Kinetics of Reactions of Catechol (*o*-Dihydroxybenzene) and Quinol (*p*-Dihydroxybenzene) with Oxidizing Metal Ions present in Excess: The Reactions with Iron(III), Vanadium(V), and Thallium(III) in Aqueous Perchloric Acid Solution

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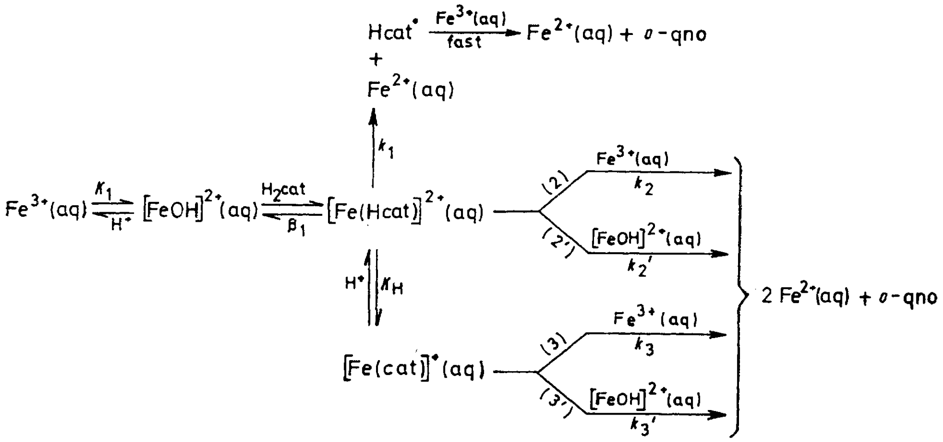
The reactions of catechol with excesses of Fe^{III}, V^{V}, and Tl^{III} ions and of quinol with an excess of V^{V} have been studied by means of a stopped-flow technique in aqueous acid solution ($HClO_4$) at 25·0 °C. Kinetic dependences on the reagent concentrations, different from those obtained in the presence of excess of the dihydroxybenzene, have been found for the reactions with Fe^{III} and V^{V} ions, while the same kinetic dependence has been found for the reaction with Tl^{III}. Proposed schemes of reaction are discussed.

THE kinetics and mechanism of oxidation of phenols with metal ions has been investigated mainly by working with the phenols present in excess. In previous papers the kinetics of oxidation of excess of catechol (*o*-dihydroxybenzene, H_2cat) with aqueous Fe^{III},[1] V^{V},[2] and Tl^{III} ions[3] were investigated. Further experiments with an excess of Fe^{III} or V^{V} ions showed a different kinetic dependence on reactant and hydrogen-ion concentrations. This prompted a kinetic study of the reaction of catechol with the above oxidants (as well as with Tl^{III}) present in large excess. It was also of interest to investigate the reaction between quinol (*p*-dihydroxybenzene, H_2quin) and an excess of V^{V} ions; this reaction, in excess of quinol, was previously studied by Wells and Kuritsyn.[4]



SCHEME 1 β_1 is the formation constant of the complex $[Fe(Hcat)]^{2+}$, K_1 the hydrolysis constant of Fe^{3+}, and K_H the acid-dissociation constant of $[Fe(Hcat)]^{2+}$

