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Kinetics of Tl(III) Oxidation of 1,2-Dihydroxybenzene in Chloride-Containing Media

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Introduction

The kinetics and mechanism of thallic ion oxidation of dihydroxybenzenes has been studied with great detail by Pelizetti *et al.* [1, 2]. The changes in rate with acidity have generally been attributed to contribution by different $Tl(OH)_n^{3-n}$ species, although the authors have underlined the possibility of a kinetically indistinguishable reaction path implying the formation of a deprotonated intermediate complex.

The present work deals with the influence of coordination of Tl(III) by Cl^- ions on the rate of oxidation of 1,2-dihydroxybenzene and the evidence obtained favors this alternate reaction path via an inner sphere complex implying Tl(III) and a deprotonated phenol OH group.

Results and Discussion

The kinetics were followed by monitoring the increase in absorbance at 400 nm due to formation of the quinone product:

$$Tl^{3+} + C_6H_4(OH)_2 \rightarrow Tl^+ + 2H^+ + C_6H_4O_2$$

The reaction was studied in pseudo-first order conditions ($[Tl(III)] \gg [(C_6H_4(OH)_2]$) and the absorbance *vs.* time data were accumulated in a data-acquisition system coupled to a Durrum stopped-flow spectrophotometer. The pseudo-first order rate constants, k_{obs}, were obtained by a least squares program. The rate law, as shown by previous work [1], is given by: Rate = $k[Tl(III)][C_6H_4(OH)_2]$. In our case it yields eqn. 1 for k_{obs}:

$$k_{obs} = k[Tl(III)] \quad (1)$$

The addition of chloride ions to the reaction medium at constant acidity and ionic strength causes the rate to decrease as shown by Table I. For Cl/Tl = 1, k_{obs} decreases by a factor of ~8 as compared to the value obtained in the absence of chloride ions. Further addition of chloride has even greater effect and for Cl/Tl ~ 3, the rate is reduced by a factor of $\sim 10^4$.

TABLE I. Observed and Calculated Rate Constant at Various Cl/Tl Ratios.

T = 25 °C; $[C_6H_4(OH)_2] = 3.0 \times 10^{-4}$ *M*; [Tl(III)] = 2.75×10^{-3} *M*; $[HClO_4] = 1.1$ *M*

Cl/Tl	k_{obs} (s^{-1})	k_{calc} (s^{-1})
0	23.4	22.8
0.11	20.4	20.4
0.22	18.2	18.0
0.33	15.3	15.6
0.44	13.9	13.4
0.55	11.6	11.3
0.66	9.6	9.3
0.77	7.5	7.5
0.88	6.2	5.9
0.99	4.1	4.5
1.10	2.9	3.4
1.32	1.03	1.68
1.54	0.47	0.73
1.65	0.35	0.44
1.76	0.23	0.25
2.20	1.5×10^{-2}	1.7×10^{-2}
2.64	3.9×10^{-3}	4.6×10^{-3}
3.09	2.2×10^{-3}	2.2×10^{-3}
3.31	1.6×10^{-3}	1.6×10^{-3}
3.85	8.2×10^{-4}	8.4×10^{-4}

Affinity of Tl(III) for Cl^- is well documented and the stability constants of $TlCl_n^{3-n}$ complexes are known [3]. The concentrations of the different species at equilibrium have been calculated using an iterative program and the rate constants have been fitted by eqn. 2.

$$k_{obs} = k_0[Tl^{3+}] + k_1[TlCl^{2+}] + k_2[TlCl_2^+] \quad (2)$$

A multiple weighted regression program, with weight factors proportional to $1/k_{obs}^2$, has been used to determine k_0, k_1 and k_2. Inclusion of contributions by $TlCl_3$ and $TlCl_4^-$ into eq. 2 does not improve significantly the correlation factor, their possible contribution to k_{obs} is negligible over the whole concentration range. Contribution by $TlOH^{2+}$, whose concentration represents a constant fraction (of a few percent) of Tl^{3+} in 1.1 *M* $HClO_4$ [4], is included in the term $k_0[Tl^{3+}]$.

The regression leads to the following rate constants at 25 °C: $k_0 = 8.3 \times 10^3$ M^{-1} s^1, $k_1 = 1.2 \times 10^2$ M^{-1} s^{-1}, $k_2 \cong 1$ M^{-1} s^{-1} and to the conclusion that reactivities decrease in the order $Tl^{3+} > TlCl^{2+} > TlCl_2^+$. The calculated rate constants by means of eqn. 2 show a good agreement with the observed values as shown in Table I.

The contribution to the rate by Tl^{3+}, $TlCl^{2+}$ and $TlCl_2^+$ (in %) is shown in Fig. 1. Due to its considerably higher rate constant, Tl^{3+} is the main reacting

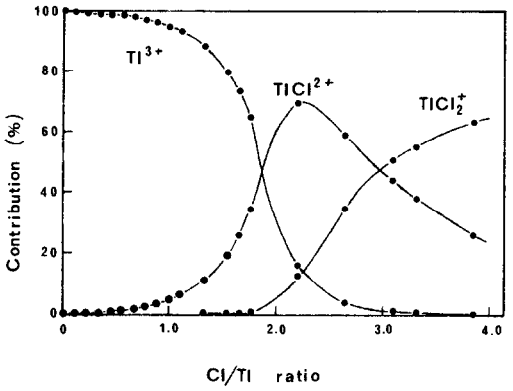

Fig. 1. Contribution of Tl(III) species to k_{obs} at different Cl/Tl ratios (T = 25 °C; [Tl(III)] = 2.75 × 10^{-3} *M*; [$C_6H_4(OH)_2$] = 3.0 × 10^{-4} *M*; [$HClO_4$] = 1.1 *M*).

