Kinetics of Oxidation of 1,4-Dihydroxy-, 1-Hydroxy-4-methoxy-, and 1,4-Dihydroxy-2-methyl-benzene by Thallium(III) in Aqueous Perchlorate Media

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The reactions of Tl^{III} with 1,4-dihydroxybenzene (H_2quin), 1-hydroxy-4-methoxybenzene (Hhmb), and 1,4-dihydroxy-2-methylbenzene (H_2dhmb) have been investigated in aqueous perchlorate media at various temperatures and acidities with $I = 2{\cdot}0$M. The reaction rates are first order in the concentration of both reactants. The dependence on acidity suggests that two paths contribute to the reaction. Rate constants for Hhmb are about one half those of H_2quin, while the methyl group of H_2dhmb increases the reaction rate. A comparison is drawn between the kinetic behaviour of a series of related oxidation reactions.

In previous studies in this laboratory the kinetics and mechanism of the Tl^{III} oxidation of 1,2-dihydroxybenzene (catechol, H_2cat),[1] 1-hydroxy-2-methoxybenzene (guaiacol),[2] and substituted 1,2-dihydroxybenzenes [2,3] to the corresponding *o*-benzoquinones have been investigated in aqueous perchlorate media. When H_2cat was oxidized with Fe^{III} or V^V (generally one-electron oxidants) [4] a different mode of reaction was found depending on which reagent was present in excess.[5] However, with Tl^{III} (two-electron oxidant) the mechanism was the same regardless of which reagent was in excess. The second-order rate constants showed a dependence on $[H^+]^{-1}$ and/or $[H^+]^{-2}$ in the case of H_2cat and its derivatives (substituted on the ring) [1,3] while guaiacol exhibited also a term independent of acidity.

Several papers deal with the kinetics of oxidation of 1,4-dihydroxybenzene (quinol, H_2quin) with several one-electron oxidants such as Fe^{III},[6,7] Ce^{IV},[8a] V^V,[8b] Co^{III},[9,10] Mn^{III},[11,12] Np^{VI},[13] and Pu^{VI} and Pu^{IV}.[14] The oxidation with Ce^{IV} and V^V is believed to proceed through an inner-sphere mechanism, while evidence for a similar mechanism has not been obtained in Fe^{III} oxidation, and in the cases of Mn^{III} and Co^{III} different behaviour has been suggested. The different dependences on acidity found were explained in terms of protonated intermediate complexes or hydrolysed metal-ion species. With the above oxidants the reaction gives rise to semiquinone formation and then to the corresponding quinone. The oxidation of H_2quin and 1-hydroxy-4-methoxybenzene, Hhmb, with

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periodate in excess[15a] shows no evidence of intermediate-complex formation (in contrast to the I^{VII}–H_2cat reaction[15b]). The mode of reaction of H_2quin with V^V,[5] as in the case of H_2cat, differs according to which reagent is present in excess. In this case there are two different paths involving the formation of **1 : 1** and **1 : 2** activated complexes between the organic molecule and metal ion; similar behaviour has been pointed out in the Pu^{VI} oxidation of quinol.[14]

It seemed of particular interest to investigate the reaction of H_2quin, Hhmb, and 1,4-dihydroxy-2-methylbenzene (H_2dhmb) with Tl^{III}. In fact this metal ion, which can behave as a two-electron oxidant, can oxidize these organic substrates in a single step so that no intermediate semiquinone formation need be advanced.

EXPERIMENTAL

Reagents.—Thallium(III) solutions were prepared by dissolving in aqueous perchloric acid either Tl_2O_3 (B.D.H.) or thallium(III) hydroxide freshly precipitated by treating a thallium(III) nitrate (E. Merck) solution with an excess of ammonia. Solutions prepared by the two methods showed similar kinetic behaviour. Twice-distilled water was used throughout. Solutions of 1,4-dihydroxybenzene (H_2cat), 1-hydroxy-4-methoxybenzene (Hhmb) (C. Erba), and 1,4-dihydroxy-2-methylbenzene (H_2dhmb) (E. Merck) were prepared immediately before use. Sodium perchlorate (C. Erba) was used for adjustment of ionic strength. Thallium(I) perchlorate solutions were prepared by dissolving the corresponding carbonate (B.D.H.) in perchloric acid (Merck). All the above materials were reagent grade.

