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Note

The kinetics and mechanism of oxidation of maltose and lactose by Tl(III) in acidic media

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The oxidation kinetics of maltose and lactose in alkaline[1] and ammoniacal[2] media have been described, but few studies in acidic media have been reported. Thallium(III), which is a two-electron oxidising agent, has a moderately high reduction potential (1.25 V) which lies between those of mercury(II) and lead(IV). The kinetics of oxidation of α-hydroxy acids[3], phenols[4], and esters[5] by thallium(III) have been studied in acidic medium, and we now report on the oxidation of maltose and lactose by thallium(III), in the presence of sulphuric acid, in aqueous acetic acid.

The kinetic experiments were initiated by mixing equal volumes of solutions at the reaction temperatures containing (*a*) thallic acetate (prepared[6] from thallic oxide) and (*b*) disaccharide (D) and H_2SO_4 in the presence of 60% acetic acid. The experiments were conducted at a constant ionic strength of 2.715. The progress of the reaction (up to 20–30%) was followed by monitoring unreacted Tl(III) by an iodometric procedure[6]. The rate constants (k_1) were evaluated by using an integrated first-order rate equation. The percentage of the probable errors in the rate-constant measurement did not exceed ±3% for maltose and ±5% for lactose. The second-order rate constants (k_2) were computed by dividing k_1 by [Substrate]. The order with respect to [Tl(III)] was found by the isolation method, whereas that with respect to [D] and [H_2SO_4] was found by van't Hoff's differential method.

Under the conditions [$Tl(OAc)_3$] and [H_2SO_4] $\gg$ [D], the disaccharide and thallic acetate reacted in a 1:1 molar ratio:

$$\text{R-}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{-H} + H_2O + Tl(OAc)_3 \rightarrow \text{R-}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{-OH} + TlOAc + 2\,HOAc.$$

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TABLE I

RATE DEPENDENCE OF OXIDATIONS[a] ON [Tl(III)], [D], AND [H_2SO_4]

[Tl(III)] × 10^3 (M)[b]	k × 10^6 (s^{-1})		[D] × 10 (M)[c]	k_1 × 10^6 (s^{-1})		[H_2SO_4] × 10 (M)[d]	k_1 × 10^6 (s^{-1})	
	Maltose	*Lactose*		*Maltose*	*Lactose*		*Maltose*	*Lactose*
0.75	67.98	23.66	0.3	6.75	3.49	9.00	33.83	9.74
1.00	50 98	16.28	0.6	13.52	6.59	8.55	32.18	9.27
1.50	33 83	9.74	0.9	20.28	9.74	8.10	30.46	8.76
2.00	26 46	7.48	1.5	33.83	15.80	7.65	28.65	8.42
3.00	16 21	4.91	2.0	45.75	20.94	7.20	27.47	7.76
4.00	12 82	3.68	2.5	55.81	25.59	6.75	25.34	7.31
5.00	10 15	2.93	3.0	67.65	31.36	6.30	23.51	6.77

[a][CH_3COOH] 60% (v/v), ionic strength (μ) 2.715, temperature 323 (maltose) and 333 K (lactose). [b][Maltose] × 10 = 1.5M, [lactose] × 10 = 0.9M, [H_2SO_4] × 10 = 9M. [c][Tl(III)] × 10^3 = 1.5M, [H_2SO_4] × 10 = 9M. [d][Maltose] × 10 = 1.5M, [lactose] × 10 = 0.9M, [Tl(III)] × 10^3 = 1.5M.

The resulting aldonic acid was unstable and was hydrolysed to D-gluconic acid and D-glucose (from maltose) and D-galactose (from lactose) [identified by p.c., using 1-butanol–acetic acid–water (4:1:5) and detection with aniline hydrogen phthalate[7]].

When [Tl(III)] ≪ [D], the reaction exhibited first-order dependence on [Tl(III)]. The first-order rate constant k_1 for the disappearance of Tl(III) at constant [D], acidity, and ionic strength decreased with increasing [Tl(III)]. This uncommon observation was also made earlier[3] and is attributed to the formation of less-reactive [Tl^{3+}]acetate complex-ion. The reaction also exhibited a clear first-order dependence on [D] as indicated by the linear plot of log k_1 *vs.* log [D] with unit slope (Table I). The linear plot of $1/k_1$ *vs.* 1/D, with a small +ve intercept on the y-axis, confirmed the second-order behaviour and indicated the formation of a less-stable complex[8] between the substrate and the oxidant. The empirical rate law conforming to the second-order reaction is $-d/dt\,[Tl(III)] = k[Tl(III)]\,[D]$.

The reaction was acid-catalysed since the pH did not change even after the reaction. The reaction also exhibited first-order dependence on [H_2SO_4] up to 0.9M. Oxidation did not occur in the absence of sulphuric acid[9] at any concentration of acetic acid in the binary solvent mixture. The reactivity of the two disaccharides with Tl(III) was maltose > lactose.

The average heat of activation and entropy of activation values for the oxidation of maltose, at five different temperatures (313–333 K), were $\Delta H^{\ddagger}$ 21246 cal.mol^{-1} and $\Delta S^{\ddagger}$ −9.63 cal.degree^{-1}.mol^{-1}, whereas, for lactose, at five different temperatures (323–343 K), they were $\Delta H^{\ddagger}$ 22880 cal.mol^{-1} and $\Delta S^{\ddagger}$ −8.21 cal.degree^{-1}.mol^{-1}. The heat of activation values are characteristic of a second-order reaction and suggest non-cleavage of the parent molecule[10]. The moderately negative values of the entropy of activation suggest the reaction to be slow, involving an activated complex that is more rigid than the reactants.

