*Inorganica Chimica Acta,* 45 (1980) L217–L218

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

R. MENARD and M. ZADOR

*Département de Chimie, Université de Montréal, C.P. 6210, Succ. A, Montreal, Que., Canada*

Received June 24, 1980

## 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 $k_{obs}$:

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

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 ~$10^4$.

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*; $[Tl(III)] = 2.75 \times 10^{-3}$ *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 | $1.5 \times 10^{-2}$ | $1.7 \times 10^{-2}$ |
| 2.64 | $3.9 \times 10^{-3}$ | $4.6 \times 10^{-3}$ |
| 3.09 | $2.2 \times 10^{-3}$ | $2.2 \times 10^{-3}$ |
| 3.31 | $1.6 \times 10^{-3}$ | $1.6 \times 10^{-3}$ |
| 3.85 | $8.2 \times 10^{-4}$ | $8.4 \times 10^{-4}$ |

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.

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

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

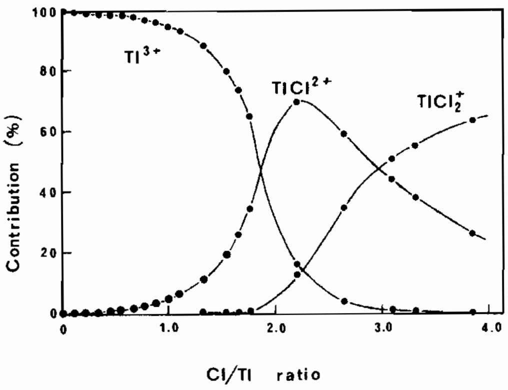

Fig. 1. Contribution of Tl(III) species to $k_{obs}$ at different Cl/Tl ratios (T = 25 °C; [Tl(III)] = $2.75 \times 10^{-3}$ *M*; $[C_6H_4(OH)_2]$ = $3.0 \times 10^{-4}$ *M*; $[HClO_4]$ = 1.1 *M*).

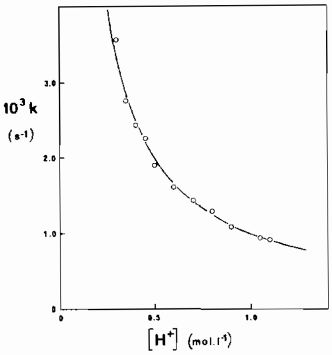

Fig. 2. Influence of acidity on $k_{obs}$ at Cl/Tl = 3(T = 25 °C; [Tl(III)] = $2.75 \times 10^{-3}$ *M*; $[C_6H_4(OH)_2]$ = $3.0 \times 10^{-4}$ *M*; ionic strength = 1.1 *M*); open circles represent experimental data; curve is calculated.

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.

## References

1 E. Pelizetti, E. Mentasti and G. Saini, *J. Chem. Soc. Dalton*, 721 (1974).

2 E. Pelizetti, E. Mentasti, M. E. Carlotti and G. Giraudi, *J. Chem. Soc. Dalton*, 794 (1974).

3 D. Peschanski, S. Valladas-Dubois, *Bull. Soc. Chim. France*, 1170 (1956).

4 F. Ya. Kul'ba, Yu. B. Yakovlev and V. E. Mironov, *Russ. J. Inorg. Chem. (Engl. Ed.)*, *9*, 1390 (1964).

5 E. Pelizetti, E. Mentasti and G. Giraudi, *Ann. di Chimica*, *69*, 355 (1974).

6 R. Favier and M. Zador, *Can. J. Chem.*, *48*, 2407 (1970); L. Nadon and M. Zador, *Can. J. Chem.*, *55*, 3590 (1977).