TABLE 1

Pseudo-first-order rate constants, $k_{obs.}$ (s^{-1}), for the oxidation of 1,4-dihydroxybenzene, H_2quin, under various experimental conditions with $[Tl^{III}] = 5·0 \times 10^{-4}$ and $I = 2·0$M

		[HClO$_4$]/M						
θc/°C	$10^2[H_2quin]$/M	0·30	0·50	0·70	1·00	1·20	1·50	2·00
18·0	0·50	3·8		2·8			2·3	2·2
	0·70	5·7		3·9			3·7	3·2
	1·0	7·7		5·5			4·8	4·3
	2·0	15		10			9·4	9·0
	3·0	19		16			14	13
	4·0	26		19			18	17
	5·0	31		26			22	20
25·0	0·50	5·2	4·9	4·2	4·5		4·3	4·0
	0·70	6·5	6·2	5·8	6·1		6·0	5·3
	1·0	8·9	10	9·2	9·5		7·5	7·0
	2·0	18	17	15·5	15		15	13
	3·0	27	25	22	23		22	22
	4·0	39	35	33	31		27	27
	5·0	45	43	41	38		36	36
35·0	0·50	11		9·6		8·7		8·0
	0·70	15		15		11		10
	1·0	20		22		16		13
	2·0	34		40		28		27
	3·0	50		58		38		40
	4·0	64		74		57		48
	5·0	67		82		65		62

Procedure.—Thallium(III) was determined by ethylenediaminetetra-acetic acid (H_4edta) titrations [1-(2-pyridylazo)-2-naphthol as indicator]. The kinetic runs were carried out with a Durrum–Gibson stopped-flow spectrophotometer. *p*-Benzoquinone (*p*-qno) formation was followed by recording the variation in transmittance at 430 nm with time. (At this wavelength the other species in solution, although in large excess, do not absorb significantly.) The resulting traces on the storage screen of a 564 Tektronix oscilloscope were photographed. The acidity and temperature ranges investigated were 0·30—2·00M ([HClO$_4$]) and 3·5—35·0 °C, respectively; the organic substrate was generally present in excess ($5·0 \times 10^{-3}$—$5·0 \times 10^{-2}$M) with $[Tl^{III}] = 5·0 \times 10^{-4}$M.* Kinetic data were evaluated with a weighted least-squares method, previously described.[16] The stoicheiometry of the reactants was determined using a Hitachi–Perkin-Elmer EPS 3T spectrophotometer.

RESULTS

Stoicheiometry.—Spectra of the products of reaction and of H_2quin (or Hhmb), Tl^{III}, Tl^I, and *p*-qno were recorded. They showed that both organic substrates are oxidized to *p*-qno regardless of which reactant is in excess. In order to assess the stoicheiometry, known amounts of Tl^{III} were mixed with a slight excess of H_2quin (or Hhmb) and the concentration of *p*-qno was evaluated spectrophotometrically at 248 nm (ε $2·2 \times 10^4$ l mol^{-1} cm^{-1}) taking into account the slight contribution of the unchanged H_2quin (or Hhmb) to the measured absorbance (Tl^I does not interfere). The overall reactions can be represented as in (1) and (2). Similarly the stoicheiometry

$$Tl^{III} + H_2quin \longrightarrow Tl^I + p\text{-qno} + 2H^+ \qquad (1)$$

$$Tl^{III} + Hhmb + H_2O \longrightarrow Tl^I + p\text{-qno} + 2H^+ + MeOH \qquad (2)$$

of reaction of H_2dhmb accords with equation (1) giving the corresponding *p*-benzoquinone.

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* 1M = 1 mol dm^{-3}, 1 cal = 4·184 J.

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[16] G. Giraudi, E. Mentasti, and E. Pelizzetti, *Atti Accad. Sci. Torino*, in the press.

