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

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In an attempt to develop new oxochromium(VI) reagents for effective and selective oxidation of organic substrates under mild conditions, the oxidation kinetics of D-galactose with tetraethylammonium chlorochromate $(C_2H_5)_4NCrO_3Cl$ has been studied in aqueous acetic acid medium 50% (v/v) in the presence of perchloric acid at constant ionic strength. The reaction, under pseudo-first order condition, is first-order with respect to both the [oxidant] and the [substrate]. The reaction is markedly catalyzed by $[H^+]$ and the effect of $[NaClO_4]$ is negligible. Increasing the dielectric constant of medium decreases the reaction rate. A 1 : 1 stoichiometry is observed and the reaction did not induce the polymerization of acrylonitrile. The reaction has been carried out at different temperatures and the various activation parameters have been computed.

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

INTRODUCTION

The kinetics of oxidation of reducing sugars which contain a large number of functional groups is of considerable interest from the mechanistic point of view and have been studied fairly well[1–10].

Tetraethylammonium chlorochromate[11] adds to the selected list of new Cr(VI) reagents introduced recently as oxidizing agent for the effective and selective oxidation of organic substrate under mild conditions. A survey of literature, however, revealed that no work has been carried out on the kinetics of oxidation of D-galactose with tetraethylammonium chlorochromate.

EXPERIMENTAL

Tetraethylammonium chlorochromate was prepared[11] by anhydrous chromium(VI) oxide dissolved in 6 M HCl and stirred at 0°C for 5 min followed by the addition of tetraethylammonium hydroxide (20%) solution. The resulting orange yellow solid was washed and dried under reduced pressure. Chromium content was determined iodometrically. Solution of D-galactose was always freshly prepared in aqueous acetic acid 50% (v/v).

Kinetic measurements: The reactions were performed under pseudo-first order conditions by keeping a large excess of [D-galactose] with respect to [TEACC]. The medium of the reaction was always 1 : 1 (v/v) acetic acid-water in the presence of perchloric acid. Kinetic measurements were made in Shimadzu UV160A spectrophotometer at 350 nm. The optical density was measured at various intervals of time. Computation of rate constants was made from the plot of log [TEACC] against time.

RESULTS AND DISCUSSION

Stoichiometry and product analysis: The stoichiometry of reaction was performed by conducting the oxidation of D-galactose under the conditions of a known excess of tetraethylammonium chlorochromate. A mixture of D-galactose (0.01 mol dm^{-3}) and TEACC (0.10 mol dm^{-3}) was kept for several hours at 30°C for the reaction to go to completion. The unconsumed oxidant was estimated iodometrically at the end of the reaction. The stoichiometry was found to be 1 : 1 consistent with the following equation:

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

For product analysis the reaction mixture containing D-galactose and tetraethylammonium chlorochromate in the stoichiometric proportion of 1 : 1 was left as to equilibrate at 30° for 24 h. The reaction mixture was neutralized with $NaHCO_3$, extracted with chloroform, washed with water and dried over anhydrous $MgSO_4$. The formation of lyxose was confirmed by phenylhydrozone formation[12]. The presence of formic acid was confirmed by spot test[13].

Empirical rate law: The pseudo-first order rate constants were determined at various initial concentrations of reactants. The results obtained are given in Table-1. Plots for different concentrations of TEACC *vs.* time were linear and the rate constants were independent of initial concentration of TEACC, showing first order dependence of the rate on [TEACC]. The reaction is first order with respect to [D-galactose], too. A plot of log k_1 against log [D-galactose] was linear with a slope of unity thereby confirming first order dependence in [D-galactose] (Fig. 1).

Rates of oxidation were found to increase with increase in [H^+] and the slopes of the plots of log k_1 *vs.* log [$HClO_4$] were approximately unity showing that the reaction is acid catalyzed and follows the first order dependence in [$HClO_4$] (Fig. 2).

