Kinetics of Oxidation of Catechol (*o*-Dihydroxybenzene) by Thallium(III) in Aqueous Perchlorate Media

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The reaction of Tl^{III} aquo-ions with catechol (H_2cat) in excess, giving *o*-quinone (qno), has been studied at $[HClO_4] = 0.30$—2.00, $I = 2.00$M, and 12·0, 18·0, 25·0, and 35·0 °C, by means of a stopped-flow technique. No spectrophotometric evidence of intermediate-complex formation has been found. The rate of oxidation is first order in both $[Tl^{III}]$ and $[H_2cat]$. The rate increases with decreasing $[H^+]$ and this is explained by assuming that the reactive species is $[TlOH]^{2+}(aq)$ or a deprotonated intermediate complex. The overall activation parameters have also been evaluated. Possible reaction mechanisms are discussed with reference to other Tl^{III} oxidations and two alternative reaction paths are suggested.

PREVIOUS work on the kinetics of oxidation of catechol (H_2cat) to *o*-quinone (qno) has been carried out with aquoiron(III),[1] aquovanadium(V)[2] (catechol being in excess), and with periodate ions.[3] Periodate-ion oxidation studies showed that the reaction proceeds through an intermediate, probably a cyclic diester of periodic

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[1] E. Mentasti and E. Pelizzetti, *J.C.S. Dalton*, 1973, 2605; E. Mentasti, E. Pelizzetti, and G. Saini, *ibid.*, p. 2609.

[2] E. Pelizzetti, E. Mentasti, and G. Saini, *Gazzetta*, in the press.

[3] S. W. Weidman and E. T. Kaiser, *J. Amer. Chem. Soc.*, 1966, **88**, 5820.

acid. The kinetic investigation of the oxidation with aquoiron(III) ions in a strongly acidic medium showed that the reactants give a 1 : 1 complex of low stability which then reacts further. The suggested mechanism of the latter redox reaction involves formation of iron(II) and the semiquinone radical which reacts with a further aquoiron(III) ion giving qno. The dependence of the rate on [H$^+$] alternatively suggests that iron(III) reacts in its hydrolysed form [FeOH]$^{2+}$(aq).

On the other hand, the kinetics of oxidation of catechol with aquovanadium(V) ions showed fast and nearly quantitative formation of a 1 : 1 complex (probably cyclic) followed by formation of 1 : 2 complexes V$^{\text{V}}$(H$_2$cat)$_2$ of low stability; the latter products decompose giving qno, and two indistinguishable mechanisms involving the exchange of one or two electrons were suggested. Moreover the overall rate of disappearance of V$^{\text{V}}$ contains a term independent of [H$^+$] and a term proportional to [H$^+$]; this was explained in terms of complexes possessing different degrees of protonation.

It seemed of interest to undertake an investigation of the kinetics of oxidation of catechol with aquothallium(III), because this ion can act as a two-electron oxidant, although in some cases intermediate formation of Tl$^{\text{II}}$ has been proposed. Moreover, dependences on [H$^+$] studied in some works suggest the possibility of Tl$^{\text{III}}$ reacting in a hydrolysed form [equation (1)]. The

$$\mathrm{Tl^{3+} + H_2O \overset{K_1}{\rightleftharpoons} [TlOH]^{2+} + H^+} \tag{1}$$

kinetics of oxidation of Tl$^{\text{III}}$ has been extensively studied with inorganic reagents (Fe$^{\text{II}}$,[4] Hg$^{\text{I}}$,[5] Os$^{\text{II}}$,[6] U$^{\text{IV}}$,[7,8] V$^{\text{II}}$,[9] V$^{\text{III}}$,[10a] V$^{\text{IV}}$,[10b] Sb$^{\text{III}}$,[11] Sn$^{\text{II}}$,[12] H$_3$PO$_2$,[13a] and H$_3$PO$_3$ [13b]) while a few studies have been carried out with organic substrates in aqueous media (formic acid,[14] cyclohexanone,[15] cyclohexanol,[16] olefins,[17] oxalic acid,[18] and aliphatic alcohols [19]).

