

The study of the Kinetics of D-mannose Oxidation with Imidazolium Fluorochromate in Aqueous Acetic Acid Medium through Spectrophotometric Analysis

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Keywords: *Oxidation, kinetics, mechanism, D-mannose, imidazolium fluorochromate.*

Kinetics and mechanism of oxidation of D-mannose with imidazolium fluorochromate (IFC) have been studied in a 1:1 volume ratio aqueous acetic acid medium. The oxidation study revealed first-order relationship on concentration of D-mannose, imidazolium fluorochromate, and perchloric acid. The reaction rates were enhanced by perchloric acid, and maintained a 1:1 stoichiometric ratio. A constant ionic strength was ensured across the reaction mixture. Further, variations in ionic strength values reflected shallow effect on oxidation rates. The reaction rates decreased in the solvent of high dielectric constant (δ). The observed results were in agreement with the Amis and Kirkwood plots, namely ($\log K_1$ vs $(1/\delta)$ and $(\delta-1/2\delta+1)$). Polymerization of acrylonitrile was absent in the reaction. The oxidation rates were recorded across the range of temperatures, and several thermodynamic variables were computed. The products of the oxidation reaction were arabinose and formic acid. A reaction mechanism supported by observed findings was suggested.

Introduction

In environmental chemistry, Sugars and their derivatives might significantly influence chromium chemistry, mainly due to their mutative and oncogenic characteristics [1]. Consequently, the sugar oxidation has been explored by various chromium-based oxidants [2-6]. Notably, the oxidation reaction of D-mannose with chromium (VI) is highly captivating because it is a vital constituent of polysaccharides, and commonly used in avian agriculture, medicinal products, and the food

industry [7]. Imidazolium fluorochromate (IFC), a gentle, durable, and specific Cr(VI) derivative, has been reported and used as an oxidant in the kinetic study of several organic compounds [8-12]. Earlier studies demonstrated that the oxidation reaction involving D-mannose and IFC have been overlooked [12]. Hence, a kinetic and mechanistic study of D-mannose oxidation with IFC was conducted.

Experimental part

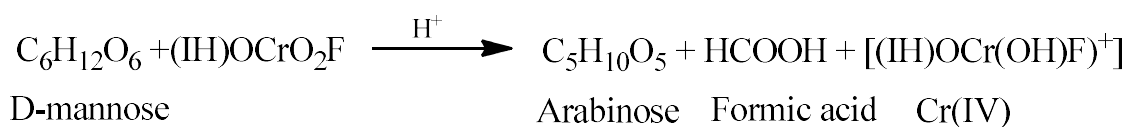
Materials and methods. IFC was derived by adding powdered chromium trioxide (S.R.L.)

to a clear solution of imidazole (S.R.L.) in 40% Hydrofluoric acid (C.D.H.) kept in an ice chamber. This afforded a bright orange solid, filtered and dried under vacuum. The product was stable and stored in a sealed container [8]. A standard solution of Mohr's salt (S.R.L.) [(NH₄)₂Fe (SO₄)₂·6H₂O] was used to determine the purity of IFC. Fresh solution of IFC and D-mannose were always prepared in a 1:1 volume ratio aqueous acetic acid (S.R.L.) medium. An unaltered ionic strength in the reaction was achieved by the addition of sodium chlorate (VII) (NaClO₄) (C.D.H.). All remaining chemicals were used directly in the experiment.

Kinetic studies and measurements. To analyze the kinetics, the reaction was carried out in a 1:1 volume ratio aqueous acetic acid

medium, with surplus [D-mannose] (2.66 x 10⁻² M) over [IFC] (1.33 x 10⁻³ M). The advancement of the IFC-mannose reaction was observed by recording absorbance values at 350 nm at different time points using a visible spectrophotometer.