TABLE II

EFFECT OF ADDITION OF SULPHURIC ACID ON OXIDATION OF DISACCHARIDES[a]

$[H_2SO_4]$ (M)	$-H_o$	$k_2 \times 10^4$ ($L.mol^{-1}.s^{-1}$)		$(4 + \log k_2 + H_o)$		$-\log a_{H_2O}$
		Maltose	*Lactose*	*Maltose*	*Lactose*	
0.90	0.1840	2.26	1.08	0.1693	−0.1503	0.0160
1.35	0.4700	4.06	2.05	0.1388	−0.1578	0.0264
1.80	0.7280	6.95	3.52	0.1139	−0.1816	0.0378
2.25	0.9800	11.43	5.94	0.0781	−0.2065	0.0530
2.70	1.2240	18.35	9.78	0.0398	−0.2338	0.0718
3.15	1.4520	27.89	15.44	−0.0067	−0.2633	0.0928
3.60	1.6660	40.82	23.28	−0.0551	−0.2990	0.1172

[a]$[Tl(III)] \times 10^3$ = 1.5M, [Maltose] × 10 = 1.5M at 323 K, [Lactose] × 10 = 0.9M at 333 K, $[CH_3COOH]$ = 60% (v/v).

The rate of reaction was almost independent of the ionic strength produced by addition of such neutral salts as K_2SO_4, KNO_3, $Mg(NO_3)_2$, or $MgSO_4$. A plot of log k_2 *vs.* $\sqrt{\mu}$ was non-linear, which suggested the absence of a primary salt effect and that the reaction involved an ion and a dipole. However, the rate decreased considerably on the addition of sodium acetate, which is attributed to the formation of less-reactive $Tl(OAc)_4^-$. There was an inverse relationship between k_2 and $[CH_3COO^-]$ in the concentration range studied. The reaction was strongly inhibited by potassium chloride, which is attributed to the formation of the covalent species $Tl(OAc)_2Cl$ and the inactive ions $TlCl^{2+}$ and $TlCl_2^+$ (ref. 11). A plot of log k_2 *vs.* log $[Cl^-]$ was linear with a slope equal to −1, showing an inverse first-order dependence[12] on $[Cl^-]$.

The rate increased with increase in the percentage of acetic acid (v/v). A plot of log k_2 *vs.* $1/D$ (where D is the dielectric constant of the solvent) was linear with a positive slope, showing the reaction to be between a cation and a dipole[13].

At $[H_2SO_4]$ >0.9M, the concept of pH fails. However, the reaction rate increased over 18–21 times with a rise in $[H_2SO_4]$ from 0.9 to 3.6M (Table II). A plot of (log k_2 + H_o) *vs.* log a_{H_2O} was linear and the slope varied from +1.5 to +2.3 which, according to Bunnett[14], conforms to the nucleophilic attack of a water molecule (the values of log a_{H_2O} and H_o are taken from the literature[14]).

Nature of the Tl(III) species. — The Tl(III) species that may be involved in the oxidation are $Tl(OAc)_2^+$, $Tl(OAc)_2^+HSO_4^-$, $Tl(OAc)_3$, $Tl(OAc)_4^-$, $Tl(OAc)_2^+$ OAc^-, and $Tl_2(OAc)_4$. The ion-pair $Tl(OAc)_2^+$ OAc^- and the double salt $Tl_2(OAc)_4$ do not play any important role in the redox reactions[6], and $Tl(OAc)_4^-$ is not a reactive species. The results discussed above suggest a positive thallic ion species as the active oxidant. If a proton abstracts an acetate group from the co-ordination sphere of thallium, the following equilibria could be responsible for giving the most-reactive, electrophilic, $Tl(OAc)_2^+$ ion species[3,5,9].

$$Tl(OAc)_3 + H^+ \rightleftarrows Tl(OAc)_2^+ + CH_3COOH$$

$$Tl(OAc)_2^+ HSO_4^- + H^+ \rightleftarrows Tl(OAc)_2^+ + H_2SO_4$$

Mechanism. — No turbidity was produced on addition of acrylamide to the reaction mixture, indicating the absence of free radicals. On the basis of the kinetic and non-kinetic evidence reported here and taking into account the previous work on Tl(III) oxidations[3–5,9], the following mechanistic steps are proposed for the reaction with the probable intermediate complex

$$[\mathrm{R}\text{-}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\text{-}\overset{+}{\mathrm{Tl}}\text{-}\mathrm{OAc}].$$

$$Tl(OAc)_3 + H^+ \overset{K}{\rightleftarrows} Tl(OAc)_2^+ + HOAc \tag{1}$$

$$\underset{\text{Disaccharide}}{\mathrm{R}\text{-}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\text{-}\mathrm{H}} + Tl(OAc)_2^+ \underset{\text{(slow)}}{\overset{k'}{\rightarrow}} \underset{\text{Intermediate complex}}{[\mathrm{R}\text{-}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\text{-}\overset{+}{\mathrm{Tl}}\text{-}\mathrm{OAc}]} + HOAc \tag{2}$$

$$\underset{\text{Intermediate complex}}{[\mathrm{R}\text{-}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\text{-}\overset{+}{\mathrm{Tl}}\text{-}\mathrm{OAc}]} + H_2O \underset{\text{(fast)}}{\rightarrow} \underset{\text{Bionic acid}}{\mathrm{R}\text{-}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\text{-}\mathrm{OH}} + H^+ + TlOAc \tag{3}$$

Considering steps *1* and *2*, the following rate law is obtained:

$$-\frac{d}{dt}[Tl(OAc)_3] = k_2 [Tl(OAc)_3][D],$$

where ($k_2 = Kk'[H^+]/[HOAc]$), which is constant at any fixed $[H^+]$ and [HOAc], is the experimental second-order rate constant.

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