EXPERIMENTAL

The reagents and procedure were as described previously.[1-4] In the present experiments, the oxidation product of catechol (H_2cat) was *o*-quinone (*o*-qno), as shown by its absorption spectrum. The reaction between quinol (H_2quin) and V^{V} ions was followed at 370 nm; the reaction product was *p*-quinone (*p*-qno). Concentration ranges were: $[Fe^{III}] = 1·0 \times 10^{-2}—3·0 \times 10^{-2}$, $[H_2cat] = 2·0 \times 10^{-4}$, $[H^+] = 0·10—0·40$ ($HClO_4$), and $I = 1·00$M ($NaClO_4$), for the reaction Fe^{III} + catechol; $[V^{V}] = 1·0 \times 10^{-3}—1·0 \times 10^{-2}$, $[H_2cat] = 1·0 \times 10^{-4}$, $[H^+] = 0·50—1·00$ ($HClO_4$), and $I = 1·00$M ($NaClO_4$), for the reaction V^{V} + catechol; $[V^{V}] = 1·5 \times 10^{-3}—7·0 \times 10^{-3}$, $[H_2quin] = 2·0 \times 10^{-4}$, $[H^+] = 0·30—5·00$ ($HClO_4$), and $I = 5·00$M ($NaClO_4$), for the reaction V^{V} + quinol; and $[Tl^{III}] = 1·0 \times 10^{-3}—3·0 \times 10^{-3}$, $[H_2cat] = 1·0 \times 10^{-4}$, $[H^+] = 1·00—2·00$ ($HClO_4$), and $I = 2·00$M ($NaClO_4$), for the reaction Tl^{III} + catechol. Measurements were carried out at 25·0 ± 0·1 °C.

RESULTS

Fe^{III} + *Catechol*.—The increase in absorbance at 390 nm (due to *o*-qno) was first order with respect to $[H_2cat]$ (the reagent not in excess). Observed rate constants k_{obs} at various $[H^+]$ and $[Fe^{III}]$ values are given in Table 1.

The rate of reaction depends on $[Fe^{III}]^n$, where n is a number between 1 and 2, which in turn is a function of $[H^+]$. By recalling the previously suggested scheme of reaction,[1b] in excess of catechol, and taking into account the fact that, when Fe^{III} ions are present in large excess, the reverse reduction due to Fe^{II} can be neglected, Scheme (1) can be proposed. No account has been taken of dissociated species of catechol because of its low dissociation constant (pK_1 *ca.* 10).[5] Also the complex $[Fe(H_2cat)]^{3+}$(aq)

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

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

[3] E. Pelizzetti, E. Mentasti, and G. Saini, *J.C.S. Dalton*, 1974, 721.

[4] C. F. Wells and L. V. Kuritsyn, *J. Chem. Soc. (A)*, 1970, 1372.

[5] L. G. Sillen and A. E. Martell, ' Stability Constants of Metal-ion Complexes,' Special Publ. No. 17, The Chemical Society, London, 1964.

can either react with another Fe^{III} ion giving the final products of reaction (Fe^{II} and *o*-qno) or decompose into Fe^{II} and $Hcat^{\bullet}$; $Hcat^{\bullet}$ is rapidly oxidized to *o*-qno by another Fe^{III} ion (as shown previously).

TABLE 1

Values of the observed rate constant k_{obs} (s^{-1}) for the oxidation of catechol with Fe^{III} ions (25·0 °C, $I = 1{\cdot}00$, $[H_2cat]_0 = 2{\cdot}0 \times 10^{-4}M$)

$10^2[Fe^{III}]$/M	$[HClO_4]$/M						
	0·10	0·12	0·14	0·17	0·20	0·25	0·40
1·0	0·042	0·029	0·024	0·018	0·014	0·0078	0·0055
1·3	0·063	0·043	0·039	0·029	0·021	0·015	0·0080
1·5	0·079	0·055	0·045	0·032	0·026	0·016	0·0092
2·0	0·12	0·089	0·070	0·049	0·038	0·028	0·013
2·3		0·11	0·098	0·064	0·052	0·035	0·016
2·5			0·11		0·055	0·037	0·018
3·0			0·14		0·075	0·048	0·024

The kinetic expression which can be deduced, assuming that reactions of hydrolysis and complex formation are fast compared with the electron transfer and that Fe^{III}, in the $[H^+]$ range investigated, is mainly present as Fe^{3+}, is as in equation (1). Here K_{eq} is the equilibrium constant of

$$-\frac{d[H_2cat]_T}{dt} = \frac{(k_1\beta_1K_1[H^+]^{-1} + \alpha_1[Fe^{III}])[H_2cat]_T}{1 + (\beta_1K_1 + K_{eq}[H^+]^{-1})[Fe^{III}][H^+]^{-1}} \quad (1)$$

the reaction $Fe^{3+} + H_2cat \rightleftharpoons [Fe(cat)]^+(aq) + 2H^+$ ($4{\cdot}3 \times 10^{-2}$ mol l^{-1}),[1a] and α_1 is given by equation (2).