Stoichiometry and product analysis. To confirm the stoichiometry, a mixture of IFC (2 x 10⁻² M) and D-mannose (2.22 x 10⁻³ M) was made in a 1:1 volume ratio aqueous acetic acid medium and kept in the dark for many hours to achieve a complete reaction. The unreacted IFC was determined by titrating it against a standard Mohr's salt solution, taking diphenylamine as an internal indicator. The reaction followed a 1:1 stoichiometric ratio (**Table 1**), consistent with the equation shown:



For product assessment, the D-mannose and IFC mixture was taken in a 1:1 molar ratio and left to equilibrate at 303 K for a day. The pH of the medium was adjusted with sodium bicarbonate (NaHCO₃), and then separated by trichloromethane (CHCl₃) solvent, followed by water washing and dehydration using MgSO₄ [3, 4]. The phenylhydrazone derivative formation

affirmed the presence of Arabinose [13], while the existence of formic acid was ascertained by spot analysis [14].

Data Analysis. Microsoft Excel (2016) computer software was used for data analysis. The goodness of the fit was assessed using the coefficient of determination (R²) for simple linear regression.

Table 1. Stoichiometry for the oxidation of D-mannose with IFC

Unconsumed [IFC] x 10 ³ M	Consumed [IFC] x 10 ⁴ M	$\frac{\text{Consumed[IFC]}}{[\text{D-mannose}]}$	Stoichiometry
2.38	2.85	0.96	1:1

Results and discussion

Empirical rate law. When [D-mannose] was in excess over [IFC], a linear correlation was observed in the graph of $\log_e [A_o/A_t]$ against time intervals, crossing the origin, indicating a unit order relationship on the concentration of IFC {Here, A_o and A_t denotes the values of absorbance at reaction starting time and at any other particular time interval respectively} (Figure 1).

The calculated first-order rate constants (K_1) elevated their values with the base to the power of one in [D-mannose]⁽ⁱ⁾, which suggests first order dependence on [D-mannose] (Table 2, Figure 2). Therefore, second order rate constant

(k_2) values were computed according to expression (i),

$$k_2 = \frac{K_1}{[\text{D-mannose}]} \quad (i)$$

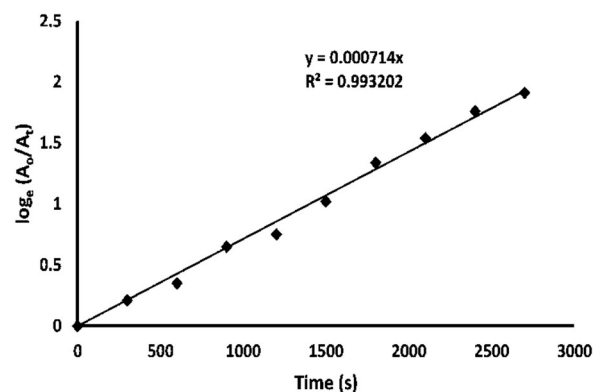


Figure 1. Plot of $\log_e (A_o/A_t)$ against Time (s) of the oxidation of D-mannose with IFC oxidant in a 1:1 volume ratio aqueous acetic acid medium at 303 K. [IFC] = 1.33 x 10⁻³ M, [D-mannose] = 2.66 x 10⁻² M, [HClO₄] = 8.90 x 10⁻¹ M, [NaClO₄] = 1.33 x 10⁻¹ M

Table 2. Concentration related rate constants of the oxidation of D-mannose with IFC oxidant in a 1:1 volume ratio aqueous acetic acid medium at 303 K

[D-mannose] x 10 ² M	[HClO ₄] x 10 ¹ M	K_1 x 10 ⁴ (s ⁻¹)	k_2 x 10 ² (M ⁻¹ s ⁻¹)	R ²
1.33	8.90	3.48	2.61	0.9956
2.66	8.90	7.14	2.68	0.9932
4.00	8.90	10.06	2.52	0.9909
5.33	8.90	13.25	2.49	0.9971
6.66	8.90	16.80	2.52	0.9986
8.00	8.90	20.13	2.52	0.9958
2.66	6.68	5.19		0.9948
2.66	11.13	8.56		0.9963
2.66	13.16	10.52		0.9916
2.66	15.58	12.98		0.9976
2.66	17.81	14.87		0.9942