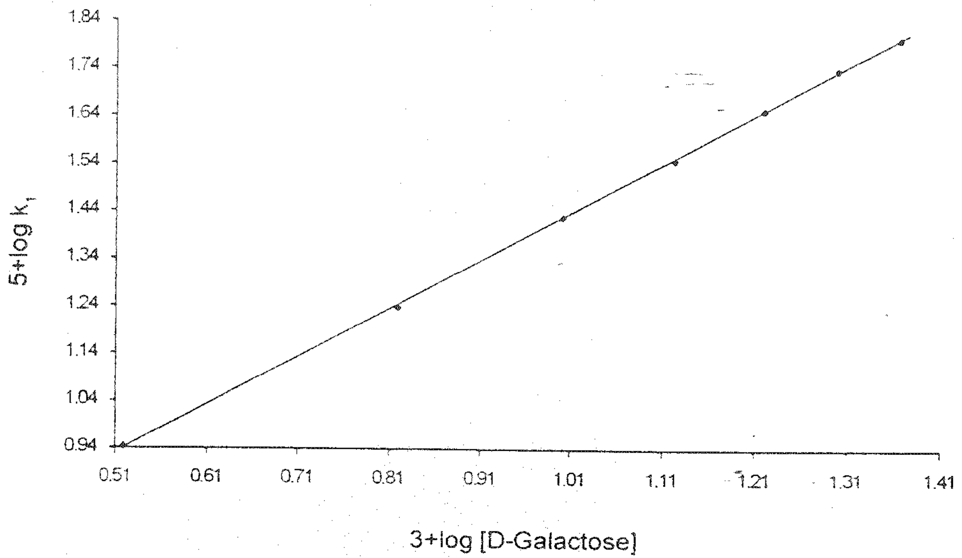


Fig. 1. Plot of log k_1 *vs.* [D-galactose]. [TEACC] = 1.11×10^{-3} mol dm^{-3}; [$HClO_4$] = 7.73×10^{-1} mol dm^{-3}; [$NaClO_4$] = 1.66×10^{-1} mol dm^{-3}; solvent: acetic adic-water (50–50% v/v); temperature = 30°C

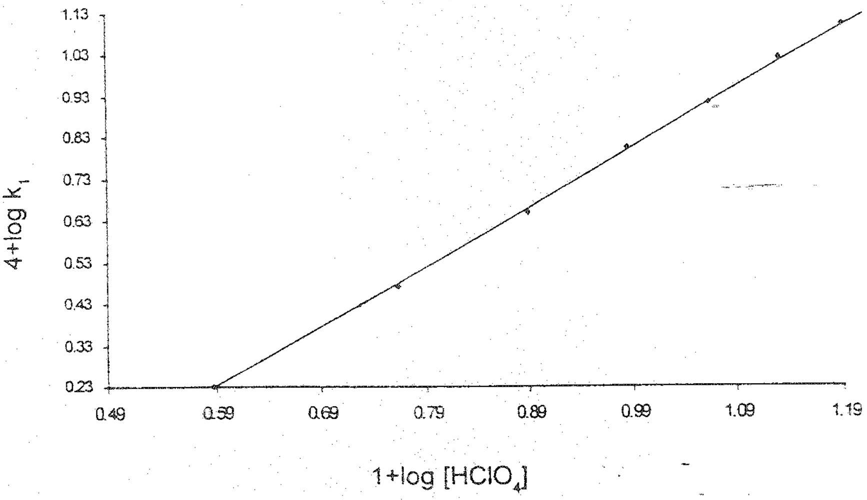


Fig. 2. Plot of log k_1 *vs.* log [H^+]. [TEACC] = 1.11×10^{-3} mol dm^{-3}; [D-galactose] = 1.66×10^{-2} mol dm^{-3}; [$NaClO_4$] = 1.66×10^{-1} mol dm^{-3}; solvent: acetic acid-water (50–50% v/v); temperature = 30°C

Consequently the empirical rate law is described as follows:

$$-\frac{d[\text{TEACC}]}{dt} = k_{obs}[\text{TEACC}][\text{D-Galactose}][\text{HClO}_4]$$

Effect of ionic strength: The reaction rate was not influenced by ionic strength when $NaClO_4$ was initially added to the reaction mixture over the range $0.83–5.00 \times 10^{-1}$ mol dm^{-3}. Similar observations were also reported earlier in the oxidation of diols by some oxochromium(VI) reagents[14] and chromic acid[15].

