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Influence of sodium dodecyl sulfate/TritonX-100 micelles on the oxidation of D-fructose by chromic acid in presence of $HClO_4$

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Abstract

The kinetics of oxidation of D-fructose by chromic acid in aqueous and aqueous surfactant (sodium dodecyl sulfate, SDS, and alkylphenyl polyethylenglykol, TX-100) media have been investigated in the presence of $HClO_4$. The reaction is acid catalyzed and is associated with an induction period which is dependent on $[H^+]$, [surfactant] and temperature. The order of oxidation during induction under [D-fructose] > [chromic acid] conditions is fractional in each reagent in both media. The rate constant was found to increase with [Mn(II)]. A mechanism has been proposed for the reaction. The micelles produce a catalytic effect in the range of SDS and TX-100 concentrations used, and the effect is explained by means of the pseudo-phase mass-action model. In the presence of SDS, the reaction is inhibited by electrolytes (NH_4Br, NaBr, LiBr), and the inhibition order $Na^+ > Li^+ > NH_4^+$ is explained on the basis of electrostatic considerations. The rate constant (k_m), binding constants (K_S and K_F), and corresponding activation parameters (E_a, $\Delta H^{\neq}$ and $\Delta S^{\neq}$) have been evaluated and discussed. The order of reactivities of different sugars is found as: D-fructose > D-arabinose > D-xylose ≈ D-glucose. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Kinetics; D-Fructose; Oxidation; Chromium(VI); Sodium dodecyl sulfate; Triton X-100

1. Introduction

Carbohydrate units are constituents of nucleic acids and play an important role in metabolism and in mammalian food supply. These are very attractive natural ligands for both toxic and essential metal ions. Oxidative degradation of sugars by different oxidizing agents have been the subject of numerous investigations.[1–15] It has been established that sugars, or their derivatives, play an important role in the chemistry of chromium, specially in the environment[16,17] and in the mechanism of chromium-induced cancer.[18] Chromium(VI) crosses the cell membrane and oxidizes cellular components in a process that leads to cellular damage, including interference with the genetic machinery. Chromium(VI) has been reported to form chromate esters with ligands containing O-, N- and S-atoms.[19]

The inhibitory/catalytic effect of organized structures (e.g., micelles) on the kinetics of a large number of reactions is well documented in the literature,[20] but there have been only a limited number of studies of chromium(VI) redox reactions in surfactant media.[21,22] We are continuing our investigations of cationic-, anionic- and non-ionic micellar effects on the electron-transfer reactions of organic acids[23] and sugars[24] with chromium(VI) as oxidant. Kinetic studies are expected to provide information on how the electron-transfer event is affected by hydrophobic and electrostatic interactions between the micelle and the chromate ester complex.

Surfactant micelles in aqueous media resemble enzymes in that they possess distinct regions of hydrophilic and hydrophobic character. The investigations of coupled systems composed of electron-transfer reaction and micelle-forming surfactants may contribute in a unique way to our understanding of the redox processes of electron-transport enzymes. This paper describes experiments designed to examine pathways for electron transfer from D-fructose to chromi-

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um(VI), and in this way we report an example where the modes of oxidation of aldo- and keto-sugars with the same oxidant are completely different.

2. Experimental

Materials.—The surfactants sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB) and Triton X-100 (TX-100) (Fluka, Switzerland) were used as received. Potassium dichromate (oxidant), D-fructose (reductant) and perchloric acid (E. Merck, India) were used as such. All other reagents ($MnSO_4 \cdot H_2O$, NH_4Br, LiBr and NaBr) used were of AR grade. The water used as solvent was previously subjected to deionization, followed by distillation (specific conductance: $(1–2) \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$).

Kinetic procedure.—The kinetic procedure used to follow the progress of the reaction has been described elsewhere.[23–25] Each kinetic run was performed under pseudo-first-order conditions using $\geq$ tenfold excess of [fructose] over [chromic acid]. A mixture containing appropriate amounts of all the reactants (except oxidant) was thermally equilibrated at the desired temperature in an oil bath (± 0.1 °C), and to this was rapidly added a measured amount of the oxidant solution (pre-equilibriated at the same temperature). The kinetics was monitored for 80% completion of the reaction by spectrophotometric determination of the decay of absorbance of chromium(VI) at 360 nm using a Bausch & Lomb Spectronic-20 spectrophotometer.[4] The pseudo-first-order rate constants (k_{obs}/k_{ψ}, s^{-1}) were computed from the slopes of log(absorbance) versus time plots ($r \geq 0.996$). The second-order rate constants (k^{11}, $mol^{-1}\ dm^3\ s^{-1}$) and initial rates (v, $mol\ dm^{-3}\ s^{-1}$) were evaluated from the relation $k^{11} = k_{obs}/[\text{fructose}]$ and $v = k_{obs} \times [\text{fructose}]$.

Stoichiometry and product analysis.—Several reaction mixtures with [chromium(VI)] > [fructose] (5×10^{-4} mol dm^{-3} oxidant: $0.5–4.5 \times 10^{-4}$ mol dm^{-3} reductant) at fixed [H^+] ($= 0.58$ mol dm^{-3}) were prepared and kept for 2 h at 60 °C. After completion of the reactions, the unconsumed oxidant was determined spectrophotometrically. In all cases the reaction stoichiometry was found to be 1:2 (chromium(VI):D-fructose). Due to the autoacceleration nature of the reaction (vide supra), the exact stoichiometry equation and products formed are difficult to predict.