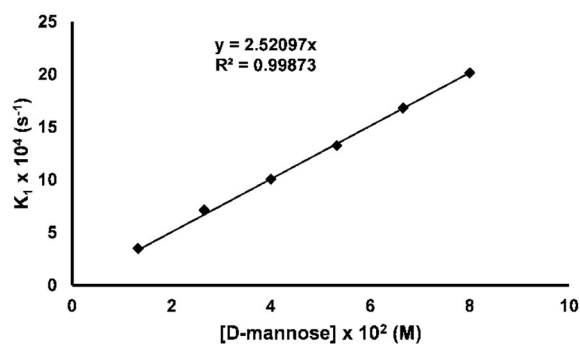


Figure 2. Plot of $K_1 \times 10^4$ versus $[D\text{-mannose}] \times 10^2$ of the oxidation of D-mannose with IFC oxidant in a 1:1 volume ratio aqueous acetic acid medium at 303 K. $[IFC] = 1.33 \times 10^{-3}$ M, $[HClO_4] = 8.90 \times 10^{-1}$ M, $[NaClO_4] = 1.33 \times 10^{-1}$ M

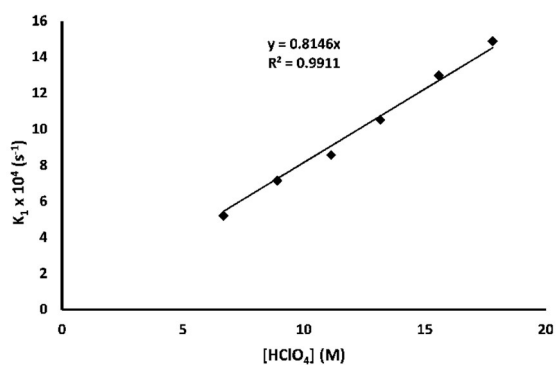


Figure 3. Plot of $K_1 \times 10^4$ versus $[HClO_4]$ of the oxidation of D-mannose with IFC oxidant in a 1:1 volume ratio aqueous acetic acid medium. $[IFC] = 1.33 \times 10^{-3}$ M, $[D\text{-mannose}] = 2.66 \times 10^{-2}$ M, $[NaClO_4] = 1.33 \times 10^{-1}$ M, $T = 303$ K

Oxidation rates were increased and showed a linear correlation with the concentration of $HClO_4$, suggesting a unit-order relationship between perchloric acid and the reaction rate. Furthermore, the linear plot of K_1 versus $[HClO_4]$ passing through the origin provided strong validation that the oxidation reactions occur mainly in the presence of $HClO_4$ (Table 2, Figure 3). Without $HClO_4$, experiments revealed that reactions were very

slow, despite elevated temperatures. As a result, all the studies were conducted while keeping the $[HClO_4]$ unchanged.

Effect of ionic strength. The variation in ionic strength with the addition of $NaClO_4$ to the reaction blend within the concentration range (0.66×10^{-1} - 4.66×10^{-1} M) had not impact the reaction rate to a considerable degree, which may suggest the involvement of both primary and secondary kinetic salt effect, indeed balancing each other. A literature survey also illustrated that the deviation in ionic strength (μ) has little or no effect on the reaction rates involving ion-polar and polar-polar interactions [15-17].

Effect of radical-forming substances. Upon adding acrylonitrile monomer to the reaction mixture, oxidation rates remained unaffected, and turbidity was absent. Therefore, the possibility of forming free radicals during the reaction was eliminated.