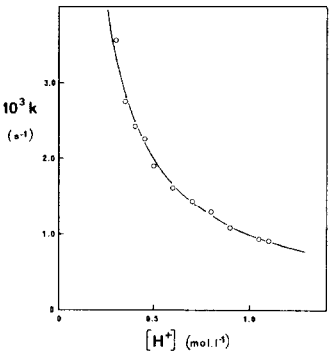

Fig. 2. Influence of acidity on k_{obs} at Cl/Tl = 3 (T = 25 °C; [Tl(III)] = 2.75 × 10^{-3} *M*; [$C_6H_4(OH)_2$] = 3.0 × 10^{-4} *M*; ionic strength = 1.1 *M*); open circles represent experimental data; curve is calculated.

species from Cl/Tl = 0 to 2. However at higher Cl/Tl ratios $TlCl^{2+}$ and $TlCl_2^+$ have the main contributions, despite their much lower rate constant, due to the fact that their concentrations largely exceed that of Tl^{3+}.

The reduction in rate has also been observed in the presence of carboxylic acids [5] where 1:1 Tl(III)–carboxylate complexes were shown to be unreactive.

The influence of acidity has been studied in conditions where Tl^{3+} (and $TlOH^{2+}$) have only minor contributions to the rate. In these conditions, the changes in the hydrolitic equilibrium: $[Tl{\cdot}OH_2]^{3+} \rightleftharpoons TlOH^{2+} + H^+$, upon changes in acidity have no significant effect on the rate of oxidation. This is achieved at Cl/Tl = 3, where Tl^{3+} represents only about 10^{-4}% of Tl(III).

As shown in Fig. 2, an increase in acidity causes the rate to decrease. The curve in Fig. 2 is calculated by using the equation $k_{obs} = k'/[H^+]$, where $k' = 9.9 \times 10^{-4}\ M^{-1}\ s^{-1}$ for Cl/Tl = 3.

The results can be accounted for by the following mechanism:

$$TlCl_n^{3-n} + C_6H_4(OH)_2 \overset{\beta_n}{\rightleftharpoons} [Cl_nTl{-}O{-}C_6H_4{-}OH]^{2-n} + H^+ \quad (3)$$

$$[Cl_nTl{-}O{-}C_6H_4{-}OH]^{2-n} \xrightarrow[\text{slow}]{k'_n} C_6H_4O_2 + nCl^- + Tl^+ + H^+ \quad (4)$$

Equation 3 implies the formation of an inner sphere complex between Tl(III) and phenol group which loses a proton. It decomposes in eqn. 4 to give the final products. Inhibition by H^+ is due to displacement of eqn. 3 to the left when acidity is increased. Combining with results in eqn. 2 one obtains: $k_0 = \beta_0 k'_0/[H^+]$; $k_1 = \beta_1 k'_1/[H^+]$; $k_2 = \beta_2 k'_2/[H^+]$ with $\beta_2 k'_0 > \beta k'_1 > \beta_2 k'_2$.

Similar results, in the absence of chloride ions, could also be accounted for by an alternate mechanism [1]. If overall reactivities are in the order $TlOH^{2+} > Tl^{3+}$, and the main reactive species is $[HOTl{-}C_6H_4(OH)_2]^{2+}$ (where deprotonation implies a Tl-coordinated water molecule) inhibition by H^+ can also be explained. However, our results strongly favor a mechanism similar to eqns. 3 and 4, even in absence of chloride ions, with reactivities of the species $Tl^{3+} > TlOH^{2+}$ and loss of phenolic proton upon coordination.

In several known cases coordination of Tl^{3+} by Cl^- or OH^- produces qualitatively the same effect [6]. Therefore it seems likely that coordination by OH^- should lead to a strong decrease in rate like that by Cl^-. It would mean that the electrostatic effect is very strong in this reaction.

Deprotonation of a phenolic OH upon coordination, although not shown by direct evidence, is also quite logical. Acidity of H_2O coordinated to Tl^{3+} is increased very strongly due to the strong electric field of the cation ($pK_a \cong 1.18$ for $Tl{\cdot}OH_2^{3+}$ [4]) and even in 1 *M* $HClO_4$ it dissociates to the extent of a few percent. 1,2-dihydroxybenzene has a K_a greater than H_2O by a factor of 10^4. Therefore, when coordinated, it should lose its proton even more readily than does H_2O.

Finally, due to the larger orbitals, the electrons of the phenolate oxygen are more easily delocalized than those of the corresponding hydroxyl, therefore their transfer to Tl(III) in the rate-determining step should also be favoured.

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