EXPERIMENTAL

Tl$^{\text{III}}$ Solutions were prepared by dissolving thallium(III) oxide in aqueous perchloric acid. Twice-distilled water was used. Catechol (H$_2$cat) solutions were prepared immediately before use. Sodium perchlorate was used for the adjustment of ionic strength. Thallium(I) perchlorate was prepared by dissolving the carbonate in perchloric acid. All the above materials were reagent grade (Carlo Erba).

Tl$^{\text{III}}$ Was determined by titrating against thiosulphate the iodine liberated after addition of KI. Kinetic runs were carried out with a Durrum–Gibson stopped-flow spectrophotometer at 390 nm [wavelength of maximum absorbance of *o*-quinone (qno), the absorbance of the other reagents being negligible] and traces photographed from the storage screen of a 564 Tekronix oscilloscope. The stoicheiometry was determined using a Hitachi–Perkin-Elmer EPS-3T spectrophotometer. Ionic strength was maintained at I = 2·00M with sodium perchlorate. The kinetic experiments were carried out at [HClO$_4$] = 0·30—2·00, [Tl$^{\text{III}}$] = 3·0 × 10^{-4}, and [H$_2$cat] 1·0 × 10^{-3}—6·0 × 10^{-3}M, and 12·0, 18·0, 25·0, and 35·0 °C.

RESULTS

Stoicheiometry.—Spectra of the final product of the reaction showed maximum absorption at 390 nm, confirming that oxidation leads to *o*-quinone.[1,2,20] To assess the stoicheiometry, known amounts of Tl$^{\text{III}}$ were mixed with an excess of catechol and the concentration of qno formed was determined spectrophotometrically at 390 nm (ε

TABLE 1

Values of the pseudo-first-order rate constant k_{obs} (s^{-1}) at I = 2·00 and [Tl$^{\text{III}}$] = 3·0 × 10^{-4}M

10^3[H$_2$cat]/M	[HClO$_4$]/M								
	0·30	0·40	0·50	0·70	1·00	1·30	1·60	1·80	2·00
12·0 °C									
6·0			37		15		12		
4·0			27		11		7·3		
2·0			12		5·5		4·0		
1·0			6·5		2·8		2·1		
18·0 °C									
4·0				29		22			
3·0				22		16			9·0
2·0				14					6·0
1·0				7·5					3·5
25·0 °C									
6·0		126	92		52	41	38	35	32
5·0		110	68		45		30	30	26
4·0		97	50		37	28	26	25	22
3·0	96	65	53	39	26	21	19	19	16
2·5	87			31					
2·0	59	47	26	24	17	14	12	12	10
1·5	50			15	13	10			7·8
1·0	39	23		11	10	6·5	5·8	5·9	5·0
35·0 °C									
4·0					96				44
3·0				105					
2·0				64	42				21
1·5				46	30				15
1·0					15				12

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$1{\cdot}46 \times 10^3$ l mol^{-1} cm^{-1}); Tl^I and the excess of catechol do not interfere in these measurements. In the investigated range of [H^+] and at 25·0 °C, it was found that $\Delta[Tl^{III}]/\Delta[qno] = 1{\cdot}01 \pm 0{\cdot}03$; thus the overall reaction can be represented as in equation (2).

$$Tl^{III} + H_2cat \longrightarrow Tl^I + qno + 2H^+ \qquad (2)$$

Kinetics.—Oscillographic traces recorded in the u.v. and visible region did not show evidence of appreciable formation of intermediates with ε values higher than those of the reactants. The increase in absorbance was found to be first order in [Tl^{III}] and Table 1 collects values of the pseudo-first-order rate constants, k_{obs}, under different experimental conditions. For runs carried out with [H_2cat] not in large excess, pseudo-first-order rate constants were evaluated from the initial parts of the kinetics traces and found to be in agreement with rate constants obtained from a second-order treatment. The first-order dependence on [H_2cat] is shown in Figure 1, for various values of [H^+]; values of the second-order rate constants, k_0, are collected in Table 2. Additional kinetic runs were carried out with lower catechol concentrations {[H_2cat] = (6·0—8·0) $\times 10^{-4}$M}; the kinetic data were computed using a second-order treatment and rate constants were in agreement with those reported in Table 2. A further set of experiments was carried out in which an excess of Tl^I was added to the catechol solutions before mixing them with the Tl^{III} solution. The experimental data showed that the reaction rate was not affected by Tl^I addition.