In order to characterize the nature of chromium(III) (reduction product of chromium(VI)), D-fructose ($= 30 \times 10^{-3}$ mol dm^3), chromium(VI) ($= 4 \times 10^{-4}$ mol dm^{-3}), and $HClO_4$ ($= 0.58$ mol dm^{-3}) were mixed at 60 °C. Spectra of the mixture were recorded at different time intervals. Fig. 1, Set A shows that as the reaction progresses, the peak at 360 nm decreases. At the end of reaction, under these experimental kinetic conditions,

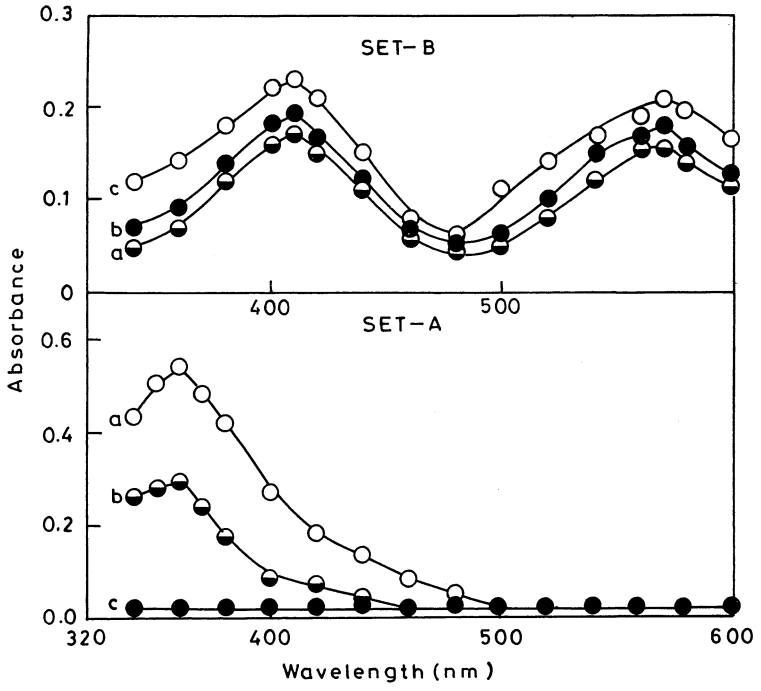


Fig. 1. (Set A) Spectra of the reaction product of the oxidation of D-fructose (30.0×10^{-3} mol dm^{-3}) by chromic acid (4.0×10^{-4} mol dm^{-3}) at 60 °C in the presence of [$HClO_4$] (0.58 mol dm^{-3}); (a) just after mixing; (b) after 30 min; and (c) after 60 min. (Set B) Effects of SDS (26.0×10^{-3} mol dm^{-3}) and TX-100 (50.0×10^{-3} mol dm^{-3}) on the spectra of aquachromium-(III) ion (the reaction product obtained after 120 min); (a) no surfactant; (b) SDS; and (c) TX-100. Other conditions were the same as in Set A with [chromic acid] $= 4.0 \times 10^{-3}$ mol dm^{-3}.

Table 1
Dependence of first-order rate constants (k_{obs}/k_{ψ}) on [Cr(VI)], [fructose], and [$HClO_4$] for the oxidation of D-fructose by chromium(VI) in the absence and presence of [SDS] and [TX-100] at 60 °C

$[Cr(VI)] \times 10^4$ (mol dm^{-3})	$[Fructose] \times 10^3$ (mol dm^{-3})	$[HClO_4]$ (mol dm^{-3})	Aqueous	SDS [a]	TX-100 [b]
			$k_{obs} \times 10^4$ (s^{-1})	$k_{\psi} \times 10^4$ (s^{-1})	$k_{\psi} \times 10^4$ (s^{-1})
2	30	0.58	3.8	6.6	8.3
3			4.0	6.8	8.5
4			4.5	7.1	9.2
5			4.3	7.0	8.9
6			4.5	7.1	9.0
4	2	0.58	0.7	1.7	3.6
	5		1.4	2.8	5.1
	10		2.3	3.8	6.0
	15		3.0	5.3	7.2
	20		3.7	5.8	8.2
	30		4.5	7.1	9.2
	40		6.1	9.6	9.8
	50		8.6	11.1	11.2
4	30	0.11	0.9	1.5	1.5
		0.23	1.8	1.8	2.0
		0.34	2.8	3.0	3.2
		0.46	3.9	4.5	5.1
		0.58	4.5	7.1	9.2
		0.69	7.2	8.4	12.8
		0.93	not observed	not observed	not observed
		1.16	not observed	not observed	not observed

[a] $[SDS] = 26.0 \times 10^{-3}$ mol dm^{-3}.
[b] $[TX\text{-}100] = 50.0 \times 10^{-3}$ mol dm^{-3}.

the chromium(VI) has no absorbance, but the chromium(III) has no absorbance either (Fig. 1(c), Set A). Hence, the spectrum of the reaction mixture was recorded at higher [chromium(VI)] (Fig. 1, Set B). The two sharp peaks observed at 410 and 570 nm are indicative of the presence of the aqua-chromium(III) species[4] in the reaction mixture as one of the reaction products.

Polymerization studies.—Upon addition of acrylonitrile to a reaction mixture ($[chromium(VI)] = 4 \times 10^{-4}$ mol dm^{-3}, $[fructose] = 30 \times 10^{-3}$ mol dm^{-3}, and $[HClO_4] = 0.58$ mol dm^3 at 60 °C), polymerization (white precipitate formation) started quickly, demonstrating that the reaction of D-fructose with chromium(VI) proceeds via free radicals. Blank experiments with either chromium(VI) or D-fructose gave no detectable white precipitates.

3. Results and discussion

General considerations.—The kinetics of the oxidative degradation of D-fructose by chromium(VI) in $HClO_4$ medium was investigated at several reactant concentrations, hydrogen-ion concentrations [H^+], and temperatures, both in the absence and presence of surfactants. The results are summarized in Tables 1–5.