$$\alpha_1 = k_2\beta_1K_1[H^+]^{-1} + (k_2'\beta_1K_1^2 + k_3K_{eq})[H^+]^{-2} + k_3'K_1K_{eq}[H^+]^{-3} \quad (2)$$

Since the data of a previous paper,[1a] where formation of the complex $[Fe(cat)]^+(aq)$ was investigated, showed that at $[H^+] = 0{\cdot}10M$ there was no evidence of formation of a protonated $[Fe(Hcat)]^{2+}(aq)$ species, it follows that the acid-dissociation constant K_H of the complex $[Fe(Hcat)]^{2+}(aq)$ should be $>0{\cdot}1$ mol l^{-1}, and $\beta_1 < 2{\cdot}6 \times 10^2$ l mol^{-1}. Thus the term $(\beta_1K_1 + K_{eq}[H^+]^{-1})[Fe^{III}][H^+]^{-1}$ in the most unfavourable case assumes the value of *ca.* 0·1 and will be neglected in the following treatment. Equations (1) and (2) can then be simplified to give (3). Figure 1 shows plots,

$$k_{obs}/[Fe^{III}] = k_1\beta_1K_1[H^+]^{-1} + \alpha_1[Fe^{III}] \quad (3)$$

according to equation (3), at various $[H^+]$. From the intercepts the value of the constant $k_1\beta_1K_1$, which has the same meaning as the constant k_1' given previously,[1b] was evaluated as 0·20 s^{-1} (*cf.* 0·19 [1b]), from which [6] $k_1\beta_1 = 1{\cdot}2 \times 10^2$ l mol^{-1} s^{-1}. Furthermore, from gradients of the plots in Figure 1, the dependence on $[H^+]^{-2}$ was assessed and a value of 2·2 s^{-1} calculated for $(k_2'\beta_1K_1^2 + k_3K_{eq})$.

It is to be noted that, in this $[H^+]$ range, the dimer species $(Fe{-}O{-}Fe)^{4+}$ is present in less than 1% of $[Fe^{III}]_T$.[6,7] The participation of this species in the redox reaction can be excluded since the rate of formation of the dimer [8] is low compared with that of the redox reaction; in fact, under the present experimental conditions, the kinetic treatment used and the suggested reaction scheme should not be applicable.

V^V + *Catechol*.—The absorbance of the solution at 505 nm increased very rapidly due to formation of a $[V^V(H_2cat)]^+(aq)$ complex whose stability constant is *ca.* 4×10^2 l mol^{-1}; [2] the absorbance then decreased with first-order kinetics with respect to H_2cat (the reagent not in excess). Values of the observed rate constant k_{obs}' at different experimental conditions are given in Table 2.

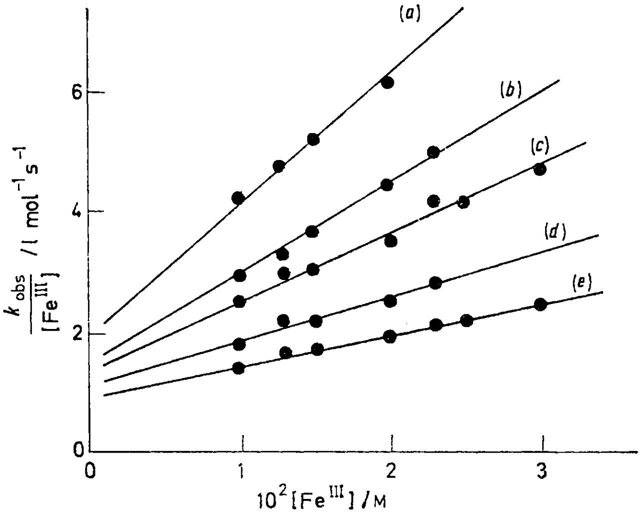

FIGURE 1 Plots of $k_{obs}/[Fe^{III}]$ against $[Fe^{III}]$ for the reaction of Fe^{III} with catechol at $[H_2cat]_0 = 2{\cdot}0 \times 10^{-4}$, $I = 1{\cdot}00M$, 25·0 °C, and $[HClO_4]$ as follows: (*a*), 0·10; (*b*), 0·12; (*c*), 0·14; (*d*), 0·17; and (*e*), 0·20M

