

Mechanistic Approach to Kinetics of Oxidation of Monosaccharides by THALLIUM(III) ACETATE

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ABSTRACT: The kinetics of oxidation of aldose sugars by thallium(III)acetate in the presence of acetic acid and sulfuric acid have been investigated. The reactions obey first order kinetics in oxidant and substrate. Increase in $[H^+]$ catalyzed the reactions. Addition of acetate ion exhibits retarding effect on the rate of oxidation. Activation parameters have been calculated. A suitable mechanism has been proposed

KEYWORDS: Kinetics, Oxidation, Aldose sugar, Thallium(III)acetate

I. INTRODUCTION

Oxidation kinetics of aldoses by different oxidants viz.. chromic acid [1,2], potassium dichromate [3], hexacyanoferrate(III) [4], quinquivalent vanadium [5], tetravalent cerium [6], trivalent thallium [7] have been investigated. Thallium(III) acetate has been employed to explore the oxidation kinetics of variety of organic substrates with different functional group such as hydrocarbons [8], aliphatic and aryl substituted secondary alcohols [9], carboxylic acids [10], alpha hydroxy acid [11]. The present investigation is carried out to study thallium(III)acetate oxidation of aldoses in aqueous acetic acid medium.

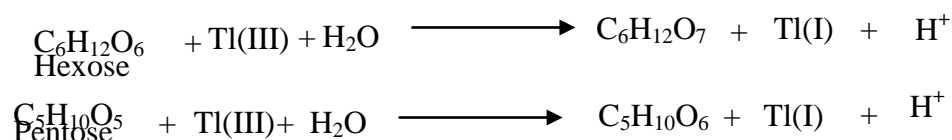
II. EXPERIMENT

A. Kinetic measurements

Kinetic studies were carried out using Ostwald's isolation method. The reaction mixture was equilibrated in a thermostat (± 0.1 °C) at desired temperature. The progress of the reaction was monitored by iodometric estimation of un-reacted thallium(III)acetate.

B. Stoichiometry and product analysis

At experimental temperature the stoichiometric results for aldose-thallium (III) system reveal that one mol of each aldose consumes one mol of oxidant. The stoichiometric reaction may be represented as



The oxidation products, corresponding aldonic acids were identified qualitatively by paper chromatography method. Aldonic acids have also been reported as product of oxidation in chromic acid oxidation of aldoses [5]. Shukla et al. [12] isolated ribonic acid as the oxidation product of ribose with potassium bromate in acid medium. In bromine oxidation of aldose, aldonic acid was reported as product of oxidation [13,14].

III-RESULTS

A. Dependence of rate on oxidant concentration

On the variation of initial concentration of *thallium(III)acetate*, the pseudo first order rate constant decreases with the increase in the concentration of oxidant (table-1). The decrease in the value of rate constant with increase in concentration in thallic acetate may be due to the formation of some less reactive species of thallium (III) acetate complex ion. The true order (n_c) was determined for each aldose-thallium acetate system by initial rate method comes to one supporting first order dependency on oxidant concentration. The slightly high values of (n_i) than the corresponding (n_c) values support the formation of such type of intermediate. Earlier workers have also reported similar observations. [15].

Table 1. Dependence of rate on the concentration of oxidant

SN	[Tl(III)] 10^3 M	GLUCOSE	GALACTOSE	XYLOSE	AROBIANOSE	RIBOSE
$k_1 \times 10^3 \text{ min}^{-1}$						
1	1.25	14.19	18.15	19.26	20.61	20.41
2	1.66	10.85	13.58	14.51	15.35	15.00
3	2.00	9.61	10.17	12.18	13.06	11.33
4	2.50	8.12	7.53	10.74	11.61	8.38
5	5.00	6.11	5.73	8.34	8.64	6.42

[Substrate] = 1.66×10^{-2} M, [H₂SO₄] = 1M, HOAc-H₂O = 40% (v/v), Temperature = 50 °C