TABLE 2

Pseudo-first-order rate constants, $k_{obs.}$ (s^{-1}), for the oxidation of 1-hydroxy-4-methoxybenzene, Hhmb, under various experimental conditions with $[Tl^{III}] = 5·0 \times 10^{-4}$ and $I = 2·0$M

		[HClO$_4$]/M					
θ$_c$/°C	10^2[Hhmb]/M	0·30	0·40	0·50	0·70	1·20	2·00
18·0	0·50	1·2			1·1	1·0	1·0
	1·0	2·4			2·4	2·1	2·2
	1·5	3·5			3·4	3·3	3·2
	2·0	4·9			4·5	4·4	3·9
	3·0	7·3			7·1	9·0	5·1
	4·0	9·8			9·6	9·0	7·6
25·0	0·50	2·4	2·5	2·2	2·5	2·2	2·0
	1·0	5·0	5·1	4·7	4·9	4·7	3·0
	1·5	7·7	8·0	8·0	7·2	6·9	4·2
	2·0	9·8	10	10	10	8·5	7·2
	3·0	14	15	14	12	12	10
	4·0	19	18·5	18	18	15	12
35·0	0·50	4·6			4·3	4·0	3·9
	1·0	10			9·0	8·0	7·9
	1·5	13			13	12	11
	2·0	16			16	15	14
	3·0	25			24	22	18
	4·0	30			30	28	24

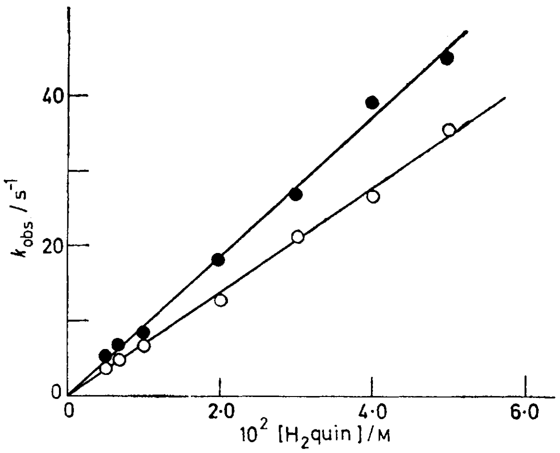


FIGURE 1 Plot of the pseudo-first-order rate constant $k_{obs.}$ against [H$_2$quin] at $I = 2·0$M, 25·0 °C, and [HClO$_4$] = 0·30 (●) and 2·00M (○)

TABLE 3

Pseudo-first-order rate constants, $k_{obs.}$ (s^{-1}), for the oxidation of 1,4-dihydroxy-2-methylbenzene, H$_2$dhmb, under various experimental conditions with $[Tl^{III}] = 5·0 \times 10^{-4}$ and $I = 2·0$M

		[HClO$_4$]/M			
θ$_c$/°C	10^2[H$_2$dhmb]/M	0·30	0·70	1·20	2·00
12·0	0·50	14	8·3	5·8	4·2
	1·0	28	17	10	8·5
	1·5	38	26	18	12
	2·0	52	30	24	17
	2·5	65	37	32	22
18·0	0·50	23	14	10	7·0
	1·0	45	25	20	15
	1·5	71	40	29	22
	2·0	92	48	39	28
	2·5	100	63	52	37
25·0	0·50	46	26	19	16
	1·0	93	53	39	29
	1·5	140	86	60	41
	2·0	165	110	73	55
	2·5		133	92	73

Kinetics of the Reactions.—The increase in absorbance was always first order in [Tl^{III}] (not in excess) under the experimental conditions, up to 90% completion of reaction. Values of the pseudo-first-order rate constants, $k_{obs.}$, at different acidities and temperatures are collected in Tables 1—3. The first-order dependence in [H$_2$quin] is shown in Figure 1 and the values of the second-order rate constants, k_0, are given in Table 4. Analogous behaviour was found for Hhmb and H$_2$dhmb and the corresponding rate constants are also listed in this Table.