Effect of solvent. The kinetics has been investigated across several compositions of $CH_3COOH-H_2O$ mixture, and it was noted that the rates surged with an increase in $[CH_3COOH]$ in the blend. (Table 3). Further, the linear relationship of Amis plot [18] of $(\log K_1)$ and $(1/\delta)$ (Figure 4(a)) with a positive slope and the linear correlation of Kirkwood plot [19] of $(\log K_1)$ and $(\delta - 1/2\delta + 1)$ (Figure 4 (b)) probably indicates an ion-dipole interaction in the reaction's slowest step.

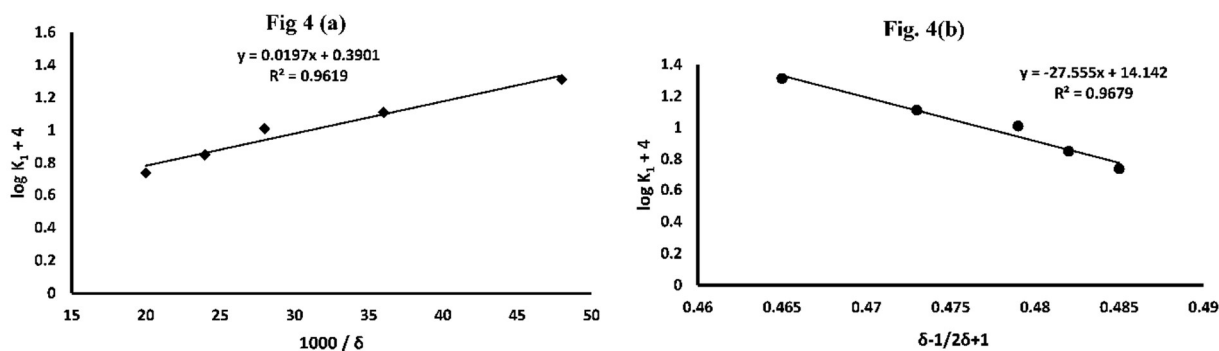


Figure 4. (a) Plot of $\log K_1 + 4$ against $(1000/\delta)$ [Amis]

(b) Plot of $\log K_1 + 4$ against $(\delta - 1/2\delta + 1)$ [Kirkwood] of oxidation of D-mannose with IFC oxidant at 303 K. [D-mannose] = 2.66×10^{-2} M, [IFC] = 1.33×10^{-3} M, $[HClO_4] = 8.90 \times 10^{-1}$ M, $[NaClO_4] = 1.33 \times 10^{-1}$ M

Table 3. Solvent composition related rate constants of oxidation of D-mannose with IFC oxidant at 303 K

$CH_3COOH:H_2O$	$K_1 \times 10^4$ (s^{-1})	R^2	$1/\delta$	$\delta - 1/2\delta + 1$
40:60	5.52	0.9891	0.020	0.485
50:50	7.14	0.9932	0.024	0.482
60:40	10.33	0.9964	0.028	0.479
70:30	12.75	0.9972	0.036	0.473
80:20	20.20	0.9916	0.048	0.465

Effect of temperature. The kinetics have been studied across various temperature ranges to analyze its effect on the rates (**Table 4**). It was observed that a rise in the temperature increased the values of the second-order rate constant (k_2). The Gibb's energy (ΔG^\ddagger) was determined using Eyring's equation of reaction rates as per the expression (ii) [15-17]:

$$k_2 = K \frac{k_b T}{h} e^{-\frac{\Delta G^\ddagger}{RT}} \quad (ii)$$

In the above expression, K is defined as the transmission coefficient, typically its value set to one. Moreover, by applying logarithms on

both sides of expression (ii), it could be written as,

$$\Delta G^\ddagger = RT \log_e \frac{k_b T}{hk_2} \quad (iii)$$

Further, by substituting the values of gas constant (R), Boltzmann constant (K_b), and Plank's constant (h) in expression (iii), it could be more simplified to expression (iv) [5] as,

