3} mol dm^{-3}) in 0.58 mol dm^{-3} $HClO_4$ and a saturated solution of mercurous chloride (5.0 cm^3) at 60 °C. After ca. 40 min, a white precipitate of mercuric chloride appeared slowly. This experiment indicates the free radical intervention during the course of oxidative degradation of glucose. The control experiments (no glucose or chromium(VI) present) did not show formation of the precipitate.

Product analysis. (i) *Cr(III):* In order to identify the nature of the reaction product (chromium(III)), the spectra of the reaction mixture were recorded at different time intervals (Figure 7). The spectrum of Cr(VI) (4.0×10^{-4} mol dm^{-3}) solution in $HClO_4$ shows an absorption band at 350 nm and a shoulder at 450 nm. The spectrum of the reaction mixture containing [$K_2Cr_2O_7$] (= 4.0×10^{-4} mol dm^{-3}), [glucose] (= 30.0×10^{-3} mol dm^{-3}) and [$HClO_4$] (= 0.58 mol dm^{-3}), taken just after mixing, did not show any change in absorbance [Figure 7A(a)]. Under the experimental kinetic conditions, no noticeable absorbance was seen even after completion of the reaction

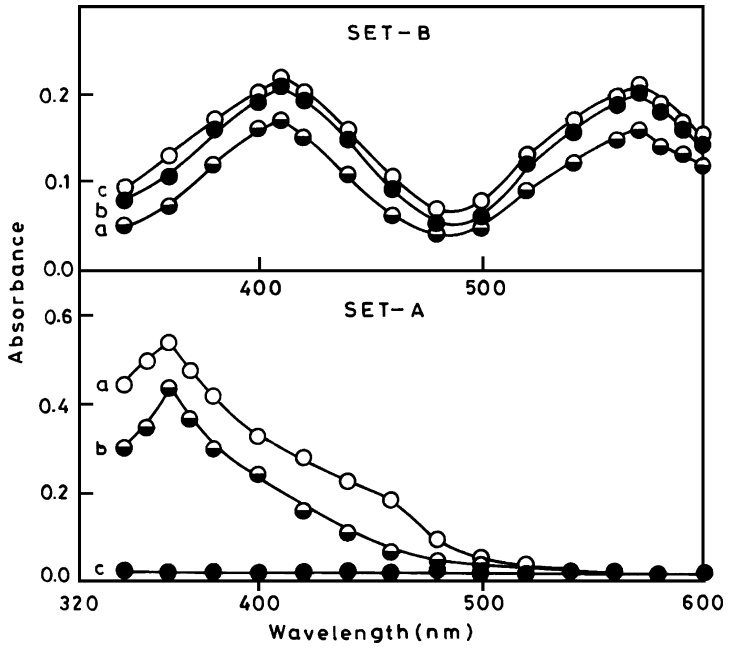

Figure 7. (**Set A**) Absorption spectra of the reaction product of the oxidation of glucose (30.0×10^{-3} mol dm^{-3}) by chromic acid (4.0×10^{-4} mol dm^{-3}) at 60 °C in presence of $HClO_4$ (0.58 mol dm^{-3}) after 0 (a), 30 (b), and 60 min (c) of mixing. (**Set B**) Effects of SDS and TX-100 on the spectra of aquachromium(III) ion (the reaction product obtained after 120 min); (a) no added surfactant, (b) SDS (26.0×10^{-3} mol dm^{-3}), and (c) TX-100 (50.0×10^{-3} mol dm^{-3}). Conditions were the same as in Set A with [chromic acid] = 4.0×10^{-3} mol dm^{-3}.

[Figure 7A(c)]. Therefore, the spectrum of the reaction mixture was recorded using higher [Cr(VI)] (Figure 7B). At the end of the reaction, the studies showed that the reaction of glucose with chromium(VI) resulted in a product having absorption bands at 405 and 575 nm (Figure 7B), which were assigned to the aqua Cr(III).[26]

(ii) *CO_2*: The experimental set up and the reaction conditions for the estimation of CO_2 were the same as detailed under the kinetic measurements. The evolved CO_2 was swept out by a constant current of purified nitrogen gas and was absorbed in standard barium hydroxide solution. But, due to the lower concentration of carbohydrate, the carbon dioxide evolved was not sufficient to be detected, even though the temperature was raised up to 90 °C. Therefore, higher carbohydrate concentrations were used to observe CO_2 evolution. The results are consistent with the report that CO_2 is one of the reaction products from the oxidation of carbohydrates by chromium(VI).[54]

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