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# Redox Reaction of 1,2-Dihydroxybenzene with Mn(III) in Aqueous Perchlorate Media. Kinetics and Mechanism

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*A stopped flow technique has been used to investigate the mechanism and kinetics of reaction of* $Mn^{III}$ *with 1,2-dihydroxybenzene in aqueous perchlorate solutions. The acidity range investigated was* $0.50 \leqq [HClO_4] \leqq 3.00$ *M, at ionic strength* $I = 3.0$ *M, and at 25.0, 18.0 and 12.0° C. The oxidation product, o-benzoquinone, is obtained according to a stoichiometry given by:*

$$2Mn^{III} + H_2cat \rightarrow 2Mn^{II} + qno + 2H^+$$

*The reaction rate was first order in both reactants and the variation of the rate on acidity pointed out that the overall reaction takes place through two paths, one independent and one dependent on* $[H^+]^{-1}$*. These paths are discussed in terms of alternative inner or outer-sphere mechanisms due to the lack of evidence of intermediate complexes formation.*

## Introduction

Catechol (1,2-dihydroxybenzene, later referred to as $H_2cat$) is rapidly oxidized to *o*-quinone (qno) by $Fe^{III}$,[1] $V^V$,[2] and $Tl^{III}$,[3] through quite different mechanisms. In the case of $Fe^{III}$, the reaction rate dependence on acidity and the increase of reaction order by respect to the oxidizing ion, when in excess, enabled us to point out that the reaction progress goes through intermediate complexes and the rate determining step has been found to be the *o*-semiquinone radical formation[1,4] furtherly oxidized to *o*-quinone.

Similarly for $V^V$, evidence of stabile intermediate complexes formation was achieved, and an inner-sphere mechanism was pointed out; moreover the reaction order in respect to $[V^V]$ was increased from one, in defect of oxidant, to two when in excess,[2,4] in agreement with a direct participation of the complex to the reaction progress. On the contrary, no spectrophotometric evidence of intermediate complexes was achieved in the oxidation of catechol by $Tl^{III}$; moreover the invariance of first order in both oxidizing agent and substrate, irrespective of reagent in excess, showed that an intermediate complex formation, if present, has a very small extent.[3,4] The examination of kinetic behaviour of guaiachol (1-hydroxy-2-methoxybenzene) with $Tl^{III}$ showed however, that the reaction rate dependence on acidity (a single term proportional to $[H^+]^{-1}$ for catechol and a term dependent on $[H^+]^{-1}$ and another independent for guaiachol) was changed as the substrate had diminished co-ordination capabilities, so that the organic substrate was expected to be responsible of the loss of $H^+$, with co-ordinative bonds formation prior of the activated complex attainment.[5]

Pursuing the study on the kinetics and mechanism of oxidation of dihydroxyaromatic compounds with oxidizing metal ions it seemed of interest to investigate to reaction of catechol with $Mn^{III}$. This is an oxidant ($E_0$ 1.56 V, in $HClO_4$ 3*M*)[6] which, as shown by previous investigations, has a strong capability to inner substitution also in highly acidic media.[6]

## Experimental

### *Materials*

$Mn^{III}$ was prepared by electrooxidation, at a platinum anode, of $Mn^{II}$ in perchloric acid.[7]

$Mn^{II}$ perchlorate was prepared by dissolution of $MnCO_3$ (C. Erba) in aqueous perchloric acid (C. Erba), the product was then recrystallized twice from water. Catechol solutions were prepared by dissolving weighted amounts of the product (C. Erba) in aqueous perchloric acid. These solutions were prepared daily before use and protected from direct light.

Perchloric acid and sodium perchlorate (C. Erba) were used for bringing the solutions (prepared in twice distilled water) to the proper acidity and ionic strength. All the above products were reagent grade.

### *Procedure*

$Mn^{II}$ was estimated by EDTA titration with Erio T as indicator.[8] $Mn^{III}$ was estimated by thiosulphate titration of the iodine liberated after addition of excess KI. The method described by Wells and Davies[7] was also used

($Mn^{III}$ sampled into a solution of $Fe^{II}$ perchlorate with subsequent spectrophotometric determination at 260 nm, $\varepsilon_{Fe^{III}} = 2.88 \times 10^3$ l $mol^{-1}$ $cm^{-1}$) giving results in satisfactory agreement with thiosulphate method.

The rate of reaction was followed with a Durrum–Gibson stopped-flow spectrophotometer. $Mn^{III}$ was mixed in the apparatus with excess catechol in perchloric acid and the concentration of *o*-benzoquinone produced was monitored at 390 nm (wavelength of maximum absorption).