B. Dependence of rate on substrate concentration

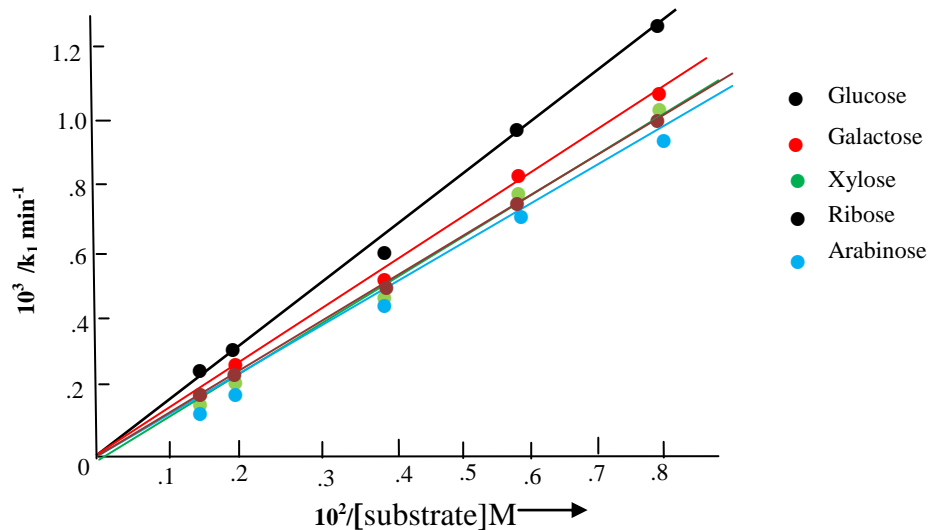
The pseudo first order rate constant increases with increase in the concentration of saccharides (Table 2). The plot between k_1 and [substrate] is linear passing through origin (Figure 1) suggesting that the order with respect to substrate is one. It is further substantiated by slope values (Glucose = 0.98, Galactose = 1.03, Xylose = 1.01, Arabinose = 1.02, Ribose = 1.00) of log-log plot between k_1 and [substrate]. The double reciprocal plot between k_1 and [substrate] is linear passing through origin suggesting that there is no kinetic evidence for complex formation.

Table 2. Dependence of rate on the concentration of Aldose Sugar

SN	[substrate] 10^2 M	GLUCOSE	GALACTOSE	XYLOSE	AROBIANOSE	RIBOSE
$k_1 \times 10^3 \text{ min}^{-1}$						
1	1.25	8.25	10.24	11.16	11.73	11.25
2	1.66	10.85	13.58	14.51	15.00	15.35
3	2.50	17.05	20.90	23.48	23.86	22.54
4	5.00	33.31	41.10	46.39	46.30	45.10
5	6.66	44.29	54.88	61.23	62.74	59.75

[Tl(III)] = 1.66×10^{-3} M, [H₂SO₄] = 1M, HOAc-H₂O = 40% (v/v), Temperature = 50 °C

Plot of $1/k_1$ VS $1/[\text{Substrate}]$



C . Dependence of rate on acid concentration

The pseudo first order rate constant increases with increase in the concentration of sulphuric acid (Table 3) suggesting that each oxidation is acid catalyzed. The slope value of log-log plot between *thallium(III)acetate* and $[H_2SO_4]$ is nearly one. These kinetic results suggest that the order with respect to $[H_2SO_4]$ is one. Hammett’s plots between $\log k_1$ versus H_0 are obtained non linear whereas the Bunnett’s plot $\{(\log k_1 + H_0) \text{ and } \log a_{H_2O}\}$ values for all the aldoses range from -9.45 to -10.57 suggest that water molecule do not take part in the slow step of the reaction.

D. Dependence of rate on the dielectric constant of the medium

The dependence of rate on dielectric constant of the medium was investigated by using acetic acid – water binary mixtures of different compositions. Table 3 shows that the rate of oxidation increases with increase in the composition of acetic acid i.e. with the decrease in dielectric constant of the medium.

Table 3. Dependence of rate on the dielectric constant of the medium

SN	HOAc-H ₂ O % [v/v]	10 ³ /D	GLUCOSE	GALACTOSE	XYLOSE	AROBINOSE	RIBOSE
$k_1 \times 10^3 \text{ min}^{-1}$							
1	30	18.81	8.99	12.06	13.23	12.48	13.77
2	40	21.53	10.85	13.58	14.51	15.00	15.35
3	50	25.17	13.33	16.24	16.51	17.58	18.41
4	60	30.36	17.39	19.78	19.77	23.58	22.50
5	70	38.08	-	-	25.07	-	-

$[Ti(III)] = 1.66 \times 10^{-3} M, [H_2SO_4] = 1M, [Substrate] = 1.66 \times 10^{-3} M, \text{Temperature} = 50^\circ C$

E. Dependence of rate on Sodium Acetate

The effect of sodium acetate on the reaction was studied by taking different concentrations of sodium acetate. The first order rate constant slightly decreases with increasing concentration of sodium acetate.

