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KINETICS OF OXIDATION OF ALDOSES BY THALLIUM(III) IN ACID PERCHLORATE MEDIUM

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ABSTRACT

The kinetics of oxidation of aldoses by thallium(III) in acid perchlorate medium have been investigated under pseudo-first-order conditions. The oxidation rate of different aldoses, which is in the order D-ribose > D-arabinose > D-xylose > D-galactose > D-mannose > D-glucose, is explained on the basis of its correlation with the percentage of free aldehydo sugar. The rate decreases with increase in the acidity, and is strongly inhibited by chloride and acetate ions. Thermodynamic parameters are reported, and suitable mechanistic steps are proposed on the basis of the kinetic and stoichiometric results.

INTRODUCTION

The kinetics of oxidation of aldoses have been reported for various metal-ion oxidants: vanadium(V)[1–4], cerium(IV)[5,6], cobalt(III)[7], and manganese(III)[8] in acid medium, and copper(II)[9] and silver(I)[10] in alkaline medium.

Some studies of the oxidation of organic[11–13] and inorganic compounds[14] have been made with Tl(III), a less-utilized, metal-ion oxidant. We now report the kinetic results of oxidation of aldoses by thallium(III) in acid perchlorate medium.

EXPERIMENTAL

Materials. — Commercially available chemicals of pure quality were used without purification. Stock solutions of aldoses (BDH Biochemical; BDH/AR) were prepared fresh daily in double-distilled water. Tl(III) oxide (BDH/AR) was used for preparing the oxidant solution in 70% perchloric acid.

Kinetic method. — The kinetic experiments were performed in stoppered, glass vessels in a temperature-controlled (±0.1 °C) water-bath. The reaction was monitored by iodometrically determining the concentration of unused Tl(III) in the presence of excess concentrations of the aldose and perchloric acid.

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TABLE I

DEPENDENCE OF RATE CONSTANTS, k_{obs} (s^{-1}), ON INITIAL ALDOSE CONCENTRATIONS[a]

$[Aldose]_0$ (M)	$k_{obs} \times 10^4$ (s^{-1})		
	D-*Glucose*[b] (70°)	D-*Galactose*[c] (65°)	D-*Mannose*[c] (65°)
0.1	0.79	1.72	1.55
0.2	1.59	2.90	2.08
0.3	1.76	5.24	4.02
0.4	1.83	8.35	4.99
0.5	2.97	9.81	6.60
0.6	3.72	12.69	—

[a] $[Tl(III)]_0 = 0.01$M. [b] $[HClO_4]_0 = 0.68$. [c] $[HClO_4]_0 = 1.00$.

TABLE II

DEPENDENCE OF RATE CONSTANT, k_{obs} (s^{-1}), ON INITIAL Tl(III) CONCENTRATION[a]

$[Tl(III)]$ (mM)	$k_{obs} \times 10^4$ (s^{-1})		
	D-*Glucose* (70°)	D-*Galactose* (65°)	D-*Mannose* (65°)
10.0	0.63	2.29	2.44
12.9	0.70	2.39	2.60
16.2	0.75	2.48	2.80

[a] [Aldohexoses] = 200mM; $[HClO_4] = 1.0$M.

In all experiments, duplicate rate-measurements were reproducible to within $\pm\sim2\%$.

Stoichiometry. — The stoichiometry was studied in the presence of an excess of D-glucose (to avoid further oxidation of more-reactive products). Arabinose and formic acid as products were confirmed by paper chromatography. Formic acid was also estimated quantitatively from the distillate collected at 100–102°. The results may be explained by the stoichiometric equation *1* (under kinetic conditions).

$$C_6H_{12}O_6 + Tl(III) + H_2O \rightarrow C_5H_{10}O_5 + HCO_2H + 2\,H^+ + Tl(I) \qquad (1)$$

When Tl(III) is present in large excess (20–25-fold), the sugar molecule is completely oxidized to CO_2. Formic acid and formaldehyde were confirmed as intermediate products by the usual spot tests, an aliquot of the reaction mixture being quenched by adding KCl solution during the studies. The presence of free radical was confirmed by the polymerization reaction with acrylonitrile in the dark.

Kinetic results, and discussion. — The disappearance of [Tl(III)] with time

TABLE III

SECOND-ORDER RATE-CONSTANT, k_o ($dm^3.mol^{-1}.s^{-1}$), FOR DIFFERENT ALDOSES[a]

Aldose	$k_o \times 10^4$ ($dm^3.mol^{-1}.s^{-1}$)
D-Glucose	2.18
L-Rhamnose	9.46
D-Mannose	10.42
D-Galactose	14.53
D-Xylose	22.34
D-Arabinose	42.30
D-Ribose	48.19

[a] $[Tl(III)]_o$ = 0.01M; $[HClO_4]_o$ = 1.0M; $[aldose]_o$ = 2.0M; temp. = 65°.