TABLE 2

Values of the observed rate constant $10^2k_{obs}'$ (s^{-1}) for the oxidation of catechol with V^V ions (25·0 °C, $I = 1{\cdot}00$, $[H_2cat]_0 = 1{\cdot}0 \times 10^{-4}M$)

	$[HClO_4]$/M				
$10^3[V^V]$/M	0·50	0·60	0·70	0·85	1·00
1·0		1·3	1·4	2·1	2·3
2·0		4·0	4·2	6·0	7·4
3·0		7·6	8·3	13	14
4·0	6·1	10	11	17	19
5·0	9·5	17	18	23	26
7·0	15	26	29	38	44
10·0	24	39	45	55	63

The order with respect to $[V^V]_T$ does not correspond to a whole number (first order was found when V^V was not in excess). A mechanism consistent with the experimental results, taking into account the scheme suggested for catechol in excess, is shown in Scheme (2). The corresponding kinetic expression which can be deduced, assuming that reactions of protonation and complex formation are fast compared with electron transfer, is in equation (4), where α_2 is given by (5). Since $K_2[H^+] \ll 1$ (ref. 2) and

$$-\frac{d[H_2cat]_T}{dt} = \alpha_2\beta_2\frac{([V^V]_T)^2}{(1 + K_2[H^+])^2}\cdot\frac{[H_2cat]_T}{1 + \{\beta_2[V^V]_T(1 + K_3[H^+])/(1 + K_2[H^+])\}} \quad (4)$$

$$\alpha_2 = k_4 + (k_4'K_2 + k_5K_3)[H^+] + k_5'K_2K_3[H^+]^2 \quad (5)$$

$K_3[H^+] \ll 1$, equation (6) is obtained. According to

$$k_{obs}' = \frac{\alpha_2\beta_2([V^V]_T)^2}{1 + \beta_2[V^V]_T} \quad (6)$$

equation (6), by plotting $[V^V]_T/k_{obs}'$ as a function of $1/[V^V]_T$ a straight line is obtained with intercept $1/\alpha_2$ and gradient $1/\alpha_2\beta_2$. Such a plot, corresponding to $[H^+] = 1{\cdot}00M$, is

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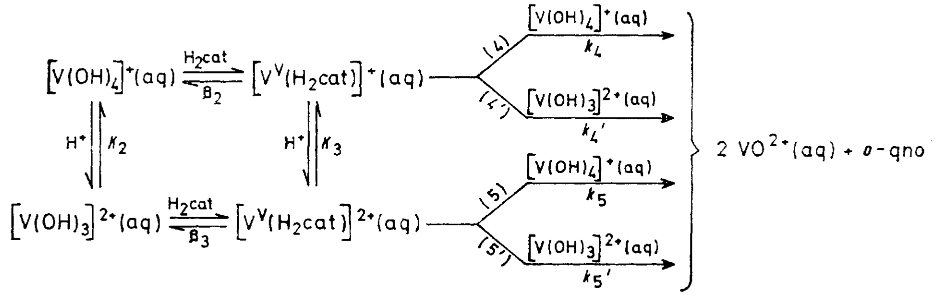
[6] R. M. Milburn, *J. Amer. Chem. Soc.*, 1957, **79**, 537.

[7] R. M. Milburn, *J. Amer. Chem. Soc.*, 1955, **77**, 1352; D. D. Perrin, *J. Chem. Soc.*, 1959, 1710.