Table 4. Dependence of rate on Sodium Acetate

SN	[CH ₃ COONa]10 ³ M	GLUCOSE	GALACTOSE	XYLOSE	AROBINOSE	RIBOSE
				k ₁ X10 ³ min ⁻¹		
1	0.00	10.85	17.58	14.51	15.00	15.35
2	3.33	10.46	12.33	12.09	13.58	13.61
3	4.00	10.07	11.52	11.51	12.28	12.73
4	5.00	9.90	10.82	10.30	12.21	12.03
5	6.66	9.82	10.56	9.70	11.98	11.36
6	10.00	9.70	10.30	8.57	11.31	11.63

[Tl (III)] =1.66×10⁻³M, [H₂SO₄] =1M ,[Substrate] 1.66x10⁻³M ,Temperature =50 °C,
HOAc-H₂O= 40% (v/v)]

F. Dependence of rate on temperature

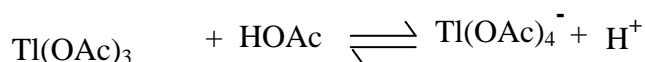
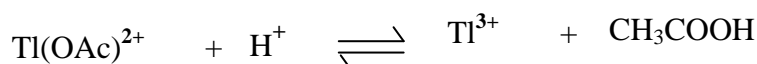
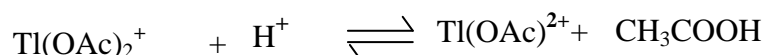
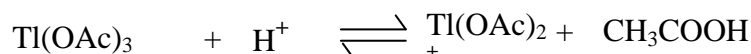
Dependence of rate on temperature was studied .The oxidation rate increases with increase in temperature. Various activation parameter are calculated from the data of the effect of temperature on rate of reaction.

Table 5. Thermodynamic parameters

Substrate	Ea kJ mol ⁻¹	A sec ⁻¹	ΔH* kJ mol ⁻¹	ΔG* kJ mol ⁻¹	ΔS* JK ⁻¹ mol ⁻¹
Glucose	87.66	2.67x10 ¹⁰	80.61	90.54	-33.58
Gelactose	62.74	3.15 x10 ⁶	58.95	91.13	-98.85
Xylose	54.36	1.49 x10 ⁵	57.45	90.85	-102.61
Arabinose	48.59	1.79 x10 ⁴	46.59	90.95	-136.27
Ribose	42.67	2.06 x10 ³	38.76	90.90	-160.19

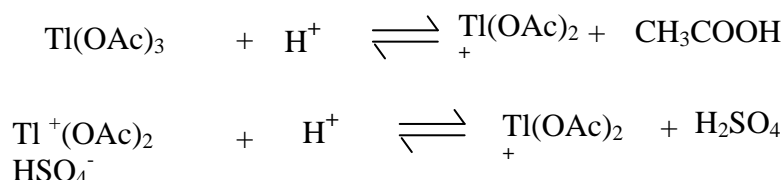
IV-DISCUSSION

A. Reactive Species and Mechanism: The nature of thallium (III) species in aqueous acetic acid depends on the concentration of acetic acid and hydrogen ion. The following equilibria are possible:



In addition to the above species thallium (III) may exist as $Tl(OAc)_2^+HSO_4^-$ in sulphuric acid medium, $Tl(OAc)_2^+ClO_4^-$ in perchloric acid medium, the ion-pair $Tl(OAc)_2^+OAc^-$ and the double salt $Tl_2(OAc)_4$. $Tl(OAc)_2^+OAc^-$ and $Tl_2(OAc)_4$ do not play any role in redox reactions and $Tl(OAc)_4^+$ is less reactive species. By pH measurements and equilibrium constants for both ionization of one acetate ion and coordination of one acetate ion have been calculated [16] and it was suggested that the important reactive species for wide range of concentration is $Tl(OAc)_2^+$.

In the present investigation the observed acceleration in the rate with increased acidity can be attributed to the removal of acetate group from the coordination sphere of thallic acetate to form electrophilic thallium(III) species [17]. The first order dependence of reaction rate on $[H_2SO_4]$ points $Tl(OAc)_2^+$ to be the reactive oxidant.



B. Nature of Aldose species :

Medium effect studies formulate the involvement of positive ion and dipole in slow step. Since the oxidant species taking part in slow step is an electrophilic, the aldose species must be a dipole. In aqueous solution an aldose molecule exists in acyclic (aldehyde and hydrated) and cyclic (furanose and pyranose) forms in dynamic equilibrium. Furanose is kinetically stable and pyranose thermodynamically stable form. Hence the rate determining step may involve aldehyde, hydrated and pyranose form. These forms are interconvertible due to mutarotation, anomersation and epimerization. Thus it is difficult to separate the individual rates.