Kinetics in the absence of surfactants.—Before dealing with the actual observed results, it is necessary to point out that in the present study the reaction showed an induction period which was entirely eliminated when the experiments were carried out at higher [H^+] (Fig. 2). Another feature, i.e., autocatalysis, is due to the catalytic role of one of the oxidation products of D-fructose produced during the kinetic runs. As the extent of the induction period depended on the reaction conditions, i.e., [D-fructose], [H^+], and temperature, choice of the best experimental conditions had been a crucial problem. Taking into consideration their effects on the induction period (see Fig. 2; the induction period diminished analogously with increase in temperature also) and the cloud-point of nonionic TX-100 (= 66 °C),[26] a compromise was made to perform the reactions at 60 °C with $[H^+] = 0.58$ mol dm^{-3}. $HClO_4$ was used as the acidifying agent due to the non-complexing nature of ClO_4^-. The rate constants of the initial stages of the reaction were obtained from the slopes of the lines (vide infra) extended over the induction period. Secondly, no

Table 2
The rate constants (k_{obs}, k_{ψ}, and k_m), activation parameters (E_a, $\Delta H^{\neq}$, and $\Delta S^{\neq}$), and binding constants (K_S and K_F) for the oxidation of D-fructose (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

Temperature (°C)	Aqueous	SDS [a]	TX-100 [b]
	$k_{obs}\times10^4$ (s^{-1})	$k_{\psi}\times10^4$ (s^{-1})	$k_{\psi}\times10^4$ (s^{-1})
30	1.0	1.4	1.9
40	1.9	2.3	3.3
50	3.0	3.8	5.1
60	4.5	7.1	9.2
70	8.3	9.2	
80	12.1	13.4	
Parameters			
cmc (mol dm^{-3})		10.2 (8.2) [c]	(0.3) [c]
$k_m\times10^3$ (s^{-1})	1.9	2.4	
K_S (mol^{-1} dm^3)	144	122	
K_F (mol^{-1} dm^3)	78	74	
E_a (kJ mol^{-1})	41	39	36
$\Delta H^{\neq}$ (kJ mol^{-1})	38	37	34
$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	−301	−299	−297

[a] [SDS] = 26.0×10^3 mol dm^{-3}.
[b] [TX-100] = 50.0×10^3 mol dm^{-3}.
[c] Literature values (quoted in parentheses) are taken from Ref. 47.

electrolyte (to maintain ionic strength) was used as applied by previous investigators,[1,2] because Tondre et al.,[27] in their pioneering work, has advised to avoid the use of even buffer solutions to maintain the pH of micellar solutions. Our main interest was to observe the behavior of surfactants in the redox chemistry of carbohydrates and compare the results with those in aqueous medium under similar reaction conditions.

Effect of [oxidant] on k_{obs}. The reactions were carried out at various fixed [oxidant] keeping other variables, viz. [fructose], [H^+] and temperature constant. The independence of k_{obs} over a range of $[Cr(VI)]_T$ (Table 1) is in agreement with a first-order dependence on $[Cr(VI)]_T$. The rate law is, therefore, given as:

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

Effect of [reductant] on k_{obs}. In the presence of fixed [oxidant] (4×10^{-4} mol dm^{-3}) and [H^+] (0.58 mol dm^{-3}) at 60 °C, the rate of oxidation increased non-linearly with the increase in [fructose] (Fig. 3(a)). The plot of log k_{obs} versus log[fructose] was linear with slope = 0.56, indicating fractional-order dependence on [fructose].

Effect of [H^+] on k_{obs}. The oxidation rate increased by increase in [H^+]. For example, under the conditions [fructose] = 30×10^{-3} mol dm^{-3} and [oxidant] = 4×10^{-4} mol dm^{-3} at 60 °C, the rate increased from 0.9×10^{-4} to 7.2×10^{-4} s^{-1} when [H^+] was increased from 0.11 to 0.69 mol dm^{-3} (Table 1). The slope of the plot between log k_{obs} versus log[H^+] is ca. 0.947, which indicates that the order is fractional with respect to [H^+]. It was also observed that the induction period

Table 4
Comparison of k_{obs} and k_{cal} values for the oxidative degradation of fructose by chromium(VI) [a]

[Fructose]$\times10^3$ (mol dm^{-3})	$k_{obs}\times10^3$ (s^{-1})	$k_{cal}\times10^4$ [b] (s^{-1})	$k_{obs}-k_{cal}/k_{obs}$
2	0.7	0.6	+0.14
5	1.4	1.4	0.00
10	2.3	2.4	−0.04
15	3.0	3.2	−0.06
20	3.7	3.9	−0.05
30	4.5	4.9	−0.08
40	6.1	5.7	+0.06
50	8.6	6.3	+0.26

[a] Conditions were the same as given in Table 1.
[b] Calculated by using Eq. (6).

Table 3
Second-order rate constants (k^{11}) for the oxidation of monosaccharides by chromium(VI) [a]

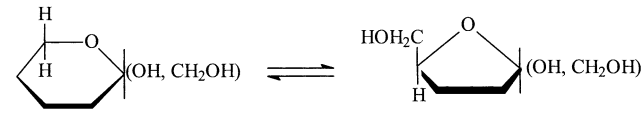
Monosaccharides	$HClO_4$ (mol dm^{-3})	Temperature (°C)	10^3 k^{11} (s^{-1} mol^{-1} dm^3)	Reference
D-Fructose	0.58	40	6.33	present work
D-Glucose	0.50	25	1.79	48
	0.50	22	1.88	49
	0.58	40	1.66	24
L-Arabinose	0.58	40	8.3	50
D-Xylose	0.50	25	2.11	48
	0.58	30	1.0	51
L-Rhamnose	0.50	33	9.87	4

[a] [oxidant] = 4.0×10^{-4} mol dm^{-3} for D-glucose, D-xylose, L-arabinose and D-fructose; 8.0×10^{-4} mol dm^{-3} for L-rhamnose.

decreased (Fig. 2), and at higher $[H^+]$ (≥ 0.93 mol dm^{-3}), the plot of log(absorbance) versus time became linear (Fig. 2).