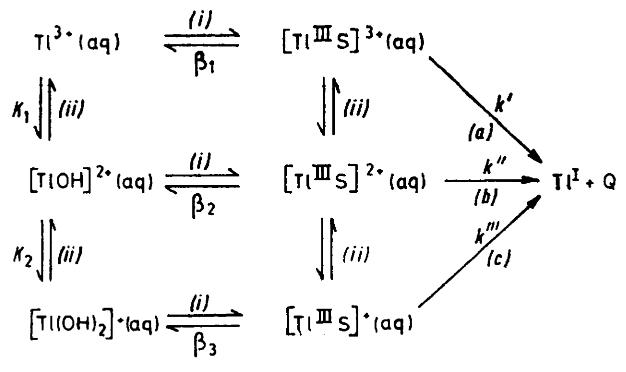
TABLE 4

Values of the second-order rate constants, k_0 (l mol^{-1} s^{-1}), at various temperatures and acidities ($I = 2·0$M)

	θ$_c$/°C			
[HClO$_4$]/M	12·0	18·0	25·0	35·0
(*a*) H$_2$quin ($10^{-2}k_0$)				
0·30		6·6	9·0	17
0·50			8·8	
0·70		5·4	8·5	19
1·00			8·2	
1·20				14
1·50		4·7	7·6	
2·00		4·3	7·1	13
(*b*) Hhmb($10^{-2}k_0$)				
0·30		2·6	5·0	8·4
0·40			5·0	
0·50			4·8	
0·70		2·4	4·7	8·2
1·20		2·1	4·0	7·4
2·0		1·9	3·2	6·8
(*c*) H$_2$dhmb($10^{-3}k_0$)				
0·30	2·6	4·6	9·0	
0·70	1·6	2·6	5·4	
1·20	1·2	2·0	3·7	
2·00	0·85	1·5	2·9	

A further set of experiments was carried out in which Tl^{III} was mixed with solutions of organic substrates containing thallium(I) perchlorate ($1·0 \times 10^{-3}$—$5·0 \times 10^{-3}$M); the results showed that reverse reactions are not kinetically relevant. Other runs were carried out with an excess of Tl^{III} over the organic substrates: the values of $k_{obs.}$ and k_0 obtained were consistent with those previously found, thus showing that the reaction mechanism does not depend on the reactant in excess.

Taking into account the above features and previous findings,[1,2] the following scheme can be proposed where K_1 and K_2 are hydrolytic equilibrium constants, β_1—β_3 are formation equilibrium constants of the precursor complexes, S is the organic substrate, and Q the corre-



(*i*) + S, (*ii*) + H$^+$

sponding quinone. Protons involved in the electron-transfer steps have been omitted and Hhmb gives rise to MeOH as reaction product. From this scheme, when $\mathrm{Tl^{III}}$ is not in excess and assuming that protolytic and complex-formation reactions are fast compared to the electron-transfer steps, equation (4) can be deduced.

$$-\frac{\mathrm{d}[\mathrm{Tl^{III}}]}{\mathrm{d}t} = \frac{(k'\beta_1 + k''\beta_2K_1[\mathrm{H^+}]^{-1} + k'''\beta_3K_1K_2[\mathrm{H^+}]^{-2})[\mathrm{T^{III}}]_\mathrm{T}[\mathrm{S}]}{1 + K_1[\mathrm{H^+}]^{-1} + K_1K_2[\mathrm{H^+}]^{-2} + (\beta_1 + \beta_2K_1[\mathrm{H^+}]^{-1} + \beta_3K_1K_2[\mathrm{H^+}]^{-2})[\mathrm{S}]}$$

$$\text{where } k_\mathrm{obs.} = \frac{(k'\beta_1 + k''\beta_2K_1[\mathrm{H^+}]^{-1} + k'''\beta_3K_1K_2[\mathrm{H^+}]^{-2})[\mathrm{S}]}{1 + K_1[\mathrm{H^+}]^{-1} + K_1K_2[\mathrm{H^+}]^{-2} + (\beta_1 + \beta_2K_1[\mathrm{H^+}]^{-1} + \beta_3K_1K_2[\mathrm{H^+}]^{-2})[\mathrm{S}]} \qquad (4)$$