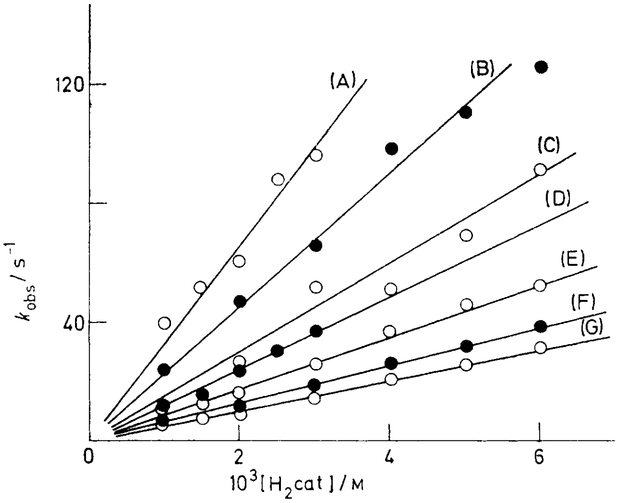

FIGURE 1 Plot of first-order rate constants k_{obs} against [H_2cat] at 25·0 °C and I = 2·00M, with [$HClO_4$] = 0·30 (A), 0·40 (B), 0·50 (C), 0·70 (D), 1·00 (E), 1·60 (F), and 2·00M (G)

DISCUSSION

The experimental data do not provide evidence of intermediate-complex formation between Tl^{III} and catechol in the above [H^+] range. This seems rather unexpected, if one takes into account the fact that intermediate complexes were found to occur in the oxidation of formic acid,[14] oxalic acid,[18] cyclohexanol,[16] H_3PO_2,[13a] and H_3PO_3 [13b] with Tl^{III} and, on the other hand, that catechol showed its co-ordination ability with Fe^{III} [1] and V^V.[2] The lack of spectrophotometric evidence does not however rule out that a complex with low stability occurs between the reacting species, so that the following scheme can be suggested. In the [H^+] range investigated protonated and deprotonated (anionic) forms of catechol may be ignored.[1,2] Because of the small value of the second hydrolysis constant of Tl^{III},[21] the species [$Tl(OH)_2$]$^+$ can also be neglected (in

TABLE 2

Values of the second-order rate constant 10^{-3} k_0 (l mol^{-1} s^{-1}) at various temperatures and I = 2·00M

	t/°C			
[H^+]/M	12·0	18·0	25·0	35·0
0·30			32	
0·40			23	
0·50	6·4		18	
0·70		7·7	13	33
1·00	2·6		8·7	24
1·30		4·1	7·0	
1·60	1·9		6·3	
1·80			6·1	
2·00		2·8	5·5	10

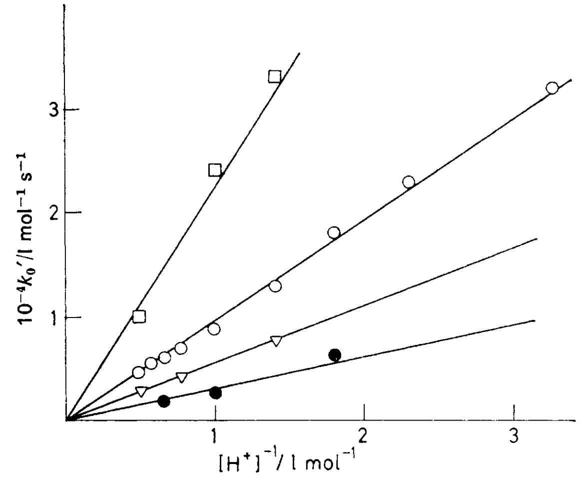

FIGURE 2 Plot of k_0', *i.e.* $k_0(1 + K_1[H^+]^{-1})$, against [H^+]$^{-1}$ at I = 2·00M and 35·0 (□), 25·0 (○), 18·0 (▽), and 12·0 °C (●)