[8] H. Wendt and H. Strehlow, *Z. Elektrochem.*, 1960, **34**, 131.

shown in Figure 2. The average value obtained for β_2 from the experimental data was $(3{\cdot}7 \pm 0{\cdot}7) \times 10^2$ l mol^{-1}, in agreement with that obtained directly from spectrophotometric data (*ca.* 4×10^2 l mol^{-1}).[2] α_2 Values showed a dependence on [H$^+$], indicating that, in the [H$^+$] range investigated, paths (4′) and/or (5) are preferred. Accordingly $(k_4'K_2 + k_5K_3)$ has been estimated to be 74 l^2 mol^{-2} s^{-1}.



SCHEME 2 $K_2 = [\mathrm{V(OH)_3}^{2+}]/[\mathrm{V(OH)_4}^+][\mathrm{H}^+]$, $K_3 = [\mathrm{V^V(H_2cat)}^{2+}]/[\mathrm{V^V(H_2cat)}^+][\mathrm{H}^+]$, and β_2 and β_3 are formation constants of the intermediate complexes

V$^\mathrm{V}$ + *Quinol*.—Even in excess of V$^\mathrm{V}$, as previously reported for reaction in the presence of excess of quinol,[4] an initial rise in absorbance followed by a decay was observed at 370 nm. This can be ascribed to formation of intermediate complexes.

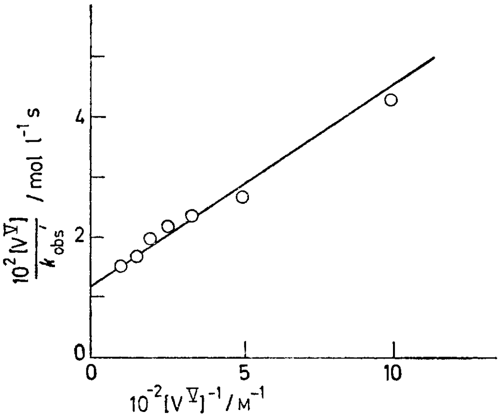


FIGURE 2 Plot of $[\mathrm{V^V}]_\mathrm{T}/k_\mathrm{obs}'$ against $1/[\mathrm{V^V}]$ for the reaction of V$^\mathrm{V}$ ions with catechol at $[\mathrm{H_2cat}]_0 = 1{\cdot}0 \times 10^{-4}$, $[\mathrm{HClO_4}] = 1{\cdot}00$, $I = 1{\cdot}00$M and 25·0 °C

TABLE 3

Values of the pseudo-first-order rate constant k_obs'' (s^{-1}) for the oxidation of quinol by V$^\mathrm{V}$ ions (25·0 °C, $I = 5{\cdot}00$, $[\mathrm{H_2quin}] = 2{\cdot}0 \times 10^{-4}$M)

	[HClO$_4$]/M					
$10^3[\mathrm{V^V}]_\mathrm{T}$/M	0·30	0·50	1·00	2·00	3·00	5·00
1·5	3·4	5·3	6·2	10	16	26
2·0	4·5	7·1	8·6	14	23	37
2·5	5·7	9·0	12	17	30	46
3·0	7·1	11	15	23	40	60
3·5	8·4	14	18	26	55	81
4·0	10	16	22	33	58	96
5·0	13	21	28	46	80	138
7·0	20	30	42	69	118	207

The decay in absorbance is first order in [H$_2$quin] (the reagent not in excess) and values of the pseudo-first-order rate constant k_obs'' are given in Table 3. It is to be noted that k_obs'' is proportional to $[\mathrm{V^V}]^n$, where n is a number between 1 and 2. By applying to this system the considerations previously suggested, Scheme (3) can be proposed. The corresponding kinetic expression which can be deduced with the same previous assumptions is as in equation (7)

$$-\frac{\mathrm{d}[\mathrm{H_2quin}]_\mathrm{T}}{\mathrm{d}t} = \frac{\beta_4\{(k_6 + k_6'K_5[\mathrm{H}^+]) + [\mathrm{V^V}]_\mathrm{T}(k_7 + k_7'K_4[\mathrm{H}^+] + k_8K_5[\mathrm{H}^+] + k_8'K_4K_5[\mathrm{H}^+]^2)\}[\mathrm{V^V}][\mathrm{H_3quin}]_\mathrm{T}}{1 + \beta_4[\mathrm{V^V}]_\mathrm{T}(1 + K_5[\mathrm{H}^+])} \quad (7)$$

where $K_4\beta_5 = \beta_4K_5$. Assuming that $[\mathrm{V(OH)_4}^+] = [\mathrm{V^V}]_\mathrm{T}$ $\{K_4[\mathrm{H}^+] \ll 1$ (refs. 2 and 4)$\}$, equation (8) is then obtained.

