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Kinetic and Mechanistic Study of the Oxidation of D-Mannose by Tetraethylammonium Chlorochromate in Aqueous Acetic Acid Medium

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The kinetic and mechanistic study of the oxidation of D-mannose by tetraethylammonium chlorochromate $(C_2H_5)_4NCrO_3Cl$ is reported. The reaction has been carried out in aqueous acetic acid 50% (v/v) medium in presence of perchloric acid at constant ionic strength. The reaction has been found to be first order with respect to each of the oxidant and substrate under pseudo-first order conditions. The reaction is catalyzed by acid and follows a first order dependence on H^+ concentration. The ionic strength variation has no effect on the reaction rate. The decrease in dielectric constant of the medium increases the rate of reaction. A 1 : 1 stoichiometry is observed in the oxidation and the reaction rate is not retarded by the addition of radical trapping agent acrylonitrile. The effect of temperature is studied and the various activation parameters are also determined. The products of oxidation are identified to be arabinose and formic acid. On the basis of observed facts, a hydride ion transfer mechanism is proposed.

Key Words: Kinetic, Oxidation, D-Mannose, Tetraethylammonium chlorochromate.

INTRODUCTION

It is of considerable interest to determine the mechanism of oxidation of reducing sugars which have a large number of functional groups unlike most organic substrates, and in which the functional groups and competing reactions frequently occur. Oxidation of some reducing sugars including D-mannose has been investigated with the aid of several oxidants[1–12]. The mechanism of oxidation of carbohydrates have been reported and reviewed[13, 14], wherein metal ions are used as oxidants. Tetraethylammonium chlorochromate[15] is the recently developed Cr(VI) oxidant which resembles pyridium chlorochromate[16] and quinolinium chlorochromate[17] and has an immense versatility as a mild and selective oxidising agent[18].

EXPERIMENTAL

The oxidant tetraethylammonium chlorochromate (TEACC) was synthesized according to the reported procedure[15]. The stock solution of TEACC and D-mannose was prepared in aqueous acetic acid 50% (v/v).

Solution of $NaClO_4$ (CDH, India) was used to maintain a constant ionic strength of 1.0 M perchloric acid (CDH, India). The reactions were performed under pseudo-first order conditions, [D-mannose] ≫ [TEACC]. The medium of reactions was always 1 : 1 (v/v) acetic acid-water in the presence of perchloric acid. The reactions were performed at constant temperature (± 0.1°C). The progress of the reaction was followed spectrophotometrically by monitoring the decrease in absorbance of TEACC at 350 nm using a Shimadzu UV-160A spectrophotometer.

RESULTS AND DISCUSSION

Reaction stoichiometry and product analysis: The stoichiometry of the reaction was carried out by taking [TEACC] ≫ [D-mannose]. A mixture of D-mannose (0.01 mol dm^{-3}) and TEACC (0.10 mol dm^{-3}) were allowed to react for 24 h at 30°C in a solvent. The unconsumed TEACC was determined iodometrically. The stoichiometry was found to be 1 : 1, consistent with the following equation:

$$C_6H_{12}O_6 + (C_2H_5)_4NCrO_3Cl \xrightarrow{H^+} C_5H_{10}O_5 + HCOOH + (C_2H_5)_4NCl + CrO_2$$

This equation entails a two electron transfer which is in good agreement with the proposals of Brown *et al.*[19] D-arabinose and formic acid were identified as the products of oxidation. The formation of D-arabinose was confirmed by phenylhydrazone formation[20] and the presence of formic acid was confirmed by spot test[21].

Empirical rate law: The kinetics of oxidation process was studied under pseudo-first order conditions in 1 : 1 (v/v) acetic acid-water mixture in the presence of perchloric acid at constant ionic strength. The pseudo-first order rate constants were determined at various initial concentrations of reactants. The results obtained are given in Table-1.

The order in oxidant is unity as the plots of log [TEACC] against time were linear in all the runs studied and pseudo-first order rate constants are independent of initial concentration of TEACC (Table-1).