The linearity of the plots in Figure 2 and the lack of spectrophotometric complex-formation evidence suggest that, in the investigated concentration range, $(\beta_1 + \beta_2K_1[\mathrm{H^+}]^{-1} + \beta_3K_1K_2[\mathrm{H^+}]^{-2})[\mathrm{S}] \ll 1$. Hence from equation (4) we obtain (5) where k_0' is the second-order rate constant at different acidities. From Figure 2 it can

$$k_0'([\mathrm{H^+}] + K_1 + K_1K_2[\mathrm{H^+}]^{-1}) = k'\beta_1[\mathrm{H^+}] + k''\beta_2K_1 + k'''\beta_3K_1K_2[\mathrm{H^+}]^{-1} \qquad (5)$$

be seen that the term $k'''\beta_3K_1K_2[\mathrm{H^+}]^{-1}$ can be neglected for the investigated compounds, and that the paths contributing to the reaction are (*a*) and (*b*) of the above scheme; values of $k'\beta_1$ and $k''\beta_2$ (calculated by using the K_1 and K_2 values previously adopted)[1,17] are given in Table 5. From data at various temperatures the activation parameters were evaluated (Table 5).

TABLE 5

Values of $k'\beta_1$ and $k''\beta_2$ ($\mathrm{l\ mol^{-1}\ s^{-1}}$) and overall activation parameters for the reaction of quinols with $\mathrm{Tl^{III}}$ at various temperatures ($I = 2{\cdot}0\mathrm{M}$)

Compound		θ_c/°C				$\Delta H^‡$	$\Delta S^‡$
		12·0	18·0	25·0	35·0	kcal $\mathrm{mol^{-1}}$	cal $\mathrm{K^{-1}\ mol^{-1}}$
$\mathrm{H_2quin}$	$10^{-2}k'\beta_1$		4·1 ± 0·4	6·8 ± 0·7	12 ± 1	11 ± 2	−10 ± 7
	$10^{-3}k''\beta_2$		1·4 ± 0·1	2·1 ± 0·2	3·3 ± 0·3	8 ± 2	−15 ± 7
Hhmb	$10^{-2}k'\beta_1$		1·8 ± 0·2	3·1 ± 0·3	5·1 ± 0·5	10 ± 2	−13 ± 7
	$10^{-3}k''\beta_2$		0·92 ± 0·09	1·6 ± $0{\cdot}1_5$	2·4 ± 0·2	9 ± 2	−12 ± 7
$\mathrm{H_2dhmb}$	$10^{-2}k'\beta_1$	4·6 ± 0·3	8·0 ± 0·5	16 ± 1		16 ± 2	+10 ± 7
	$10^{-4}k''\beta_2$	1·2 ± 0·1	2·1 ± 0·2	4·0 ± 0·3		15 ± 2	+16 ± 7

TABLE 6

Values of the pseudo-first-order rate constants for the reaction of catechol, $\mathrm{H_2cat}$, and quinol, $\mathrm{H_2quin}$, with $\mathrm{Tl^{III}}$ at 3·5 °C ($I = 2{\cdot}0\mathrm{M}$)

$[\mathrm{H_2cat}]$/M	$k_\mathrm{obs.}/\mathrm{s^{-1}}$ *	$[\mathrm{H_2cat}]$/M	$k_\mathrm{obs.}/\mathrm{s^{-1}}$ *
0·050	49	0·18	165
0·070	68	0·20	180
0·10	98	0·23	192
0·13	126	0·25	198
0·15	140		

	$[\mathrm{HClO_4}]$/M		
$[\mathrm{H_2quin}]$ †/M	0·15	0·50	2·00
0·030	4·7	4·4	4·0
0·050	7·6	7·4	7·0
0·070	10·8	10·9	10·3
0·090	14·2	14·0	13·6
0·110	17·3	16·8	16·3

* $[\mathrm{HClO_4}] = 2{\cdot}00$, $[\mathrm{Tl^{III}}] = 2{\cdot}0 \times 10^{-4}\mathrm{M}$; the rate constant given is the average value from at least three separate measurements. † $[\mathrm{Tl^{III}}] = 5{\cdot}0 \times 10^{-4}\mathrm{M}$.