No interference from absorption due to $Mn^{III}$, $Mn^{II}$ and catechol has been found at this wavelength, at the concentrations investigated.

Reaction traces stored on the memorized screen of a 564 Tektronix oscilloscope, were photographed.

The reaction stoichiometry was determined with an Hitachi–Perkin Elmer EPS-3T spectrophotometer.

The acidity range investigated was 0.50–3.00*M* ($HClO_4$) and the kinetic runs were carried out with initial [$Mn^{III}$] in defect ($1.0 \times 10^{-4}$ *M*).

The experiments were carried out at 25.0, 18.0 and 12.0° C. All the solutions were brought to ionic strength I = 3.0 *M*.

## Results and Discussion

### *Mn*$^{III}$

This oxidation state of Mn is stable only when complexed by anions such as $SO_4^{2-}$, $F^-$, $PO_4^{3-}$ or in strongly acidic solutions, due to its ease to the following disproportionation equilibrium:[6]

$$2\,Mn^{III} \rightleftarrows Mn^{II} + Mn^{IV} \qquad (1)$$

with $K_{disp} = 10^{-3}$ mol $l^{-1}$.

$Mn^{3+}$ is also easily hydrolyzed giving, in this range of concentration, $MnOH^{2+}$ as the predominant hydroxo complex, according to:

$$Mn^{3+} + H_2O \rightleftarrows MnOH^{2+} + H^+ \qquad (2)$$

with[7] $K_h = 0.93 \pm 0.03$, $\Delta H = 4.8 \pm 0.8$ kcal $mol^{-1}$ at 25.0° C and I = 4.0 ($NaClO_4$) (these data have been assumed to hold in the present experimental conditions, disregarding the small difference in ionic strength).

$Mn^{III}$ was stabilized by adding a large excess (at least 100-fold) of $Mn^{II}$ with respect to $Mn^{III}$ so that equilibrium (1) could be regressed avoiding decomposition and $MnO_2$ precipitation. Moreover the acidity ([$HClO_4$]) was kept higher than 0.5*M*; this allowed to rule out the formation of hydroxo species higher than $MnOH^{2+}$.

$Mn^{III}$ was used as perchlorate so that the oxidizing species could be able to give inner-sphere substitution.

### *Stoichiometry*

A product spectrum obtained for reaction between $Mn^{III}$ and excess catechol, in aqueous perchloric acid, is identical to that of *o*-quinone under the same conditions, with a maximum absorption at 390 nm.[1]

In order to evaluate the reaction stoichiometry, known amounts of $Mn^{III}$ were mixed with a slight excess of catechol and the concentration of *o*-benzoquinone was determined spectrophotometrically ($\varepsilon_{390} = 1.46 \times 10^3$ l $mol^{-1}$ $cm^{-1}$).[1] In the investigated acidity range it was found that $\Delta[Mn^{III}]/\Delta[qno] = 1.98 \pm 0.03$. No interference was found by varying the concentration of excess catechol, $Mn^{II}$ present and perchloric acid, thus confirming that the overall reaction can be represented as:

$$2\,Mn^{III} + H_2cat \rightarrow 2\,Mn^{II} + qno + 2H^+ \qquad (3)$$

### *Kinetics of Reaction*

After mixing the reactants in the flow apparatus, a rise of optical density at 390 nm can be observed, the oscilloscopic trace appearing as a typical monotonic kinetic display, and the same is found over a wide spread of wavelengths, so that no spectroscopic evidence can be achieved for intermediate complex species formation. This is rather unexpected due to the fact that 1,4-dihydroxybenzene has been suggested to give *p*-benzoquinone through an inner mechanism with the formation of transient complexes;[9] consequently 1,2-dihydroxybenzene, having chelation capability, was expected to undergo oxidation through a similar mechanism.

The increase of optical density, when working with a constant excess of catechol, was always of the first order in $Mn^{III}$ concentration and typical first order plots are reported in Figure 1. In Table I the experimental conditions and the pseudo-first-order rate constants, $k_{obs}$, for the performed runs, have been collected.