$$\frac{k_\mathrm{obs}}{[\mathrm{V^V}]_\mathrm{T}} \cdot \frac{1 + \beta_4[\mathrm{V^V}]_\mathrm{T}(1 + K_5[\mathrm{H}^+])}{\beta_4} = \gamma + \alpha_3[\mathrm{V^V}]_\mathrm{T} \quad (8)$$

where

$$\gamma = k_6 + k_6'K_2[\mathrm{H}^+] \quad (9)$$

and

$$\alpha_3 = k_7 + (k_7'K_4 + k_8K_5)[\mathrm{H}^+] + k_8'K_4K_5[\mathrm{H}^+]^2 \quad (10)$$

Figure 3 shows plots of the experimental data according to equation (8), calculated by using values of β_4 (5·5 l mol^{-1}) and K_5 (3·2 l mol^{-1}) reported by Wells and Kuritsyn.[4] Figure 4 shows the dependence of $\alpha_3/[\mathrm{H}^+]$ on [H$^+$]; it can

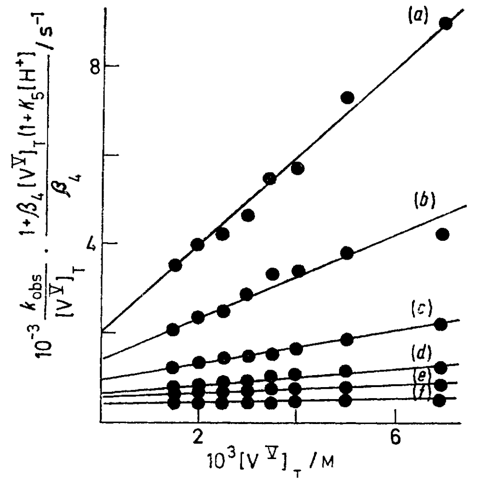
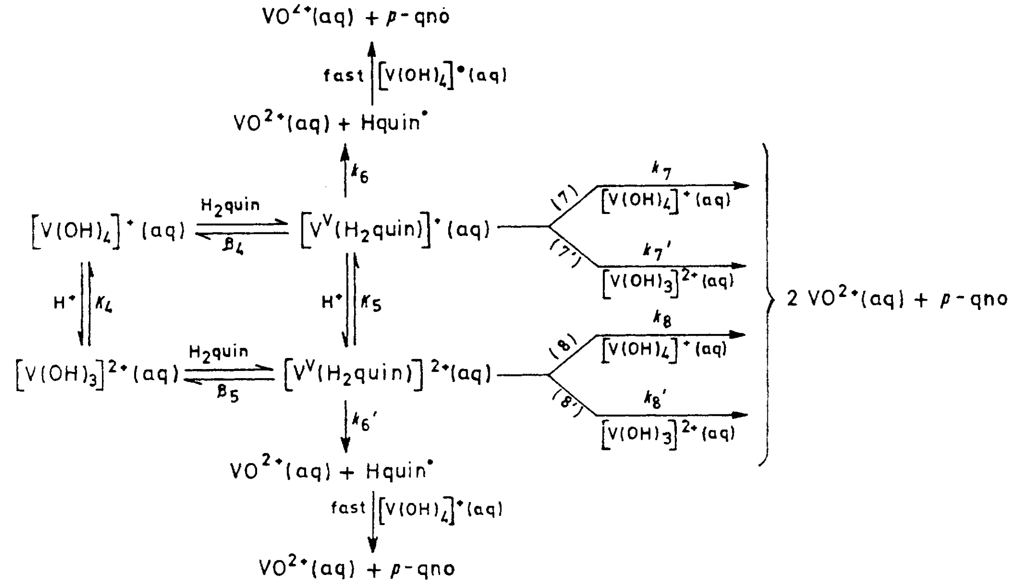