Kinetics of Oxidation of $\mathrm{H_2cat}$ *and* $\mathrm{H_2quin}$ *at High Concentration*.—In order to achieve information about the order of magnitude of the formation constants of the precursor complexes, series of runs at high concentrations of the organic substrates were carried out. In the case of $\mathrm{H_2cat}$ the experiments were made at 3·5 °C and $[\mathrm{HClO_4}] = 2{\cdot}0\mathrm{M}$; under these conditions the half time of the reaction at the highest $\mathrm{H_2cat}$ concentration was at the limit of the resolution time of our stopped-flow apparatus. The results are collected in Table 6 (each value is the average of at least three separate measurements). A plot of $k_\mathrm{obs.}$ against [S] was not linear at higher values of $[\mathrm{H_2cat}]$. Taking into account that under these conditions $(K_1[\mathrm{H^+}]^{-1} + K_1K_2[\mathrm{H^+}]^{-2}) \ll 1$ and for $\mathrm{H_2cat}$ $k'\beta_1 \ll k''\beta_2K_1[\mathrm{H^+}]^{-1} \gg k'''\beta_3K_1K_2[\mathrm{H^+}]^{-2}$,[1] equation (4) can be written as (6).

$$\frac{1}{k_\mathrm{obs.}} = \frac{1}{k''\beta_2K_1[\mathrm{H^+}]^{-1}} \cdot \frac{1}{[\mathrm{S}]} + \frac{\beta_1 + \beta_2K_1[\mathrm{H^+}]^{-1}}{k''\beta_2K_1[\mathrm{H^+}]^{-1}} \qquad (6)$$

Assuming that $\beta_1 \ll \beta_2K_1[\mathrm{H^+}]^{-1}$, the intercept and gradient of a plot of $1/k_\mathrm{obs.}$ against $[\mathrm{S}]^{-1}$ gave $k'' = 6 \times 10^2\ \mathrm{s^{-1}}$ and $\beta_2 = 60\ \mathrm{l\ mol^{-1}}$ respectively.

Kinetic runs at 3·5 °C were also carried out with $\mathrm{H_2quin}$ the upper concentration (0·11M) of which was limited by its solubility. The runs were carried out at 0·15, 0·50, and 2·00M-$\mathrm{HClO_4}$. As it can be seen from Table 6, no deviation from linearity in the plot of $k_\mathrm{obs.}$ against [S] was observed, so that for $\mathrm{H_2quin}$ $(\beta_1 + \beta_2K_1[\mathrm{H^+}]^{-1}) \leqslant 1\ \mathrm{l\ mol^{-1}}$.

DISCUSSION

Different mechanisms of oxidation of quinol with metal ions have been assessed or proposed. An inner-sphere mechanism has been suggested by Wells and Kuritsyn for the oxidation with $\mathrm{V^V}$, $\mathrm{Ce^{IV}}$, $\mathrm{Co^{III}}$, and $\mathrm{Mn^{III}}$,[8,9,11] while Davies for the last two ions (particularly for $\mathrm{Co^{III}}$)[10,12] suggested an outer-sphere mechanism. In the oxidation of catechols by $\mathrm{Tl^{III}}$,[2] the dependence on acidity ($[\mathrm{H^+}]^{-2}$) suggested an inner-sphere mechanism; in the present case no definite assignment of the nature of the precursor complexes can be made. Because the ratios of the overall specific rate constants $k''\beta_2$ [path (*b*)] and $k'\beta_1$ [path (*a*)] have values ranging from 4—5 (for $\mathrm{H_2quin}$ and Hhmb) to 25 $\mathrm{l\ mol^{-1}\ s^{-1}}$ (for $\mathrm{H_2dhmb}$), it is evident that the OH ligand has a much larger influence than expected

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[17] 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.

for an electrostatic effect alone. It is possible that the hydroxy-group can act as a bridge for the electron transfer.