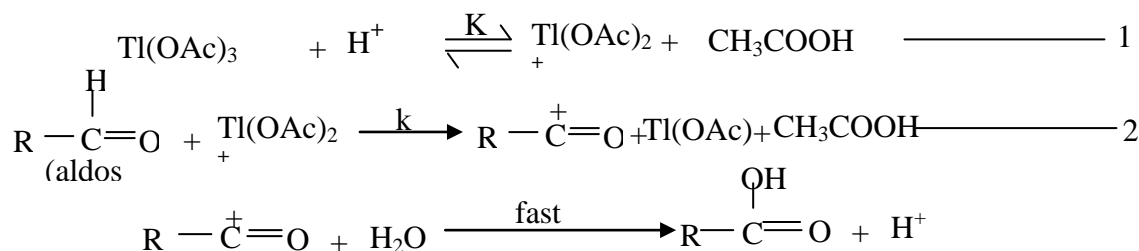
To determine whether the oxidation of aldose is taking place via pyranose form or acyclic form an attempt using graphical method was made. In consistent with the following equation:

$$k_2 = k [G] + K' [\text{aldehyde sugar}]$$

(where [G] = sugar concentration in pyranose form)

A graph was plotted between second rate constant k_2 ($k_2 = d[Tl(III)]/dt / [\text{aldose}] [Tl(III)]$) and [aldehyde]. The plot was linear with an intercept on rate axis suggesting that the observed rate is sum total of rate contributing by the pyranose form together with aldehyde form. Further the ratio of slope and intercept of the linear plot is nearly $10^3 : 1$. This clearly suggest that most of the aldose is oxidized in aldehyde form. Further there is significant difference in the rate constant values of different aldoses selected for the present investigation. This difference in reactivity order clearly points out that the reaction proceeds through aldehyde form. In the kinetic oxidation studies of aldoses by vanadium (V) [18] and thallium (III) [7] by using graphical method the workers have suggested the involvement of aldehyde form. The dependence of reaction rate on aldose concentration rules out the involvement of intermediate complex formation. Hence a rate determining step involving the attack of electrophilic thallium species on acyclic aldose species may be formulated. The failure of each aldose – thallium (III) system to induce polymerization of acrylonitrile suggests that the reaction does not involve free radical as reaction intermediate i.e. thallium (III) is acting as a two electron oxidant.

Based on these kinetic and non kinetic evidences a probable mechanism for thallium (III) acetate – aldose system may be proposed as:





On the basis of equation 1 and 2 the rate equation may be obtain as:

$$\text{Rate} = k_2 [\text{TI}(\text{OAc})_3] [\text{RCHO}] \quad \text{where } k_2 =$$

$$\frac{Kk_1[\text{H}^+]}{\text{CH}_3\text{COO}}$$

C. Structure and reactivity

According to Rudram [19] canter [20] et al. the percentage concentration of different forms of aldose are :

Aldose	$[\alpha - \text{pyranose}] \%$	$[\beta - \text{pyranose}] \%$	[free aldehyde]%
D- Glucose	36	64	0.024
D- Galactose	35	65	0.085
D-Xylose	29	71	0.170
D-Arabinose	63	37	0.280
D-Ribose	28	54	8.5

From the above table it is evident that the relative amounts of free aldehyde sugar decreases in the order D-ribose > D-arabinose > D-xylose > D-galactose > D-glucose. The observed order of reactivity for the present investigation is D-ribose > D-arabinose > D-xylose > D-galactose > D-glucose which is well in accordance with the percentage of aldehydic form. From the above order of reactivity it is evident that decrease in the chain length increases the oxidation rate.

The values of kinetic and thermodynamic parameters give additional support to the proposed mechanism. Since E_a is the measure of a reactivity of a compound, the more reactive compound is expected to have lower E_a values and the less reactive one, the higher E_a value. The ΔG^* values for all the thallium(III) acetate – aldose system are almost same. This may be understood in terms of isokinetic relationship [21]: according to which a series of homologous substrates of slightly different structures but undergoing reactions by the same mechanism, the free energy ΔG^* would be same with relative changes in ΔH^* and ΔS^* value. The entropy of activation for all the reactions have been found to be negative. This is due to compactness of transition state as compared to the ground state. Further, the large negative value of entropies of activation are expected for a bimolecular reaction with high polar transition state.

V-COCLUSION

The kinetic oxidation studies of aldose by thallium(III)acetate reveal that the aldose oxides into acid. Kinetic evidence also supports for the no formation of intermediate complex between active oxidant and substrate species.

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