FIGURE 3 Plot of left-hand side of equation (8) against $[\mathrm{V^V}]_\mathrm{T}$ for the reaction of V$^\mathrm{V}$ ions and quinol at $I = 5{\cdot}00$M, 25·0 °C, and [HClO$_4$] as follows: (*a*), 5·00; (*b*), 3·00; (*c*), 2·00; (*d*), 1·00; (*e*), 0·50; and (*f*), 0·30M

be seen that path (7) does not contribute significantly. From the intercept $(k_7'K_4 + k_8K_5) = (5{\cdot}6 \pm 2{\cdot}2) \times 10^4$ l^2 mol^{-2} s^{-1} and $k_8'K_4 = (9{\cdot}0 \pm 3{\cdot}6) \times 10^3$ l^2 mol^{-2} s^{-1} can be obtained. The paths (7′) and (8) are kinetically indistinguishable. Intercepts of the plots in Figure 3, plotted as a function of $[H^+]$, gave $k_6 = (3{\cdot}6 \pm 1{\cdot}3) \times 10^2$ and $k_6' = (1{\cdot}1 \pm 0{\cdot}4) \times 10^2$ s^{-1} [*cf.* $(3{\cdot}3 \pm 0{\cdot}9) \times 10^2$ and $(1{\cdot}3 \pm 0{\cdot}3) \times 10^2$ s^{-1} respectively [4]].



SCHEME 3 $K_4 = [V(OH)_3^{2+}]/[V(OH)_4^+][H^+]$, $K_5 = [V^V(H_2quin)^{2+}]/[V^V(H_2quin)^+][H^+]$, and β_4 and β_5 are formation constants of the complexes $[V^V(H_2quin)]^+(aq)$ and $[V^V(H_2quin)]^{2+}(aq)$

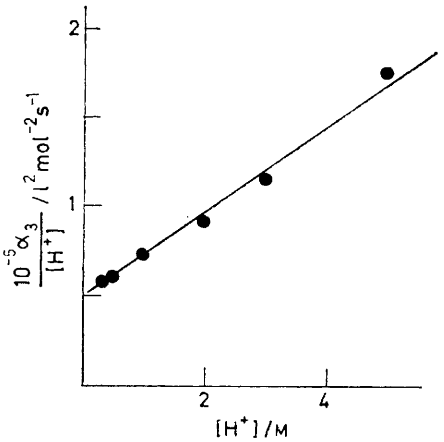


FIGURE 4 Plot of $\alpha_3/[H^+]$ against $[H^+]$ for the reaction between V^V ions and quinol at $I = 5{\cdot}00$M and 25·0 °C

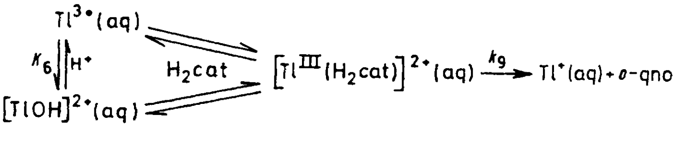
Tl^{III} + *Catechol*.—No spectrophotometric evidence of complex formation was found. Kinetic runs were monitored at 390 nm. The absorbance increased with time and the kinetics were first order in $[H_2cat]$. Pseudo-first-order rate constants k_{obs}''' are given in Table 4. The reaction was also first order in $[Tl^{III}]_T$. The expression $k_0'''(1 + K_6[H^+]^{-1})$, where k_0''' is the second-order rate constant showed a linear dependence on $[H^+]^{-1}$. The above observations are the same as those found previously with excess of catechol.[3]

Therefore the mechanism suggested for the reaction in the presence of excess of catechol can be assumed to apply also when Tl^{III} ions are in excess. From the present experiments, k_9 was found to be $(1{\cdot}3 \pm 0{\cdot}1) \times 10^5$ l mol^{-1} s^{-1}, in agreement with the value given previously.[3] (The same value, as previously, was assumed for K_6.[3,9])