The reaction rate increases with the increasing concentration of D-mannose and the plot of log k_1 *vs.* log [D-mannose] is found to be linear having a slope of 1.01 (Fig. 1), indicating first order dependence on [D-mannose]. The second order rate constants, k_2 ($k_2 = k_1$/[substrate]), are constant supporting the first order dependence on [D-mannose] (Table-1).

The reaction is acid catalyzed (Table-1) and the plot of log k_1, *vs.* log [H^+] is found to be linear having a slope of 1.03 (Fig. 2) indicating first order dependence on [H^+].

The linear increase in rate with acidity suggests the involvement of protonated Cr(VI) species in the rate determining step. Involvement of such species is well known in Cr(VI) oxidation[22] proceeding in acid media[23]. Hence, the empirical rate law may be given as below:

$$-\frac{d[TEACC]}{dt} = k_{obs}[TEACC][D\text{-mannose}][H^+]$$

TABLE-1
DEPENDENCE OF RATE CONSTANT ON [TEACC], [D-MANNOSE] AND PERCHLORIC ACID AT 30°C

$[NaClO_4] = 1.66 \times 10^{-1}$ mol dm^{-3}; solvent: acetic acid-water {50–50% (v/v)}

[TEACC] × 10^3 (mol dm^{-3})	[D-Mannose] × 10^2 (mol dm^{-3})	$[HClO_4]$ × 10 (mol dm^{-3})	$K_1 \times 10^4$ (s^{-1})	$K_2 \times 10^2$ (dm^{-3} mol^{-1} s^{-1})
0.66	1.66	7.73	3.55	—
0.88	1.66	7.73	3.52	—
1.11	1.66	7.73	3.55	—
1.33	1.66	7.73	3.57	—
1.55	1.66	7.73	3.55	—
1.33	0.66	7.73	1.42	2.15
1.33	1.00	7.73	2.13	2.13
1.33	1.33	7.73	2.88	2.17
1.33	1.66	7.73	3.55	2.14
1.33	2.00	7.73	4.29	2.14
1.33	1.66	3.80	1.62	—
1.33	1.66	5.80	2.75	—
1.33	1.66	7.70	3.55	—
1.33	1.66	9.90	4.73	—
1.33	1.66	11.60	5.62	—

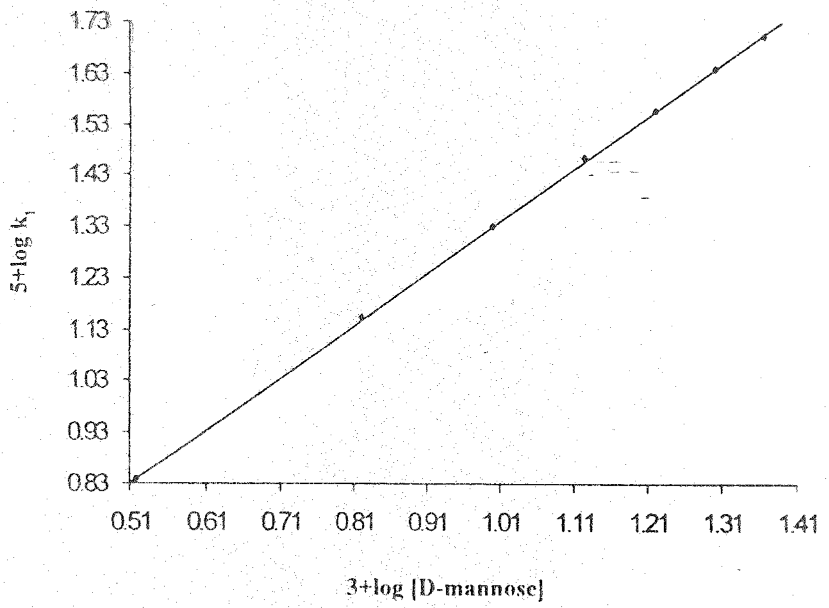


Fig. 1. Plot of log k_1 *vs.* log [D-mannose]; $[TEACC] = 1.11 \times 10^{-3}$ mol dm^{-3}; $[HClO_4] = 7.73 \times 10^{-1}$ mol dm^{-3}; $[NaClO_4] = 1.66 \times 10^{-1}$ mol dm^{-3}; solvent acetic acid-water {50-50% (v/v)}; temperature 30°C