TABLE-1

RATE CONSTANTS FOR OXIDATION OF D-GALACTOSE BY TEACC AT 30°C.

[TEACC] × 10^3 (mol dm^{-3})	[D-Galactose] × 10^2 (mol dm^{-3})	[H^+] × 10^1 (mol dm^{-3})	$k_1 \times 10^4$ (s^{-1})	$k_2 \times 10^2$ (mol^{-1} dm^3 s^{-1})
0.66	1.66	7.73	4.46	—
0.88	1.66	7.73	4.46	—
1.11	1.66	7.73	4.46	—
1.33	1.66	7.73	4.44	—
1.55	1.66	7.73	4.44	—
1.11	0.33	7.73	0.88	2.68
1.11	0.66	7.73	1.72	2.61
1.11	1.00	7.73	2.67	2.67
1.11	1.33	7.73	3.52	2.65
1.11	1.66	7.73	4.46	2.68
1.11	1.66	3.8	1.70	—
1.11	1.66	5.8	2.95	—
1.11	1.66	7.7	4.46	—
1.11	1.66	9.9	6.31	—
1.11	1.66	11.6	8.03	—

Effect of radical-forming agent: When the reaction was initiated by adding acrylonitrile into a solution containing D-galactose and TEACC, no retardation in the rate was observed. No turbidity due to the polymerization of acrylonitrile was observed. Thus, the formation of radical intermediate may be ruled out in the course of the reaction.

Effect of solvent: The reaction has been studied under various compositions of acetic acid-water mixture. It has been observed that the reaction rate increases with the increase of CH_3COOH in acetic acid-water mixture (Table-2 and Fig. 3). A linear plot between log k_1 and 1/D (inverse of dielectric constant) with a positive slope suggests an interaction between an ion and a dipole[16].

TABLE-2
DEPENDENCE OF RATE ON SOLVENT COMPOSITION

[D-Galactose] = 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}; temperature 30°C

$CH_3COOH : H_2O$	$k_1 \times 10^4$ (sec^{-1})	1/D
40 : 60	3.71	0.020
50 : 50	4.46	0.024
60 : 40	5.20	0.028
70 : 30	6.88	0.036
80 : 20	9.33	0.048