TABLE IV

DEPENDENCE OF RATE CONSTANTS, k_o ($dm^3.mol^{-1}.s^{-1}$), ON H^+ CONCENTRATION AT CONSTANT $[ClO_4^-]$ (2.17 M)[a]

$[H^+]_o$ (M)	$k_o \times 10^4$ ($dm^3.mol^{-1}.s^{-1}$)		
	D-*Glucose* (70°)	D-*Galactose* (65°)	D-*Mannose* (65°)
0.27	30.16	94.92	—
0.37	22.35	86.60	23.77
0.67	8.74	34.97	14.09
1.17	3.83	16.50	8.10
1.67	2.50	9.10	6.18
2.17	2.04	7.33	4.77

[a] $[Tl(III)]_o$ = 0.01M; [aldose] = 0.2M.

uniformly followed first-order kinetics. The values of pseudo-first-order rate-constants at different, initial concentrations of substrate and oxidant are respectively reported in Table I and II.

The rate constant k_{obs} increased proportionately with increase in aldose concentration (see Table I). The values of the slopes of linear plots of log k_{obs} *versus* log (s) are 0.87, 1.25, 1.07 for D-glucose, D-galactose, and D-mannose, respectively.

The values of the second-order rate-constant, $k_o(k_{obs}/[s])$, for different aldoses under similar experimental conditions are given in Table III.

Effect of acidity. — The rate constant k_o was found to decrease with increase in acidity (varied either by means of perchloric or sulfuric acid).

At a constant value of $[ClO_4^-]$ (2.17M), maintained by adding an appropriate quantity of $NaClO_4$ solution, the rate of oxidation (k_o) decreased with H^+ concentration, varied by means of perchloric acid (see Table IV).

TABLE V

DEPENDENCE OF RATE CONSTANTS, k_o (dm^3.mol^{-1}.s^{-1}), ON CHLORIDE AND ACETATE ION CONCENTRATION[a]

[Chloride] × *10*^{3} (M)	k$_o$ × *10*^{4} *(dm*^{3}*.mol*$^{-1}$*.s*$^{-1}$*)*	*[Acetate]* × *10*^{2} (M)	k$_o$ × *10*^{4} *(dm*^{3}*.mol*$^{-1}$*.s*$^{-1}$*)*
0.0	7.99	0.00	7.99
0.6	5.22	2.88	5.40
1.6	4.40	5.76	2.98
3.0	2.68	11.50	2.90
6.0	0.21	17.30	1.96

[a] [Tl(III)]$_o$ = 0.01M; [HClO$_4$]$_o$ = 0.68M; [glucose]$_o$ = 0.2M; temp. = 70°.

The two Hammett relations, the plots of log k_o against [H$^+$] and H$_o$, show a linear relationship, with slope values of −1.37, −1.33, −0.93, and 1.07, 0.88, and 0.62, respectively, for D-glucose, D-galactose, and D-mannose.

Reactive species of Tl(III). — In aqueous perchloric acid, Tl(III) has been described as Tl^{3+}, and its hydrolyzed forms as $Tl(OH)^{2+}$, $Tl(OH)_2^{1+}$, *etc.* In the present case, $Tl(OH)^{2+}$ may be presumed to be the reactive species of Tl(III), to explain the inverse dependence of rate (k_o) on acidity (see Table IV).

$$Tl^3 + H_2O \overset{K_h}{\rightleftharpoons} Tl(OH)^{2+} + H^+ \qquad (2)$$

Because of the very small value of the second hydrolysis-constant of Tl^{3+}, the formation of the species $[Tl(OH)_2]^+$ can be neglected.

The oxidation rate (k_o) is very strongly inhibited by the presence of chloride and acetate ion (see Table V); this is because these ions form strong, covalent complexes with Tl^{3+}, thus lowering the concentration of the reactive species $Tl(OH)^{2+}$. Furthermore, the coordination sites on Tl^{3+} are blocked by these ions, and the formation of an intermediate complex is inhibited[14].

Correlation of rate and configuration. — Aldoses have both an acyclic and cyclic forms that exist in dynamic equilibria. From the rate, the equilibrium constant, and the activation energy of mutarotation of D-glucose given in the literature[15,16], the value of the rate constant k, for the conversion of α into β forms can be computed as 0.4243 s^{-1} under the present experimental conditions, *i.e.*, a temperature of 70° and [H$^+$] = 0.68M. This value of the rate constant (k_1) is many times greater than the first-order, oxidation rate-constant value of 0.0395 × 10^{-4} s^{-1}, computed from the pseudo-first-order rate-constant, k_{obs} 0.79 × 10^{-4} s^{-1}. From this, it may be assumed that the oxidation of aldoses is not affected by the mutarotation. Thus, the observed rate of oxidation (k_{obs}) is the sum of the rates contributed by each of the α and β forms, together with that of the aldehydo form.