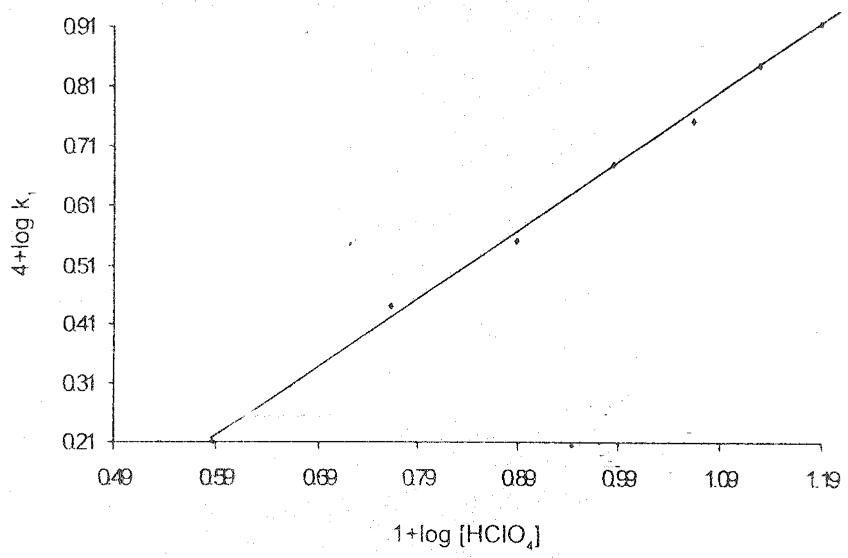


Fig. 2. Plot of log k_1 *vs.* log [$HClO_4$]; [TEACC] = 1.11×10^{-3} mol dm^{-3}; [$HClO_4$] = 7.73×10^{-1} mol dm^{-3}; [$NaClO_4$] = 1.66×10^{-3} mol dm^{-3};sSolvent: acetic acid-water {50-50% (v/v)}; temperature 30°C

Salt effect on the reaction rate: The reaction rate was not influenced by ionic strength over the range of 0.83×10^{-1} to 5.00×10^{-1} mol dm^{-3} $NaClO_4$. Similar observations have also been reported in the oxidation of hydrocarbons by other oxochromium(VI) reagents[24].

Solvent effect: The kinetics of the reaction has been studied under varying composition of acetic acid-water mixture (Table-2).

TABLE-2

EFFECT OF SOLVENT (CH_3COOH) ON THE RATE CONSTANT k_1

[TEACC] = 1.11×10^{-3} mol dm^{-3}; [D-mannose] = 1.66×10^{-2} mol dm^{-3};
[$HClO_4$] = 7.73×10^{-1} mol dm^{-3}; [$NaClO_4$] = 1.66×10^{-1} mol dm^{-3}; temperature 30°C

$CH_3COOH : H_2O$	$k_1 \times 10^4$ (sec^{-1})	1/D
40 : 60	3.20	0.020
50 : 50	3.55	0.024
60 : 40	3.91	0.028
70 : 30	4.74	0.036
80 : 20	6.15	0.048

It has been observed that pseudo-first order rate constants increase with decreases in dielectric constant (Table-2). A plot of log k_1 *vs.* 1/D (inverse of dielectirc constant) is linear with positive slope (Fig. 3). From this it is concluded that reaction is of ion-dipole type[25] and this provides convincing evidence that the active species is a protonated form of TEACC.