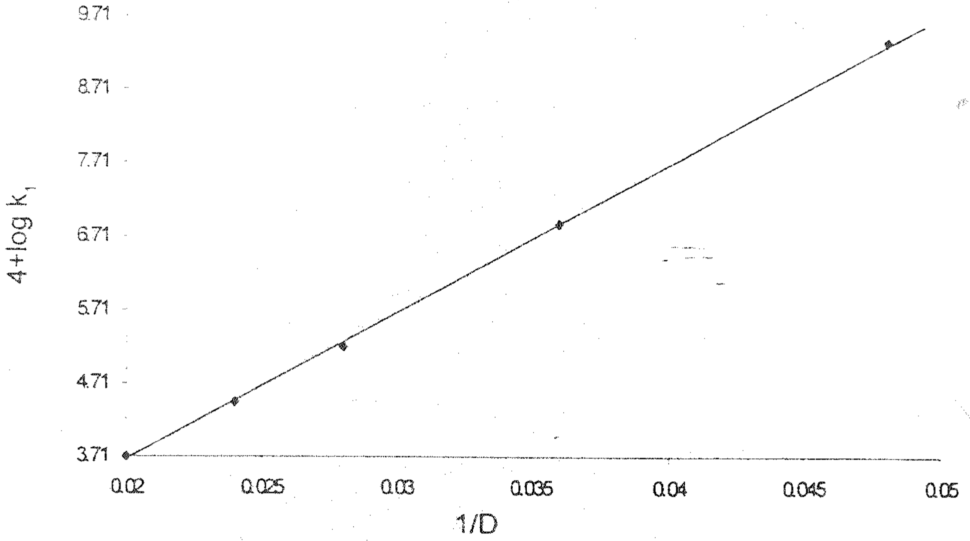


Fig. 3. Plot of log k_1 *vs.* 1/D. [TEACC] = 1.11×10^{-3} mol dm^{-3}; [D-galactose] = 1.66×10^{-2} mol dm^{-3}; [$HClO_4$] = 7.73×10^{-1} mol dm^{-3}; [$NaClO_4$] = 1.66×10^{-1} mol dm^{-3}; temperature = 30°C

Effect of temperature: The reaction rates at different temperatures were determined and the values of activation parameters were calculated from the slope of linear plot of log k_1 *vs.* T^{-1}. The data are presented in Table-3. An inspection of data (Table-3) shows that these reactions are characterized by a high negative value of entropy of activation (ΔS^*). This indicates that solvation effects are predominant in the reaction, which suggests the formation of a charged and rigid transition state. Furthermore, the high positive values of energy of activation and enthalpy of activation indicate that the intermediate is highly solvated.

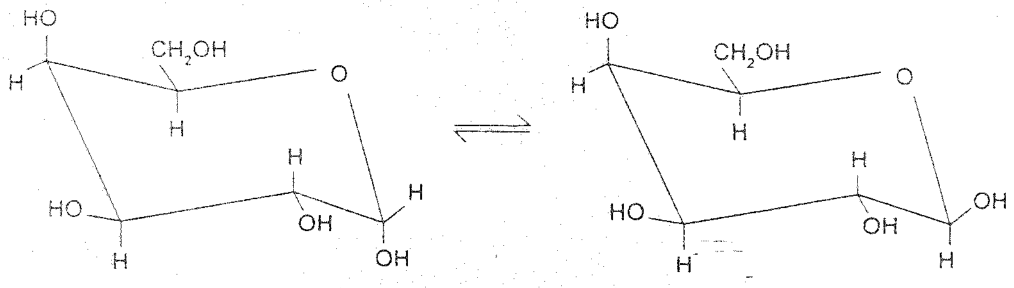
TABLE-3

TEMPERATURE DEPENDENCE AND ACTIVATION PARAMETERS OF OXIDATION OF [D-GALACTOSE] BY TEACC

[D-Galactose] = 1.66×10^{-2} mol dm^{-3}; [TEACC] = 1.11×10^{-3} mol dm^{-3};
[Perchloric acid] = 7.73×10^{-1} mol dm^{-3}; [NaClO$_4$] = 1.66×10^{-1} mol dm^{-3};

Temperature (K)	$k_1 \times 10^4$ (s^{-1})	Temperature coefficient	E_a (kJ mol^{-1})	$\log_{10} A$	ΔH* (kJ mol^{-1})	ΔS* (kJ mol^{-1})	−ΔS* (J K^{-1} mol^{-1})
293	2.24	—	—	6.27	53.25	92.20	132.95
298	3.26	1.99	50.84	6.27	53.21	92.88	133.13
303	4.46	2.11	57.11	6.25	53.17	93.70	133.76
308	6.89	2.12	59.14	6.28	53.13	94.16	133.21
313	9.44	—	—	6.27	53.09	94.92	133.66
		Mean:	55.69				
		E_a from graph:	55.68				

Aldoses in aqueous acidic solution exist as equilibrium mixture of α- and β-pyranose[17] **(Scheme-1).** The equilibrium mixture of D-galactose mainly consists of β-anomer with the equatorial orientation of the glycosidic hydroxyl group. The β-anomer is supposed to be more reactive species[18].