$$\begin{tikzcd}
{[TlOH]^{2+}(aq) + H_2cat} \arrow[r, phantom, "\rightleftharpoons"] \arrow[d, shift left, "+H^+"] & {(HOTl\text{-}H_2cat)^{2+}(aq)} \arrow[r, "k"] \arrow[d, shift left, "+H^+"] & {Tl^+(aq) + qno + H^+(aq)} \\
{Tl^{3+}(aq) + H_2cat} \arrow[r, phantom, "\rightleftharpoons"] \arrow[u, shift left, "K_1"] & {(Tl\text{-}H_2cat)^{3+}} \arrow[r, "k'"] \arrow[u, shift left] & {Tl^+(aq) + qno + 2H^+(aq)}
\end{tikzcd}$$

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[21] G. Biedermann, *Arkiv. Kemi*, 1953, **5**, 441; *Rec. Trav. chim.*, 1956, **75**, 716; G. Biedermann and L. G. Sillen, *Arkiv. Kemi*, 1956, **10**, 103; T. E. Rogers and G. M. Waind, *Trans. Faraday Soc.*, 1961, **57**, 1360.

fact at the lower [$\mathrm{H^+}$] value its concentration is *ca.* 2% of the total [$\mathrm{Tl^{III}}$]).

From this scheme equations (3) and (4) can be deduced.

$$-\frac{\mathrm{d}[\mathrm{Tl^{III}}]_\mathrm{T}}{\mathrm{d}t} = \frac{(k' + kK_1[\mathrm{H^+}]^{-1})[\mathrm{H_2cat}][\mathrm{Tl^{III}}]_\mathrm{T}}{1 + K_1[\mathrm{H^+}]^{-1}} \quad (3)$$

$$k_{\mathrm{obs}} = [\mathrm{H_2cat}]\frac{k' + kK_1[\mathrm{H^+}]^{-1}}{1 + K_1[\mathrm{H^+}]^{-1}} = [\mathrm{H_2cat}]k_0 \quad (4)$$

According to equation (4), the plots of Figure 2 are obtained. The points were calculated with values of K_1 computed for our experimental conditions from literature data [21] at various temperatures and ionic strengths; the values are reported in Table **3**, together with values of *k*.

TABLE 3

Values of the activation parameters and of K_1 and k at various temperatures ($I = 2{\cdot}00$M)

t/°C	12·0	18·0	25·0	35·0
10^2K_1/mol $\mathrm{l^{-1}}$	6·9	7·3	7·7	8·5
$10^{-4}k$/l $\mathrm{mol^{-1}\ s^{-1}}$	5·0 ± 0·4	8·2 ± 0·7	14 ± 1	29 ± 3

$\Delta H^\ddagger = 46 \pm 5$ kJ $\mathrm{mol^{-1}}$. $\Delta S^\ddagger = 25 \pm 15$ J $\mathrm{K^{-1}\ mol^{-1}}$.

A similar dependence of the rate of $\mathrm{Tl^{III}}$ disappearance on [$\mathrm{H^+}$] was pointed out in most kinetic $\mathrm{Tl^{III}}$ oxidation studies, *e.g.* those of formic acid [14] and $\mathrm{Hg^{I}}$,[5] and in the $\mathrm{Tl^{III}}$–$\mathrm{Tl^{I}}$ exchange.[22] It is worth noting that in other studies more complex dependences on [$\mathrm{H^+}$] have been found, because in addition to the ion [TlOH]$^{2+}$, the second hydrolytic species [$\mathrm{Tl(OH)_2}$]$^+$ or hydrolysed forms of the other reagent ($\mathrm{U^{IV}}$,[7] $\mathrm{V^{III}}$ [10]) are important. In some instances the observed dependence on [$\mathrm{H^+}$] can be attributed to deprotonation, kinetically indistinguishable, of the reducing agent, as in the cases of formic acid,[14] oxalic acid,[18] and $\mathrm{H_3PO_3}$.[13b]