Effect of temperature: The reaction has been studied at five different temperatures. Table-3 presents the various activation parameters calculated.

A plot of log k_1 *vs.* 1/T is linear showing that the Arrhenius equation is followed (Fig. 4).

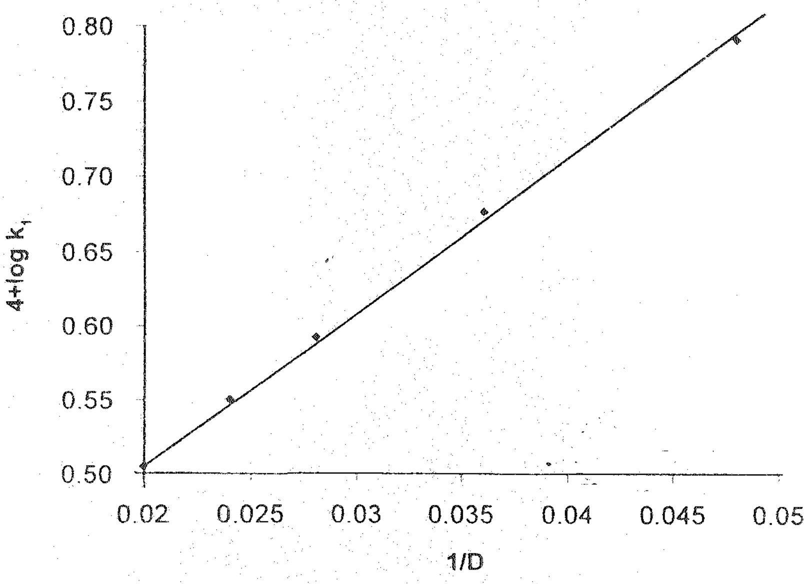


Fig. 3. Plot of log k_1 *vs.* 1/D; [TEACC] = 1.11×10^{-3} mol dm^{-3}; [$HClO_4$] = 7.73×10^{-1} mol dm^{-3}; [$NaClO_4$] = 1.66×10^{-1} mol dm^{-3}; solvent acetic acid-water {50-50% (v/v)}; temperature 30°C

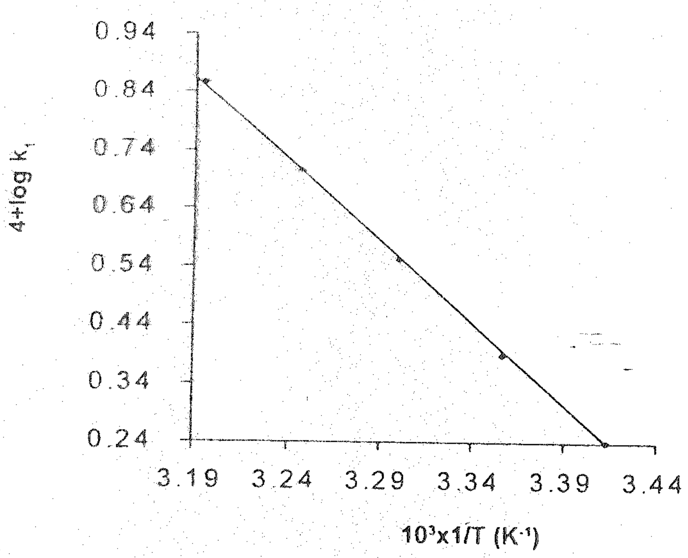


Fig. 4. Plot of log k_1, *vs.* 10^3/T; [D-mannose] = 1.66×10^{-2} mol dm^{-3}; [TEACC] = 1.11×10^{-3} mol dm^{-3}; [$HClO_4$] = 7.73×10^{-1} mol dm^{-3}; [$NaClO_4$] = 1.66×10^{-1} mol dm^{-3}; solvent: acetic acid-water {1 : 1 (v/v)}; temperature 30°C