Effect of temperature on k_{obs}. The reaction was carried out at different temperatures in the range of 30–80 °C (Table 2). Different activation parameters (E_a, $\Delta H^{\neq}$ and $\Delta S^{\neq}$) were evaluated using both Arrhenius and Eyring equations (Table 2).

The mechanism. Before proposing a mechanism it is necessary to discuss the species of D-fructose and chromic acid present in aqueous acidic solutions. It has been shown by laser-Raman spectroscopy[28] that D-fructose exists in an equilibrium mixture of pyranoid and furanoid forms. Out of these, only the pyranose form is claimed to be involved in oxidation reactions.[29] D-glucose exists in equilibrium between α- and β-pyranose



α– or β–D-fructopyranose (58%) α – or β–D-fructofuranose (42%)

(2)

forms with the free aldehydic form as intermediate.[30] As far as the conformation is concerned, the anomeric protons in α- and β-glucose are present in equatorial and axial positions, respectively.[29] It has also been

Table 5
Dependence of first-order rate constants of the oxidative degradation of D-fructose (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}) on [SDS] and [TX-100] at 60 °C

$[SDS] \times 10^3$ (mol dm^{-3})	$k_\psi \times 10^4$ (s^{-1})	$k_{\psi cal} \times 10^4$ [a] (s^{-1})	$[TX\text{-}100] \times 10^3$ (mol dm^{-3})	$k_\psi \times 10^4$ (s^{-1})	$k_{\psi cal} \times 10^4$ (s^{-1})
5	5.2		2.5	5.4	6.3
10	5.8		5	5.7	6.4
			10	6.4	7.6
15	6.4	7.0	15	6.9	7.9
20	6.7	7.3	20	7.4	8.0
26	7.1	7.8	26	7.8	8.1
30	7.3	7.8	30	8.1	8.3
35	7.6	7.9	35	8.4	8.6
40	7.8	8.1	40	8.6	8.8
45	8.0	8.2	45	8.8	9.0
50	8.2	8.4	50	9.2	10.0
60	8.4	8.6	60	10.6	10.2
			67	13.2	12.9

[a] Calculated by using Eq. (9) with the values quoted in Table 2.

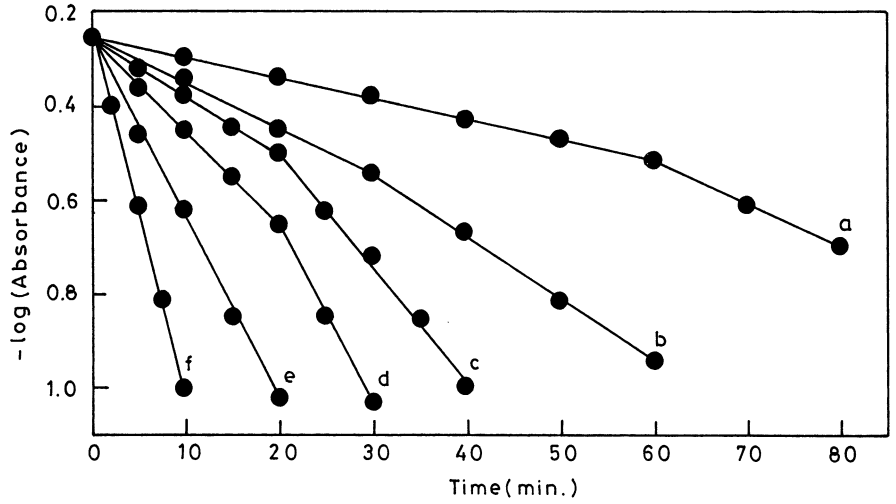


Fig. 2. Plots of log(absorbance) vs. time for the oxidative degradation of D-fructose (30.0×10^{-3} mol dm^{-3}) by chromic acid (4.0×10^{-4} mol dm^{-3}) at 60 °C; $[HClO_4]$ = (a) 0.23; (b) 0.46; (c) 0.58; (d) 0.69; (e) 0.93; and (f) 1.16 mol dm^{-3}.

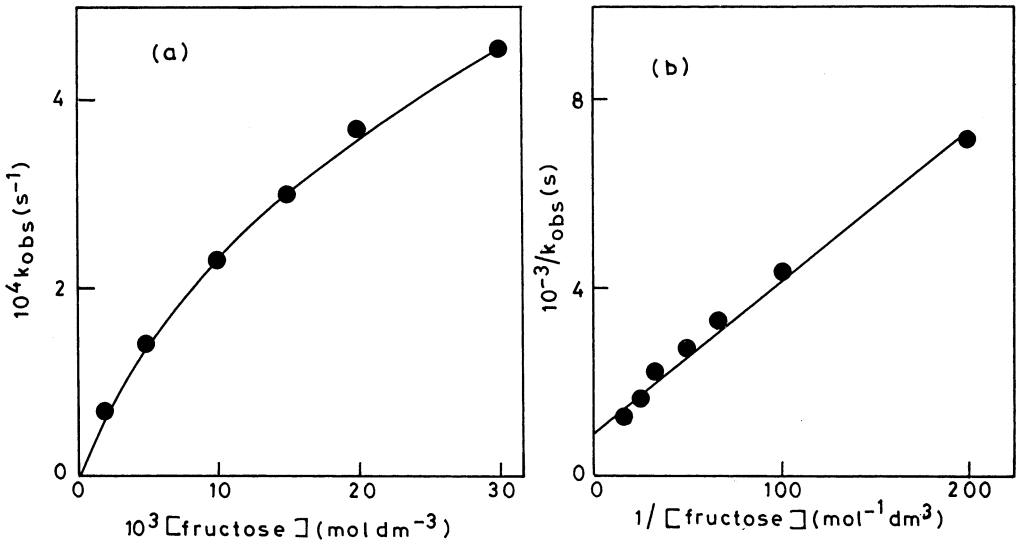


Fig. 3. k_{obs} vs. [fructose] (a) and $1/k_{obs}$ vs. 1/[fructose] (b) plots; [chromic acid] $= 4.0 \times 10^{-4}$ mol dm^{-3}, [H^+] $= 0.58$ mol dm^{-3}, and temperature $= 60$ °C.