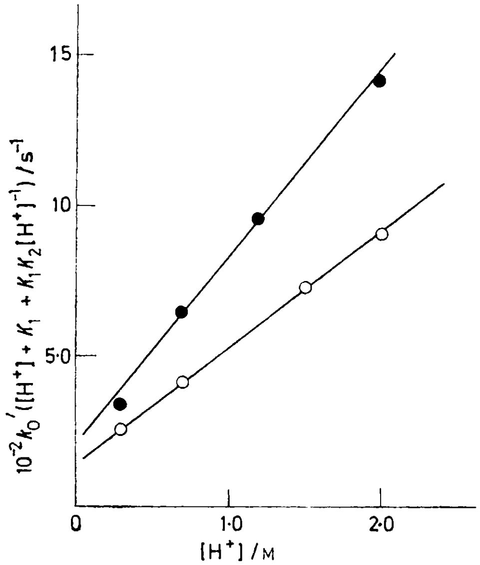

FIGURE 2 Plot of left-hand side of equation (5) against $[H^+]$ for the reactions of Tl^{III} with H_2quin at I = 2·0M and 18·0 °C (○) and with Hhmb at I = 2·0M and 35·0 °C (●)

In all the investigations with metal ions,[6-14] a free-radical mechanism was assumed. Kinetic evidence of semiquinone formation has been obtained in the oxidations with Fe^{III} (ref. 6) and Pu^{VI}.[14] In the reaction with Tl^{III} two alternative reaction mechanisms can be proposed: a two-electron transfer or two one-electron transfers, the latter mechanism giving first Tl^{II} and semiquinone then quinone. This mechanism [reaction (7)] seems to be excluded in fact. The equilibrium constant K_7, at $[H^+]$ = 1M, can be calculated,

$$Tl^{3+} + H_2\text{quin} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} Tl^{2+} + \text{Hquin}\cdot + H^+ \quad (7)$$

from the recently reported standard electrode-potential values of the Tl^{3+}–Tl^{2+} (ref. 18) and H_2quin–Hquin· couples,[14] as 1×10^{-11} mol l^{-1}. If k_{-7} is assumed to be, as an upper limit, diffusion controlled ($k_{\text{diff.}} \approx 10^{10}$ l mol^{-1} s^{-1}), k_7 should be *ca.* 1×10^{-1} l mol^{-1} s^{-1}, *i.e.* much smaller than the observed kinetic data. Thus, using the $E^\ominus$ data reported, the presence in the course of the reaction of Tl^{2+} in the bulk of the solution can be excluded. It is to be noted that in the present investigation the same mode of reaction holds regardless of which reactant is in excess. This cannot be attributed simply to the fact that Tl^{III} can react as a two-electron acceptor, but also to the small extent of precursor-complex formation.

A comparison of data concerning the oxidation of quinols with other reagents shows that with Ce^{IV} (ref. 8*a*) and V^V (ref. 8*b*) the activation energy can be attributed almost entirely to intermediate-complex formation. In the present case, it is not possible to evaluate the contribution of the single steps to the overall activation parameters. It is noteworthy that $\Delta H^\ddagger$ for Hhmb and guaiacol are very near to those found for H_2quin and H_2cat respectively in the oxidation with Tl^{III}. This seems to suggest that the presence of a methoxy-group instead of a hydroxy-group does not effect significantly the overall activation energy. Unlike H_2cat and guaiacol, the same dependence on acidity was observed for H_2quin and Hhmb, thus excluding acid catalysis in the oxidation of monomethyl ethers of H_2cat and H_2quin. In comparison to H_2quin, the rate constants for reaction of Hhmb are *ca.* 50% less; however, the methyl group in H_2dhmb increases the overall reaction rate. A similar trend was observed in the oxidation of H_2dhmb with other metal ions [Fe^{III},[7] Np^{VI} (ref. 13)].

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