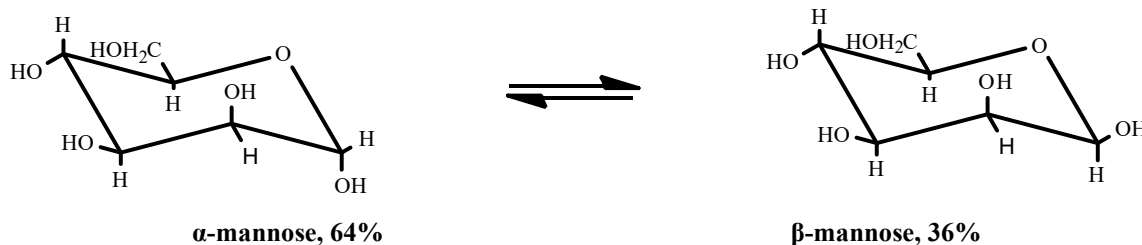
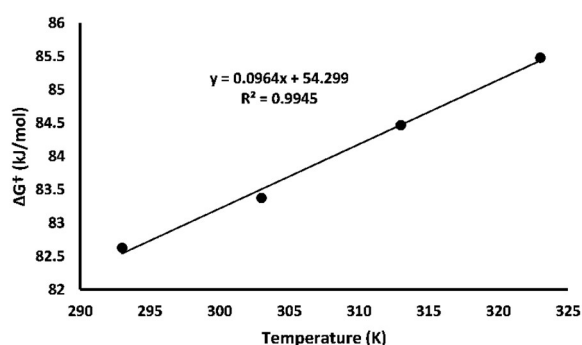
$$\Delta G^\ddagger = 8.314 T [23.7634 + \log_e (T/k_2)] \quad (iv)$$

Gibbs free energy (ΔG^\ddagger) was calculated by using expression (iv). Enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) values were calculated from the y-intercept and gradient of the linear plot of ΔG^\ddagger against temperature (T) (**Figure 5**) as per the following expression (v),

$$\Delta G^\ddagger = -T \Delta S^\ddagger + \Delta H^\ddagger \quad (v)$$

Table 4. Temperature dependent rate constants and several thermodynamic variables of oxidation of D-mannose with IFC oxidant in a 1:1 volume ratio aqueous acetic acid medium.

Temperature (K)	$k_2 \times 10^2$ (M ⁻¹ s ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	$-\Delta S^\ddagger$ (J K ⁻¹ mol ⁻¹)
293	1.14	82.63	54.30	96.4
303	2.68	83.38		
313	5.24	84.47		
323	10.14	85.48		



Scheme 1. Structures of α - and β -mannose

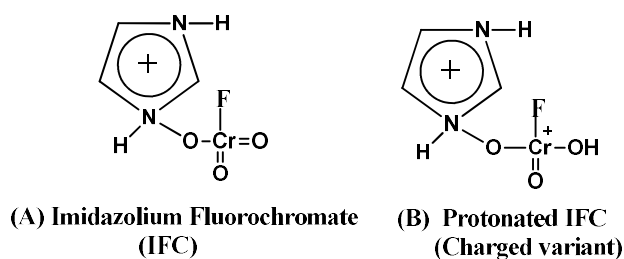
Under acidic conditions in an aqueous medium, imidazolium fluorochromate is predominantly exist in the charged variant (A) as $[(IH)OCrO(OH)F]^+$ (**Scheme 2**) (where I = imidazole; IH^+ = imidazolium ion), by selectively isolating H^+ ion released during $HClO_4$ dissociation. The study implies that the charged form of IFC ($[(IH)OCrO(OH)F]^+$) shows more significant activity compared to the neutral

Figure 5. Plot of ΔG^\ddagger against Temperature (K) of oxidation of D-mannose with IFC oxidant in a 1:1 volume ratio aqueous acetic acid medium. $[D\text{-mannose}] = 2.66 \times 10^{-2}$ M, $[IFC] = 1.33 \times 10^{-3}$ M, $[HClO_4] = 8.90 \times 10^{-1}$ M, $[NaClO_4] = 1.33 \times 10^{-1}$ M

The observed negative entropy value (ΔS^\ddagger) probably suggests that the transient intermediate is polar compared to the reactants. Further, the positive enthalpy of activation (ΔH^\ddagger) probably suggests that the intermediate is highly solvated.