confirmed that the β-anomer should be more reactive than the α-anomer.[31]

α– D-glucose β–D-glucose

On the other hand, chromic acid (chromium(VI)) exists in the following acid–base equilibria:[32]

$$CrO_4^{2-} + H^+ \overset{K_{a2}}{\rightleftharpoons} HCrO_4^- \quad (3)$$

$$HCrO_4^- + H^+ \overset{K_{a1}}{\rightleftharpoons} H_2CrO_4 \quad (4)$$

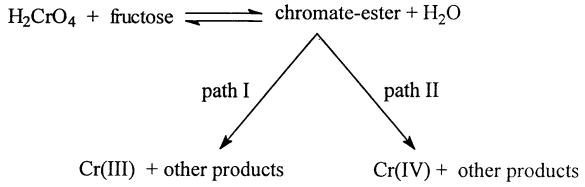
Under the experimental conditions ([H^+] $= 0.11$–0.69 mol dm^{-3}), H_2CrO_4 and $HCrO_4^-$ species exist in significant concentrations. As the [H^+] increases, the percentage of H_2CrO_4 species increases which, in turn, increases the reaction rate.

According to Sala et al.,[1] the first step of the mechanism (oxidation of aldohexoses or their derivatives by chromic acid) represents formation of a chromate ester between oxidant and reductant. This observation, coupled with our past[23–25] and present results, allows us to propose the following scheme (Scheme 1).

In this scheme, paths I and II represent, respectively, one-step, three-electron and one-step, two-electron transfers.

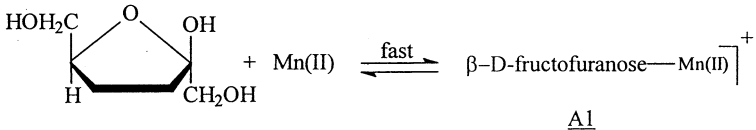
Effect of [manganese(II)] on k_{obs}. Ester formation between the chromate and the substrate is the first-step of chromium(VI) reduction. The second step generally falls into two classes characterized by reduction of chromium(VI) to chromium(IV) by two-equivalent substrates or reduction of chromium(VI) by three-equivalent substrates. Manganese(II) has been used as an analytical tool to determine the involvement of chromium(IV), if formed, in the rate-determining step.[33] In such a case (i.e., in the presence of manganese(II) and if chromium(IV) is an intermediate), the oxidation rate by chromium(VI) would decrease by half.[34] Therefore, to substantiate the formation of Cr(IV) as an intermediate during the reduction of Cr(VI) by D-fructose, the effect of [Mn(II)] was investigated at constant [fructose] ($= 30 \times 10^{-3}$ mol dm^{-3}), [Cr(VI)] ($= 4 \times 10^{-4}$ mol dm^{-3}) and [$HClO_4$] ($= 0.58$ mol dm^{-3}) at 60 °C. The k_{obs} values were 4.5, 4.9, 5.2, 5.6, 6.3, 6.7 s^{-1}, respectively, at [Mn(II)] $= 0.05$, 0.10, 0.15, 0.20, 0.25, 0.30 mol dm^{-3}. It is seen that k_{obs} increases with increase in [Mn(II)]. The observed positive catalytic effect rules out the possibility of formation of Cr(IV) (path II) in the rate-determining step. Thus, we may safely conclude that the oxidation of D-fructose by chromic acid follows a one-step, three-electron transfer mechanism. Additionally, to detect any build up of Mn(III), some experiments were also carried out by measuring the absorbance at 470 nm (λ_{max} for aquamanganese(III)[25]), but we failed to observe appearance of this ion. The following mechanism is, therefore, proposed in presence of Mn(II) (Scheme 2).

In both routes I and II, the first step represents formation of a complex (A1 or A3) between D-fructose



Scheme 1.

Route I



A1

β–D-fructofuranose

$$A1 + H_2CrO_4 \xrightleftharpoons{K_{es1}} A1\text{—chromium(VI)}$$

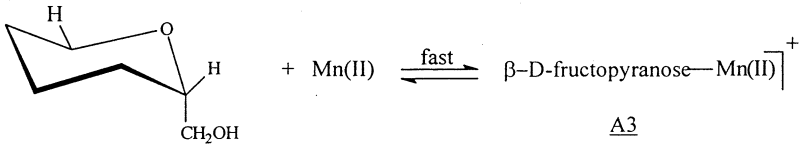
A2

$$A2 \xrightarrow{k_1} Cr(III) + Mn(III) + \text{other products}$$

$$2Mn(III) \xrightarrow{fast} Mn(II) + Mn(IV)$$

$$Mn(IV) + \text{fructose} \xrightarrow{fast} Mn(II) + \text{other products}$$

Route II



A3

β– D-fructopyranose

$$A3 + H_2CrO_4 \xrightleftharpoons{K_{es}} A3\text{—chromium(VI)}$$

A4

$$A4 \xrightarrow{k} Cr(III) + Mn(III) + \text{other products}$$

(The fate of Mn(III) is similar as postulated in route I).