α-Galactose, 30%   β-Galactose, 70%

Scheme-1

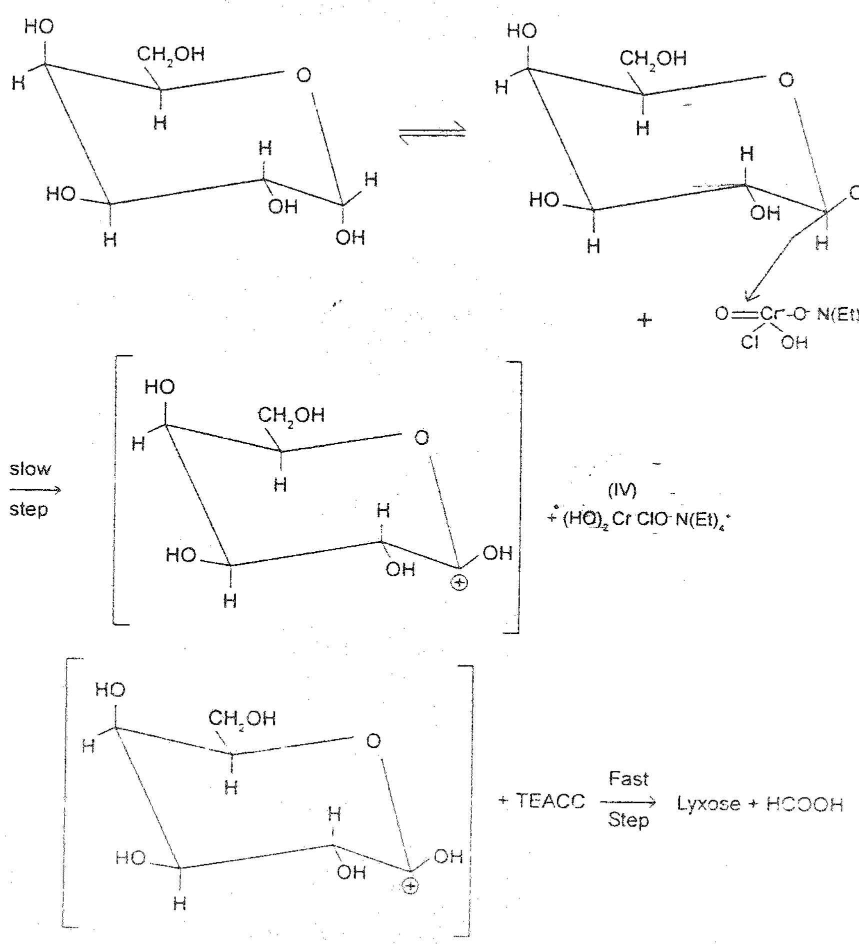
An increase in the oxidation rate with acidity suggests protonation of TEACC species. This protonated TEACC interacts with the substrate in the rate determining step. Involvement of such species is well known in chromic acid oxidation[19].

The oxidation of D-galactose may be assumed to follow the direct hydride ion transfer of the axial anomeric proton of β-galactose as shown in **Scheme-2.**

However, UV spectra recorded did notshowthe existence of intermediate complex formation. This indicates the instability of intermediate (Fig. 4).