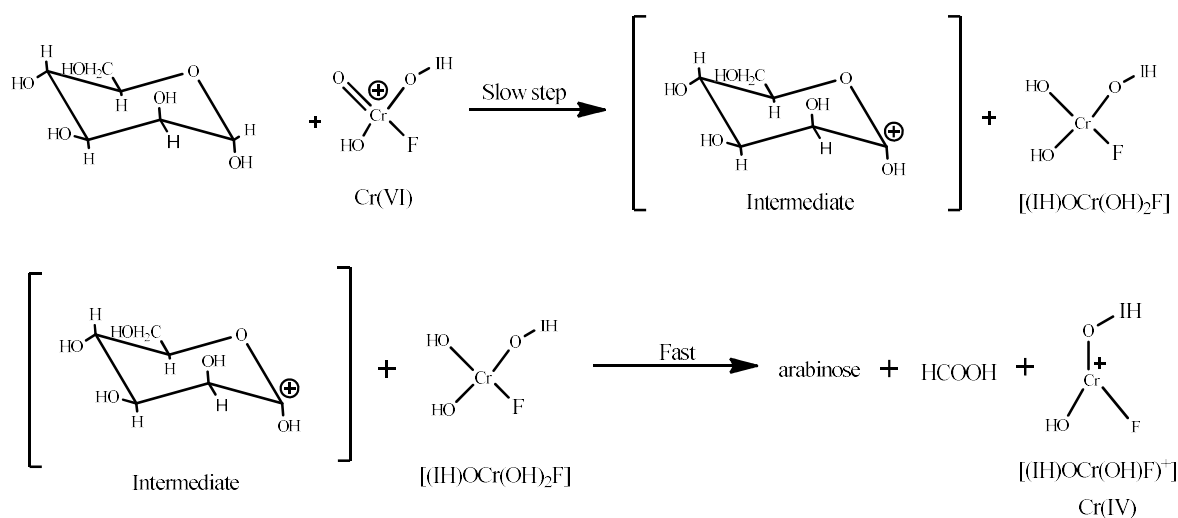
Aldoses attain equilibrium in an aqueous acidic solution, resulting in mixture of α - and β -pyranose ring forms [20] (**Scheme 1**). The α -anomer, with the epimeric OH in the axial orientation, dominates the equilibrium mixture of D-mannose. However, the β -anomer is predicted to exhibit higher reactivity.

form (B) ($[(IH)OCrO_2F]$). This charged form of IFC interacts with the D-mannose in the slowest step of the reaction. The participation of such entities is widely observed in Cr (VI) based oxidation reactions [2-6].



Scheme 2. Structures of neutral and charged variant of Imidazolium Fluorochromate (IFC)

A free radical mechanism is not feasible due to the absence of acrylonitrile



Scheme 3. Suggested mechanistic path

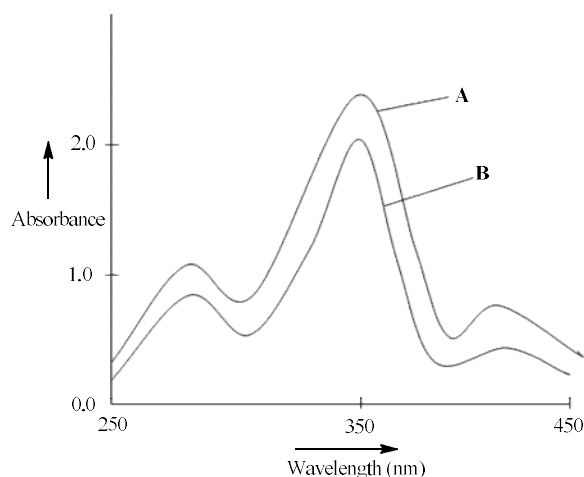
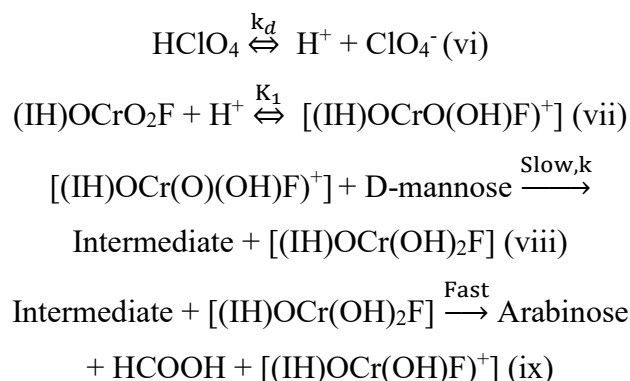