The plot of k_o, the second-order rate-constant, against the percentage of aldehydo sugar is linear, with an intercept on the k_o axis. The ratio of slope and

TABLE VI

PERCENTAGE CONCENTRATIONS OF DIFFERENT FORMS OF ALDOSES[17,18]

Aldose	*[α-Pyranose]* (%)	*[β-Pyranose]* (%)	*[Free aldehyde]* (%)
D-Glucose	~36	~64	0.024
D-Mannose	~64	~36	0.064
D-Galactose	~35	~65	0.085
D-Xylose	~29	~71	0.170
D-Arabinose	~63	~37	0.280
D-Ribose (0.1M)	~18	~54	8.5

TABLE VII

VALUES OF ACTIVATION PARAMETERS

Aldose	$\Delta H^{\ddagger}$ *(kJ.mol⁻¹)*	$\Delta S^{\ddagger}$ *(J.deg.mol⁻¹)*	$\Delta G^{\ddagger}$ *(kJ.mol⁻¹)*
D-Glucose	122.00 ±0.21	24.47 ±0.08	113.55 ±0.37
D-Galactose	122.13 ±0.25	40.81 ±0.16	108.23 ±0.42
D-Mannose	123.89 ±0.29	43.73 ±0.08	109.02 ±0.50

intercept has been found to be $10^4:1$. This clearly establishes that most of the aldose is oxidized through its aldehydo form. The differences in oxidation rate (see Table III) can be attributed to the different percentages of aldehydo form, as the percentages of α and β forms for different aldoses are almost the same (see Table VI). This linear correlation helps to explain the observed reactivity of different aldoses (see Table III), which is in the order: D-ribose > D-arabinose > D-xylose > D-galactose > D-mannose > D-glucose.

Effect of temperature. — The values of the activation parameters are given in Table VII. These values were calculated from the Arrhenius linear-plots obtained by plotting log k_r against $1/T$.

Mechanistic steps, and the rate law. — In Tl(III) oxidations, the two-electron change can take place either in a single step[11], or in two successive one-electron steps, with intermediate Tl(II) formation[12-14]. In the present case, the evidence of free-radical formation indicates the possibility of two successive, one-electron changes in Tl(III).

A linear, isokinetic plot (β = 105 K) can be obtained in accordance with the Laffler compensation law[18], and thus the following mechanistic steps can now be proposed for all of the aldohexoses.

$$C_6H_{12}O_6 + Tl(III) \overset{K}{\rightleftharpoons} \underset{\text{activated complex}}{[C_6H_{12}O_6\text{—}Tl(III)]} \qquad (3)$$

$$[C_6H_{12}O_6\text{–Tl(III)}] + H_2O \xrightarrow[\text{(slow)}]{k_s} \bar{R} + HCO_2H + H_3O^+ + \text{Tl(II)} \qquad (4)$$

$$\overset{\text{(fast)}}{}$$
$$\bar{R} + \text{Tl(II)} \rightarrow C_5H_{10}O_5 + H^+ + \text{Tl(I)}, \qquad (5)$$

where $\bar{R} = CH_2OHCHOHCHOHCHOH\dot{C}HOH$ (free radical).

From the proposed steps *2–5*, the rate law can be derived as

$$-\frac{d[\text{Tl(III)}]}{dt} = \frac{KK_hk_s[C_6H_{12}O_6]\,[\text{Tl}^{3+}]}{[H^+]} = k_{obs}[\text{Tl}^{3+}]. \qquad (6)$$

In terms of activity, Eq. *6* can be represented as

$$-\frac{d[\text{Tl(III)}]}{dt} = \frac{KK_hk_s[C_6H_{12}O_6]\,[\text{Tl}^{3+}]}{[H^+]}\cdot\frac{v\text{TlOH}^{2+}}{v\ddagger}\cdot\frac{v\text{Tl}^{3+}}{v\text{TlOH}^{2+}vH^+} = k_{obs}[\text{Tl}^{3+}], \qquad (7)$$

or

$$\frac{k_{obs}}{[C_6H_{12}O_6]} = k_o = \frac{k_r}{[H^+]}\cdot\frac{v\text{TlOH}^{2+}}{v\ddagger}\cdot\frac{v\text{Tl}^{3+}}{v\text{TlOH}^{2+}vH^+}, \qquad (8)$$

where k_o = second-order rate-constant and k_r = specific rate-constant.

The observed decrease in rate with increase in acidity (see Table III) will depend on the two activity-coefficient ratios, $v\text{Tl}^{3+}/v\text{TlOH}^{2+}/vH^+$ pertaining to equilibrium step *2*, and $v\text{TlOH}^{2+}/v$ pertaining to reaction steps *3–5*.

It can be shown that ϕ, the proportionality constant of the Bunnett–Olsen equation[20], is also a proportionality constant between the logarithms of activity coefficient ratios of Eq. *8*. From the Bunnett–Olsen plots, the values of ϕ have been computed as 4.83, 4.34, and 3.66, and that of the specific rate-constant k_r as 9.12×10^{-3}, 9.55×10^{-3}, and $28.8 \times 10^{-3}\ s^{-1}$ for D-glucose, D-mannose, and D-galactose, respectively.

Alternatively, the medium dependence on oxidation rates can be expressed by ω parameters computed from Bunnett plots. The values 4.28, 3.57, and 5.3 in the three cases suggest that the water molecule should act as a proton-transferring agent in the rate-determining step[21] *4*.

Thus, the proposed steps *2–5*, and the rate laws *6–8* explain the results obtained during this study.

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