Scheme 2.

and Mn(II), as 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.[35] The equilibrium between β-D-fructofuranose and Mn(II) is fast. In presence of chromium(VI), the equilibrium shifts towards the right-hand side because A1 is consumed and converted to A2. As the reaction proceeds, the equilibrium involving K_{es1} also shifts in the forward direction. Both complexes form an ester-like complex (A2 or A4) with chromium(VI). In analogy to our previous studies,[23] we assume that A2 and A4 decompose by a one-step, three-electron oxidation–reduction mechanism directly to chromium(III). One of the electrons transferred is donated by the manganese atom and the other two by the organic substrate.

The following rate-law is derived with the help of the mechanism in Scheme 2 (Route I):

$$v = -\mathrm{d}[Cr(VI)]_T/\mathrm{d}t = \frac{k_1 K_{es1} K_{a1}[H^+][Cr(VI)]_T[\text{fructose}][Mn[II]]}{1 + K_{a1}[H^+] + K_{es1}K_{a1}[H^+][\text{fructose}]} \quad (5)$$

or

$$k_{obs} = \frac{k_1 K_{es1} K_{a1}[H^+][\text{fructose}][Mn(II)]}{(1 + K_{a1}[H^+] + K_{es1}K_{a1}[H^+][\text{fructose}])} \quad (6)$$

which can be rearranged as

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{(1 + K_{a1}[H^+])}{k_1 K_{es1} K_{a1}[H^+][\text{fructose}][\text{Mn(II)}]} \quad (7)$$

In the above equations k_1, K_{es1} and K_{a1} are, respectively, the oxidation rate constant of intermediate A2, its ester formation constant and ionization constant of chromic acid (Eq. (4)). At constant $[H^+]$, a plot of l/k_{obs} versus l/[fructose] is linear, making an intercept on the l/k_{obs} axis (Fig. 3(b)), thus satisfying the Michaelis–Menten reciprocal relationship (kinetic proof for complex formation). Hence complex formation between H_2CrO_4 and D-fructose occurs initially. Values of $k_1 = 1.03 \times 10^{-3}$ s^{-1} and $K_{es1} = 325.8$ mol^{-1} dm^3 were calculated from the intercept (967.6) and slope (31.5) of Fig. 3(b) ($r = 0.991$). Hereby it is confirmed that the redox reaction occurs in two kinetically distinguishable steps: the first is a fairly rapid complex formation between H_2CrO_4 and D-fructose, and the second is a slower oxidative degradation of the chromate ester (A2). The values of k_1, K_{es1}, K_{a1}, and [fructose] were used to find k_{cal} (Table 3), which is in excellent agreement with the observed k_{obs}. This confirms the validity of the rate law (6) and the proposed mechanism (Scheme 2, Route I).

Interestingly, rate for ketohexose (fructose) is ca. fourfold higher in comparison to aldohexose (glucose) (Table 4), which can be explained on the basis of stability of the pryanose or furanose forms. Glucose exists in the 100% pyranose form, whereas both pyranose and furanose forms are present in the aqueous solution of D-fructose (vide infra). A six-membered ring (pyranose) is thermodynamically[34] more stable than a five-membered ring (furanose), because the latter forms more ring strain than the former. Thus, we may conclude that β-D-fructofuranose is more reactive in comparison to β-D-fructopyranose, and the reaction proceeds mainly through the Route I of Scheme 2. The possibility of Route II can be completely ruled out because glucose and fructose have different rate constants (in case of the same rate constant values, involvement of pyranose form may be considered).

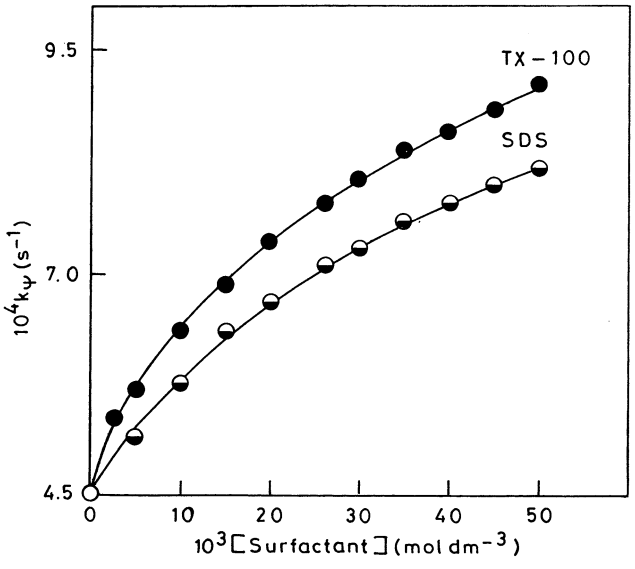


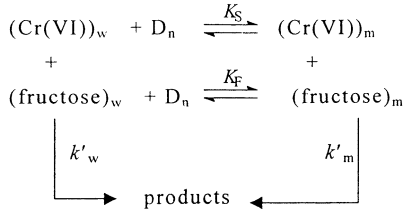
Fig. 4. Effect of [surfactant] (SDS—◒, TX-100—●) on the k_ψ. Other conditions were the same as in Fig. 1 (Set A).

Kinetics in the presence of surfactants.—Preliminary observations showed that the reaction mixture containing CTAB ($= 1.4 \times 10^{-4}$ mol dm^{-3}) and $HClO_4$ ($=$ 0.58 mol dm^3) became intense turbid at room temperature (30 °C) with a visible precipitate in the solution due to the solubility problem of CTAB, which did not become homogeneous even after raising the temperature. However, no such precipitate was formed by adding anionic SDS or nonionic TX-100 surfactants. As a result, the effect of CTAB could not be seen, and it was decided to carry out the kinetic experiments with only SDS and TX-100 surfactants.