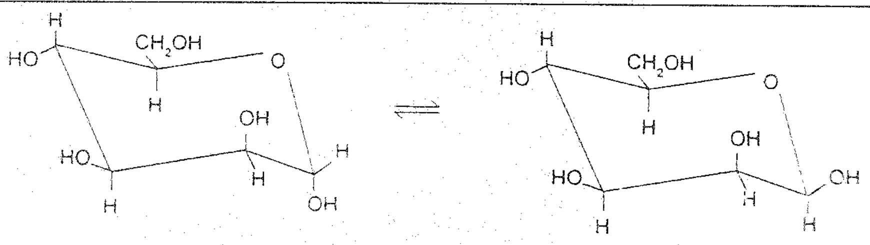
Aldoses in aqueous acidic solution exist as equilibrium mixtures of α- and β-pyranose **(Scheme-1)**[26]. The equilibrium mixture of D-manose mainly consists of the α-anomer having the epimeric H in equatorial position. The β-anomer is supposed to be more reactive species[27].

A free radical mechanism is ruled out since the polymerization of acrylonitrile is not observed.

TABLE-3
DEPENDENCE OF RATE ON TEMPERATURE AND ACTIVATION PARAMETERS IN ACETIC ACID 50% (v/v)-WATER 50% (v/v) MIXTURES

[D-Mannose] = 1.66×10^{-2} M; [TEACC] = 1.11×10^{-3} M; [Perchloric acid] = 7.73×10^{-1} M; [Sodium perchlorate] = 1.66×10^{-1} M

Temperature (K)	$k_1 \times 10^4$ (sec^{-1})	Temperature coefficient	E_a (K) (kJ mol^{-1})	$\log_{10} A$	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	$-\Delta S^*$ (J K^{-1} mol^{-1})
293	1.74	—	—	5.99	52.26	92.82	138.43
298	2.45	2.04	52.63	5.97	52.22	93.60	138.86
303	3.55	2.07	55.49	5.98	52.18	94.28	138.94
308	5.07	2.03	55.99	5.98	52.14	94.96	139.03
313	7.22	—	—	5.98	52.10	95.62	139.04
	Mean:		54.70				
	E_a from graph:		54.68				



α-mannose, 69%

β-mannose, 31%

Scheme-1

The increase in rate with acidity suggests protonation of TEACC species. This protonated TEACC interacts with the substrate in the rate-determining step. Both structural and experimental observations led to the conclusion that the reaction involves the removal of a hydride ion, leaving a carbonium ion as a transient intermediate which undergoes further changes to form the product. However, the UV-spectra did not show the existence of the intermediate complex formation (Fig. 5), indicating its instability. The process is outlined in **Scheme-2.**

Observation of earlier workers provides support for this mechanism[28-30].