Figure 7. (A) UV-spectra of IFC in a 1:1 volume ratio aqueous acetic acid at 303 K; (B) UV-spectra of IFC oxidant with D-mannose in a 1:1 volume ratio aqueous acetic acid at 303 K

polymerization. Both structural and experimental findings indicate that the reaction proceeds through the hydride ion elimination, resulting in a short-lived carbocation intermediate that undergoes successive transformations to form the product (**Scheme 3**). Meanwhile, the observed UV-spectra probably suggests the vulnerability of the intermediate (**Figure 7**). The findings of previous researchers support the basis of this mechanism [3-4].

Rate law. Considering the suggested mechanistic path, the rate term of the D-mannose oxidation with IFC may be deduced as shown:



From expression (vi), k_d could be written as,

$$k_d = [\text{H}^+] [\text{ClO}_4^-] / [\text{HClO}_4] \text{ (x)}$$

The rate law corresponding to eq. (viii) is as follows,

$$\frac{-d[IFC]}{dt} = k [(IH)OCr(O)(OH)F^+] [D\text{-mannose}] \quad (xi)$$

$[(IH)OCr(O)(OH)F^+]$ could be derived from eq. (vii) as,

$$[(IH)OCr(O)(OH)F^+] = K_1 [(IH)OCrO_2F] [H^+] \quad (xii)$$

On substituting $[H^+]$ from eq. (x) in eq. (xii),

$$[(IH)OCr(O)(OH)F^+] = K_1 k_d [(IH)OCrO_2F] [HClO_4] / [ClO_4^-] \quad (xiii)$$

Now, on substituting $[(IH)OCr(O)(OH)F^+]$ from eq. (xiii) in eq. (xi) gives,

$$\frac{-d[IFC]}{dt} = k K_1 k_d [(IH)OCrO_2F] [D\text{-mannose}] [HClO_4] / [ClO_4^-] \quad (xiv)$$

Therefore, at constant $[HClO_4]$, eq. (xiv) could be expressed as,

$$\frac{-d[IFC]}{dt} = k'' [IFC] [D\text{-mannose}] \quad (\text{where } k'' = k K_1 k_d [HClO_4] / [ClO_4^-]) \quad (xv)$$

Conclusions

Kinetics of perchloric acid enhanced oxidation of D-mannose by imidazolium fluorochromate depicted unit-order dependence on $[IFC]$, $[D\text{-mannose}]$, and $[HClO_4]$. Further, the slowest step of the oxidation reaction of D-mannose with IFC involves the association of the charged variant of IFC ($[(IH)OCr(O)(OH)F^+]$), and D-mannose pursued by hydride ion elimination, resulting in the formation of short-lived carbocation intermediate which undergoes rupture of the $C_1\text{-}C_2$ bond intrinsically to give the products.

Acknowledgements

Thanks due to the financial support provided by the Higher Education Department, Uttar Pradesh in the form of a minor research project under the "Research and Development Scheme" by Government order no. 107/2021/2584/सत्तर-4-2021-4(28)/2021 dated-28/12/2021

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