A question of general interest in multiequivalent reactions is whether they are accomplished in a single step or through successive one-electron transfers. According to Schaffer,[23] in a redox reaction in which the number of electrons involved in the two half reactions is equal reaction proceeds in a single step, whereas when the number of electrons is unequal the overall reaction involves either a succession of steps or higher-order reactions and is generally slower. Literature data concerning reduction of $\mathrm{Tl^{III}}$ with several two-electron reducing agents, such as $\mathrm{Hg_2}^{2+}$,[5] formic acid [14] (which does not give intermediate-radical formation), $\mathrm{V^{II}}$,[9] and $\mathrm{Sn^{II}}$,[12] show that reaction occurs only in a single step, in accordance with the above principle. With other two-electron reductants, however, such as oxalic acid,[18] $\mathrm{U^{IV}}$,[7] cyclohexanol,[16] $\mathrm{H_3PO_3}$,[13a] and $\mathrm{H_3PO_2}$ [13b] (oxidised to $\mathrm{H_3PO_3}$), the experimental data do not permit exclusion of two-stage one-electron oxidation with intermediate $\mathrm{Tl^{II}}$ formation. $\mathrm{Tl^{II}}$ Has been detected in the oxidation of aliphatic alcohols by $\mathrm{Tl^{III}}$ induced by γ-irradiation or u.v. photolysis.[19] It is also worth mentioning that the rate of the two-step oxidation of $\mathrm{V^{III}}$ by $\mathrm{Tl^{III}}$ [10a] is higher than that of one-step oxidation of $\mathrm{V^{II}}$ [9] with the same oxidant.

From the present data it is impossible to decide whether the reaction of catechol with $\mathrm{Tl^{III}}$ gives qno and $\mathrm{Tl^{I}}$ directly, or if reaction occurs in two steps, involving intermediate formation of $\mathrm{Tl^{II}}$ and of a semiquinone radical (Hcat˙) (produced in the oxidation of catechol by $\mathrm{Fe^{III}}$ [1] and, probably, $\mathrm{V^{V}}$ [2]) as in equations (5) and (6). In the latter case, both $\mathrm{Tl^{II}}$ and Hcat˙,

$$\mathrm{Tl^{III} + H_2cat \longrightarrow Tl^{II} + Hcat^{\bullet} + H^+} \quad (5)$$

$$\mathrm{Tl^{II} + Hcat^{\bullet} \longrightarrow Tl^{I} + qno + H^+} \quad (6)$$

being highly reactive, will react within their solvent cage before diffusing out. In this connection it is of note that while it has been found that reaction of $\mathrm{Tl^{III}}$ with $\mathrm{U^{IV}}$ in water [7] probably occurs *via* a single step mechanism, the same reaction in methanol–water (3 : 1 v/v) [8] proceeds *via* one-electron steps, a difference possibly attributed to the different solvent-cage effects in the two cases. The present experiments with $\mathrm{Tl^{I}}$ show that the mechanism of catechol oxidation does not involve any equilibrium with $\mathrm{Tl^{I}}$.

In Table **3** estimates of the activation parameters are also reported; the values are of the same order as previous data concerning other redox reactions involving $\mathrm{Tl^{III}}$ as oxidant. It is noteworthy that available data on the first hydrolysis step of $\mathrm{Tl^{III}}$ show a small ΔH of reaction (*ca.* 4 kJ $\mathrm{mol^{-1}}$); some authors, however, have postulated, by comparison with hydrolyses of other transition-metal ions (*e.g.* those of $\mathrm{In^{III}}$ and $\mathrm{U^{IV}}$) higher ΔH values for [TlOH]$^{2+}$ formation.[5,7,8,10,11,14] If these values were taken into account, a lower value for $\Delta H^\ddagger$ would be obtained for the present reaction.

[3/1548 *Received*, 23*rd July*, 1973

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