TABLE 4

Values of the observed rate constant k_{obs}''' (s^{-1}) for the oxidation of catechol with Tl^{III} ions (25·0 °C, $I = 2{\cdot}00$, $[H_2cat]_0 = 1{\cdot}0 \times 10^{-4}$M)

	[HClO$_4$]/M		
$10^3[Tl^{III}]$/M	1·00	1·50	2·00
1·0	8·7	6·4	4·9
1·5	14	9·2	7·6
2·0	18	12	10
2·5	23	15	12
3·0	30	19	15



DISCUSSION

The experimental results suggest that in the oxidation of catechol with Fe^{III} ions in excess, the rate-determining step is mainly oxidation of intermediate complexes, in equilibrium with the reactants, by means of Fe^{III}; there are two alternative paths, kinetically indistinguishable, *i.e.* the reaction of the ion $[FeOH]^{2+}(aq)$ with $[Fe(Hcat)]^{2+}(aq)$ and/or $Fe^{3+}(aq)$ with $[Fe(cat)]^+(aq)$. Of the few papers on the oxidation of organic compounds by Fe^{III} ions, a first-order dependence on the reactants

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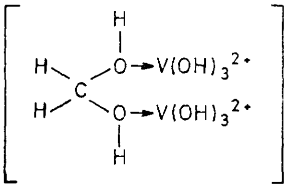
[9] G. Biedermann, *Rec. Trav. chim.*, 1956, **75**, 716; T. E. Rogers and G. M. Waind, *Trans. Faraday Soc.*, 1961, **57**, 1360.

was observed with acetoin[10] (the experiments were carried out with a large excess of organic substrate). It is noteworthy that in the oxidation of quinol with Fe^{III} ions in excess[11] (where no evidence of intermediate complexes was found), no term in $[Fe^{III}]^2$ was found. However, experimental data on the oxidation of sulphite ion (in presence of an excess of metal ion) are in agreement with an equation which includes a term proportional to $[Fe^{III}]^2$.[12]

When the oxidation of catechol is carried out with V^V ions in excess, there are two alternative paths for the rate-determining step, *i.e.* reaction of $[V(OH)_3]^{2+}(aq)$ ions with $[V^V(H_2cat)]^+(aq)$ and/or $[V(OH)_4]^+(aq)$ with $[V^V(H_2cat)]^{2+}(aq)$. Similar behaviour is proposed for the reaction of quinol with an excess of V^V ions. A second-order dependence on V^V has already been found in other oxidation reactions (formaldehyde,[13] chloral,[14] malonic acid,[15] and arsenious acid[16]). This kinetic behaviour was explained by assuming formation of intermediate complexes such as (I).



(I)

Kinetic dependences on the reactants in the oxidation of catechol with Tl^{III} ions do not change in the presence or absence of an excess of the oxidant.

The occurrence of these different mechanisms does not seem to depend simply on the number of electrons transferred. However, it is relevant that the redox reaction occurs through interaction of the oxidizing metal ion and the organic substrate, with the possibility of intermediate complex formation, the stability of which depends both on the cation and the organic molecule. In particular, for one-electron oxidants, it is suggested that, when formation of a stable complex does not occur (*i.e.* for Fe^{III} and quinol), the kinetic behaviour does not change in the presence or absence of an excess of the oxidant. On the other hand, when intermediate-complex formation occurs (*i.e.* with Fe^{III} + catechol, V^V + catechol, and V^V + quinol) two competitive paths are expected, one being direct decomposition of the complex with formation of the products of reaction, the other being further reaction of the complex with another oxidizing ion. Additional work on a number of redox reactions is required in order to clarify this point.

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[12] D. G. Karraker, *J. Phys. Chem.*, 1963, **67**, 871.

[13] T. J. Kemp and W. A. Waters, *Proc. Roy. Soc.*, 1963, **A274**, 480.

[14] T. J. Kemp in 'Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1972, vol. 7, p. 379.

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[16] M. Bobtelsky and A. Glasner, *J. Amer. Chem. Soc.*, 1942, **64**, 1462.