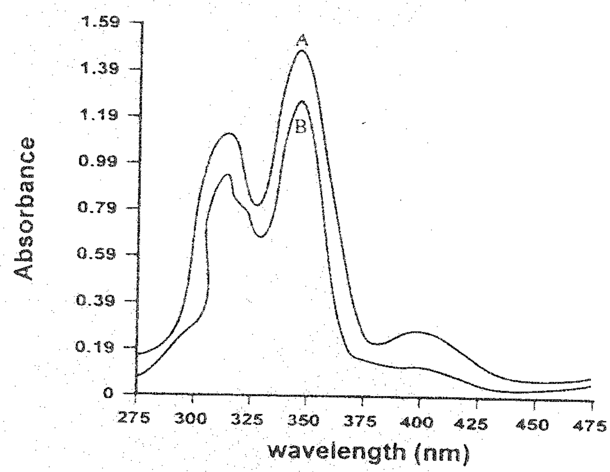
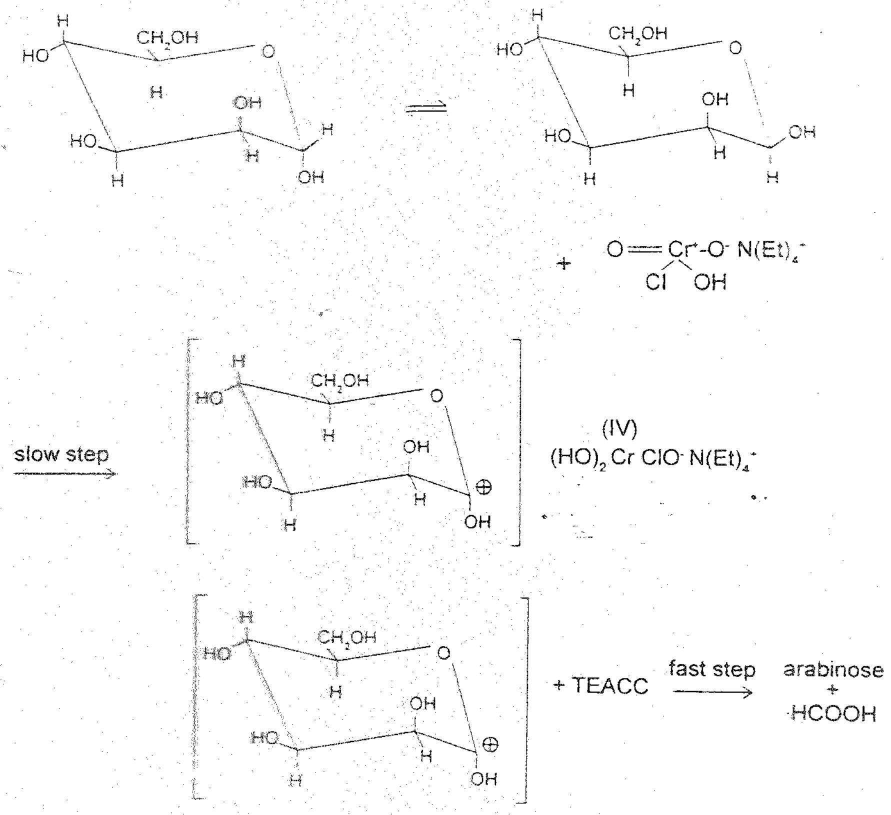


Fig. 5. UV-spectra of TEACC in aqueous acetic acid 50% (v/v) (A) and TEACC in aqueous acetic acid 50% (v/v) with D-mannose (B)



Scheme-2

Rate law:

$$\mathrm{TEACC} + \mathrm{H}^+ \underset{K_2}{\overset{K_1}{\rightleftharpoons}} \mathrm{TEACCH}^+ \qquad (1)$$

$$\mathrm{TEACCH}^+ + \mathrm{S} \xrightarrow[\text{slow step}]{k_1} \mathrm{I} + \mathrm{Cr(IV)} \qquad (2)$$

$$\mathrm{I} + \mathrm{TEACC} \xrightarrow{\text{fast}} \text{products} \qquad (3)$$

$$\text{Rate} = -\frac{d}{dt}[\mathrm{TEACCH}^+] \propto [\mathrm{TEACCH}^+][\mathrm{S}] = k_1[\mathrm{TEACCH}^+][\mathrm{S}] \qquad (4)$$

Applying law of mass action to eqn. (1) we get,

$$k_1 = \frac{[\mathrm{TEACCH}^+]}{[\mathrm{TEACC}][\mathrm{H}^+]} \qquad (5)$$

$$[\mathrm{TEACCH}^+] = K_1[\mathrm{TEACC}][\mathrm{H}^+]$$

Substituting the value of $[\mathrm{TEACC}][\mathrm{H}^+]$ from eqn. (5) into eqn. (4),

$$\text{Rate} = k_1K_1[\mathrm{TEACC}][\mathrm{H}^+][\mathrm{S}] = k_{obs}[\mathrm{TEACC}][\mathrm{H}^+][\mathrm{S}]$$

Conclusion

The oxidation of D-mannose proceeds *via* hydride ion transfer mechanism involving the specific cleavage of C_1—C_2 bond of the substrate to give the products.

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