Effect of [SDS]/[TX-100] on k_ψ. In order to explore the role of surfactant micelles on the reaction rate (k_ψ), the oxidation reaction was studied as a function of [surfactant] at constant [Cr(VI)] ($= 4 \times 10^4$ mol dm^{-3}), [fructose] ($= 30 \times 10^{-3}$ mol dm^3), and $[H^+]$ ($= 0.58$ mol dm^{-3}) at 60 °C. The variations of the k_ψ with [surfactant] are illustrated in Fig. 4. As can be seen, both the surfactants produce a catalytic effect in the entire range of their concentrations used.

Effect of other variables on k_ψ. It has been established that surfactants may change the mechanism of a reaction. Therefore, to confirm the mechanism vis-a-vis micelle-free medium, the pseudo-first-order rate constants were determined over a range of [fructose], [Cr(VI)], $[H^+]$, and temperature at fixed [SDS] and [TX-100] (Tables 1 and 2). The kinetics follow the same fractional order each in [fructose] and $[H^+]$ and are first order in [Cr(VI)]. The effect of varying [Mn(II)] on the rate was also seen at constant [SDS] ($= 26 \times 10^{-3}$ mol dm^{-3}). The k_ψ-values were found to increase with [Mn(II)] ($k_\psi \times 10^4$: 4.0, 5.1, 6.1, 7.0, 7.1 and 7.3 s^{-1} for [Mn(II)] = 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30 mol dm^{-3}, respectively). These observations undoubtedly establish that the mechanism of oxidation of D-fructose by chromium(VI) in the presence of SDS and TX-100 remains the same as in the absence of surfactants.

Binding constants and rate constants in the micellar media.—The catalytic data observed with micelles of SDS and TX-100 on the oxidation of D-fructose by chromic acid (Tables 1 and 2) allow us to determine kinetically the binding constants (K_S and K_F) and the rate constant (k_m) in the micellar media. The catalytic role of the micelles can be explained by means of the micellar pseudo-phase kinetic model proposed by Menger and Portnoy[20a] as modified by others.[20b,20c,20d,36] This model considers the micelle to be a separate phase from the aqueous and that the reaction



Scheme 3.

occurs in both the phases. Therefore, the reaction probably follows the outlined in Scheme 3.

Here D_n represents the micellized surfactant (= [surfactant]$_T$ − cmc) and k'_w and k'_m stand for rate of oxidation of fructose in non-micellar pseudo-phase and micellar pseudo-phase, respectively. The observed rate law: rate = k_ψ [Cr(VI)]$_T$, and Scheme 3 lead to Eq. (8).

$$k_\psi = \frac{k'_w + k'_m K_S[D_n]}{(1 + K_S[D_n])} \quad (8)$$

In terms of second-order rate constants (k_w and k_m), Eq. (8) can be written as

$$k_\psi = \frac{k_w[\text{fructose}]_T + (K_S k_m - k_w) M_F^S[D_n]}{(1 + K_S[D_n])} \quad (9)$$

In Eq. (9), M_F^S (= [(fructose)$_m$]/[D_n]) is the mole ratio of D-fructose bound to the micellar head groups. To obtain M_F^S, the following expression may be used

$$(\text{fructose})_w + D_n \overset{K_F}{\rightleftharpoons} (\text{fructose})_m \quad (10)$$

$$K_F = \frac{[(\text{fructose})_m]}{[(\text{fructose})_m]([D_n] - [(\text{fructose})_m])} \quad (11)$$

A quadratic Eq. (12) can be obtained with the help of Eq. (11), and the mass balance [fructose]$_T$ = [(fructose)$_w$] + [(fructose)$_m$].

$$K_F[(\text{fructose})_m]^2 - (1 + K_F[D_n] + K_F[\text{fructose}]_T)[(\text{fructose})_m] + K_F[D_n][\text{fructose}]_T = 0 \quad (12)$$

In Eq. (12), K_F is an adjustable parameter. For the calculation of k_m and K_S, the cmc values were determined under the experimental conditions (Table 2). A non-linear least-squares technique was used, and the best value of K_F was taken to be the one for which the value of Σd_i^2 turned out to be a minimum. The best-fit values are summarized in Table 2. The $k_{\psi cal}$ values were obtained by substituting the k_w, K_S, k_m, K_F and [D_n] in Eq. (9) and compared with $k_{\psi obs}$ (Table 5). The close agreement between $k_{\psi cal}$ and $k_{\psi obs}$ provides supporting evidence for the method of calculation.

Probable reaction site.—The location of reactants and degree of water penetration into the micellar structure have a major influence on reactivity.[37] It has been proved that the exact reaction site cannot be proposed because the micellar pseudo-phase is regarded as a microenvironment having varying degrees of water activity, polarity, and hydrophobicity.[38] The activity of water at the surface is not different from water activity in the aqueous pseudo-phase.[39] Therefore, at present, the localization of oxidant and reductant can be considered. As the micellar catalysis was found to increase with increase in [H^+], and as partitioning of neutral H_2CrO_4 in micellar phase has been questioned,[40] $HCrO_3^+$ seems to be the reactive species. (Oxidations of secondary alcohols,[41] benzaldehyde,[42] and *N*,*N*-dimethylformamide[43] by chromium(VI) at high [$HClO_4$] have successfully been explained by considering $HCrO_3^+$ as the reactive oxidant species.) For arguments sake, if we do consider H_2CrO_4 being partitioned in the micellar phase, as many have done so,[21,22] simultaneous partioning of H_2CrO_4 and H^+ is equivalent to the partioning of $HCrO_3^+$. In the present case, the acid concentration is not so high, but keeping in mind the well-known fact that in the presence of anionic micelles, the effective local pH in the vicinity of the micellar surface is lower (by ca. 2 units),[44] chances of H_2CrO_4 gaining another proton in the interfacial region are high (Eq. (13)). Thus, we assume that the catalytic behavior of SDS micelles are caused by the inclusion of