Rate law:

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



Scheme-2

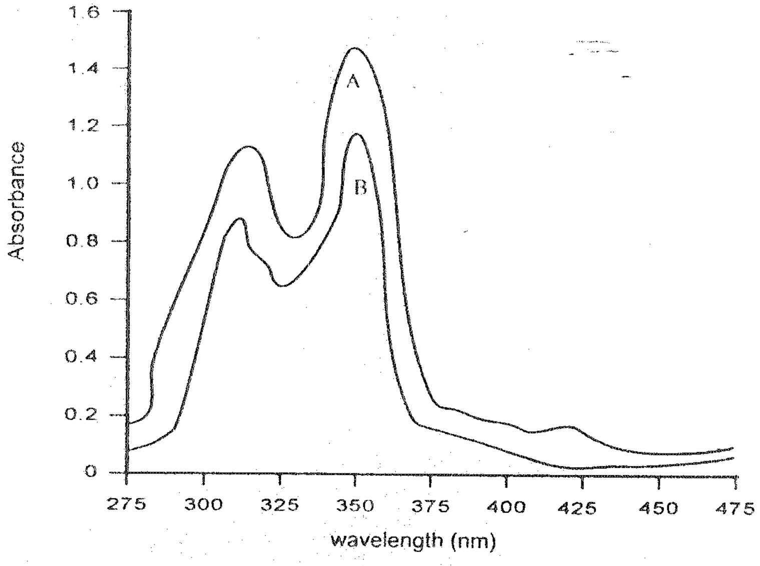


Fig. 4. UV-spectra of TEACC in aqueous acetic acid 50% (v/v) (A) and TEACC in aqueous acetic acid 50% (v/v) with D-galactose (B)

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

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

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

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

$$k_1 = \frac{[\text{TEACCH}^+]}{[\text{TEACC}][\text{H}^+]}$$

$$[\text{TEACCH}^+] = K_1[\text{TEACC}][\text{H}^+] \qquad (5)$$

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

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

Conclusion

The oxidation of D-galactose by TEACC in aqueous acetic acid medium proceeds *via* hydride ion transfer mechanism involving specific cleavage of C_1—C_2 bond of the substrate to give the products.

REFERENCES

1. E. Kasper, *Z. Physik Chem. (Leipzig)*, **224**, 427 (1963).
2. A.P. Modi and S. Ghosh, *J. Indian Chem. Soc.*, **46**, 687 (1969).
3. S.P. Mishra and K.C. Gupta, *J. Indian Chem. Soc.*, **51**, 145 (1974).
4. K.K.S. Gupta and S.N. Basu, *Carbohydrate Res.*, **72**, 39 (1979).
5. F. Anand and A. Shrivastava, *Carbohydrate Res.*, **102**, 23 (1982).
6. B. Capon, *Chem. Res.*, **69**, 407 (1969).
7. R.P. Bhatnagar and A.G. Fandis, *J. Sci. Ind. Res.*, **45**, 90 (1986).
8. R. Varadarajan and R.K. Dhar, *Indian J. Chem.*, **25A**, 474 (1986).
9. P.O.I. Virtanen and R. Lindroos-Heinanen, *Acta Chem. Scand.*, **B42**, 411 (1988).
10. V. Shashikala and K.S. Rangappa, *Oxid. Commun.*, **27**, 316 (2004).
11. A. Pandurangan and V. Murugesan, *J. Indian Chem. Soc.*, **73**, 484 (1996).
12. S. Honda and K. Takiura, *Anal. Chim. Acta*, **77**, 125 (1975).
13. F. Feigl, Spot Test in Organic Chemistry, Elsevier, Amsterdam, p. 347 (1960).
14. G.L. Agrawal and S. Jha, *Revue Roumaine de Chimie*, **34**, 1969 (1989).
15. P.S. Radhakrishanamurty, *Ind. J. Chem.*, **19**, 41 (1971).
16. E.S. Amis, Solvent Effects on Reaction Rates and Mechanism, Academic Press, New York, p. 42 (1966).
17. M.L. Wolfrom and R.S. Staurt, *Adv. Carbohyd. Chem. Biochem.*, **24**, 13 (1969).
18. A.S. Perlen, *Can. J. Chem.*, **42**, 2365 (1964).
19. K.B. Wiberg, Oxidation in Organic Chemistry, Part A, Academic Press, p. 69 (1965).

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