$$H_2CrO_4 + H^+ \rightarrow HCrO_3^+ + H_2O \quad (13)$$

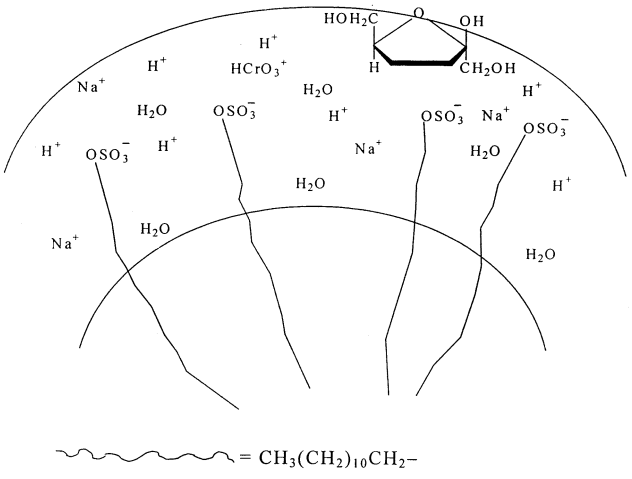
[H^+] into the Stern layer (most of the ionic micelle mediated reactions are believed to occur in this layer). Based on purely electrostatic considerations, the [H^+] increases, which in turn, increases the percentage of species $HCrO_{3+}$ into the Stern layer, and the negative head groups of SDS micelles form ion-pairs with the $HCrO_3^+$ species.

Alcohol distribution between aqueous and SDS micelles has been studied using fluorescence techniques[45] and NMR.[46] Based on these results, the possibility of partitioning D-fructose between the micellar and aqueous phases cannot be ruled out. Thus, we may safely conclude that the redox reaction between chromium(VI) and fructose takes place in the Stern layer (Scheme 4). The micelle helps in bringing the $HCrO_3^+$ and D-fructose together into a small volume, which may orient in a manner suitable for the oxidation.

As far as the role of nonionic micelles of TX-100 is concerned, hydrogen bonding between the nonionic micelles and the reactants may play an important role. Due to this, both the reactants can be concentrated in to the small volume of TX-100 micelles. Chromic acid and D-fructose both possess no hydrophobic character. D-Fructose has 5-OH groups in the cyclic structure, and there may occur hydrogen bonding between the –OH groups of fructose and the –OH groups of the nonionic TX-100. Possibility of the hydrogen bonding between H_2CrO_4 and hydrophilic part of the TX-100 micelles cannot be ruled out either. Formation of an ester-like species between the chromium(VI) and organic reduc-

tants is a characteristic feature of the mechanism of these reactions. Therefore, the associated H_2CrO_4 and D-fructose with TX-100 micelles (through hydrogen bonding) seem responsible of facilitating formation of the chromate ester. This might be the main role of TX-100 micelles toward catalysis.

Effect of added salts on k_ψ.—It is observed that the rate constant k_ψ, decreases exponentially with increase in inorganic salt (NaBr, NH_4Br, LiBr) concentrations. The salt effects in anionic micelles of SDS generally follow the expected pattern (Fig. 5). The reason for this observation may be as follows. Presence of cations around the Stern layer may result in the decrease of surface potential of the micelle, which in turn excludes the reactant species from the Stern layer as well as from the micellar surface. This will give rise to depletion of reactants in the micellar phase; hence, the retardation of the rate with increasing concentration of salts. Salt effect depends largely on the nature of counter ion to the micelle. The counter ions (Na^+, Li^+ and NH_4^+) compete for $HCrO_3^+$ for the SDS micelles so that inhibition by univalent ions typically increases with increasing hydrophobicity of the added cation ($Na^+ > Li^+ > NH_4^+$).



Scheme 4.

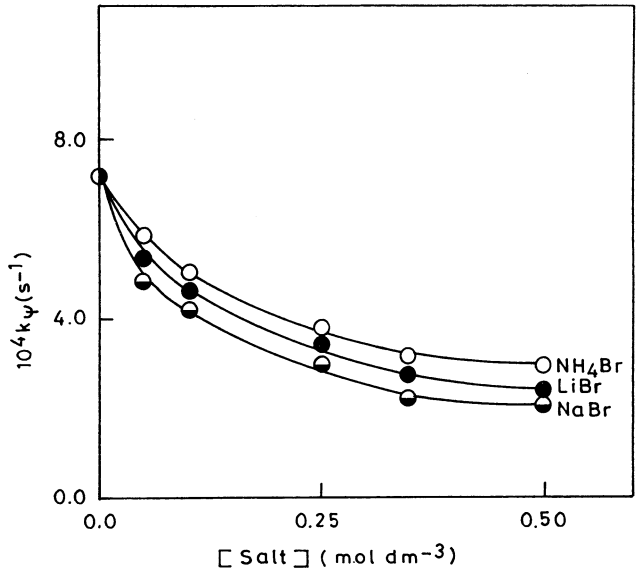


Fig. 5. Effect of salts (NH_4Br—○, LiBr—●, NaBr—◒) on the k_ψ. Other conditions were the same as in Fig. 1 (Set A) with $[SDS] = 26.0 \times 10^{-3}$ mol dm^{-3}.

Activation parameters.—The activation parameters obtained in the aqueous as well as in the SDS/TX-100 media (Table 2) show that the magnitude of $\Delta S^{\neq}$ is not significantly affected, indicating that the same mechanism is being followed in aqueous as well as in micellar media. A meaningful mechanistic explanation of the apparent values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ 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.

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