Figure 2 shows, at some acidities, that the first order rate constant $k_{obs}$ is directly proportional to $[H_2cat]_{tot}$ so that it can be concluded that the redox reaction is also of the first order on the reagent in excess, and the

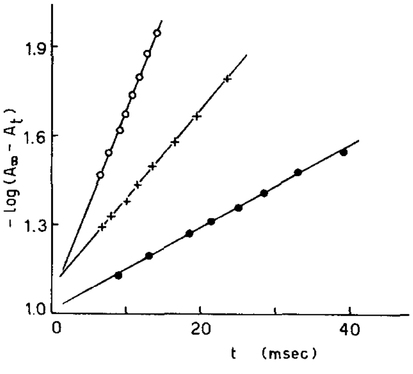

Figure1. First-order plots for the increase of optical density at [$HClO_4$] = 1.00*M*, I = 3.0*M* and 25.0° C, with initial [$Mn^{III}$] = $1.0 \times 10^{-4}$ and [$H_2cat$] as follows: ● $1.0 \times 10^{-3}$*M*, + $2.0 \times 10^{-3}$*M*, ○ $4.0 \times 10^{-3}$*M*.

TABLE I. Pseudo-first-order Rate Constants $k_{obs}$ ($sec^{-1}$) in Various Experimental Conditions; $[Mn^{III}] = 1.0 \times 10^{-4} M$, $[Mn^{II}] = 2.0 \times 10^{-2} M$, $I = 3.0M$ ($NaClO_4$).

| $10^3 \times [H_2cat]$ mol $l^{-1}$ | $[HClO_4]$, mol $l^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | 0.50 | 0.70 | 1.00 | 1.50 | 2.00 | 3.00 |
| | | | t = 25.0 °C | | | |
| 1.0 | 41 | 40 | 33 | 31 | 27 | 22 |
| 1.5 | 64 | 67 | 59 | 27 | 40 | 36 |
| 2.0 | 85 | 76 | 68 | 59 | 56 | 49 |
| 2.5 | 114 | | | | | |
| 3.0 | 130 | 127 | 111 | 98 | 88 | 72 |
| 4.0 | | 176 | 149 | 135 | 123 | 101 |
| 5.0 | | 200 | 199 | 162 | 150 | |
| | | | t = 18.0 °C | | | |
| 1.0 | | 24 | 22 | 19 | 16.5 | 15 |
| 1.5 | | 35 | 31 | 30 | 26 | 23 |
| 2.0 | | 49 | 42 | 38 | 33 | 31 |
| 3.0 | | 73 | 64 | 57 | 51 | 48 |
| 4.0 | | 97 | 85 | 75 | 66 | 60.5 |
| 5.0 | | 124 | 122 | 96 | 85 | 80 |
| | | | t = 12.0 °C | | | |
| 1.0 | | | 13 | 12 | 11 | 9.0 |
| 1.5 | | 25 | 21 | 19 | 16 | 14 |
| 2.0 | | 34 | 28 | 24 | 22 | 18.5 |
| 3.0 | | 51 | 43 | 38 | 33 | 28.5 |
| 4.0 | | 63 | 58 | 52 | 45 | 37 |
| 5.0 | | 78 | 71 | 65 | 59 | 52 |

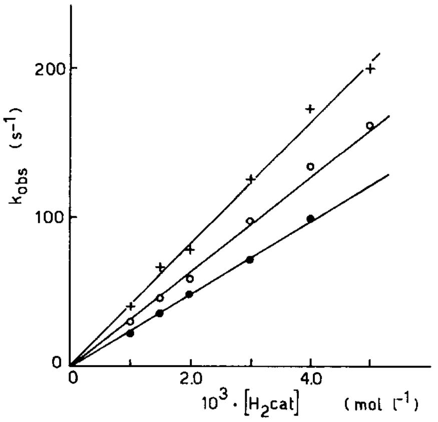

Figure 2. Dependence of $k_{obs}$ on $[H_2cat]$ at 25.0 °C and with $[HClO_4]$ as follows: + 0.7*M*, ○ 1.5*M*, ● 3.0*M*.

second order rate constants $k_0$, obtained at different perchloric acid concentrations and at 25.0 °C are collected in Table II. These values show that the overall reaction rate increases with decreasing acidity, so that deprotonation reactions should be involved in the reaction sequence, before the rate determining step. Moreover, from Table III it can be seen that no significant effect on rate has been observed when excess $[Mn^{II}]$ was varied; this last finding, together with the observed stoichiometry, points out that a back reaction is not involved.

TABLE II. Values of the Second Order Rate Constants $k_o$ at 25.0 °C and Various Acidities.

| $[HClO_4]$ mol $l^{-1}$ | $10^{-4} \times k_o$ l $mol^{-1}$ $s^{-1}$ | $10^{-4} \times k_o(1 + K_h[H^+]^{-1})$ l $mol^{-1}$ $s^{-1}$ |
|---|---|---|
| 0.50 | 4.3 | 12.4 |
| 0.70 | 4.1 | 9.6 |
| 1.00 | 3.6 | $6.9_5$ |
| 1.50 | 3.2 | 5.2 |
| 2.00 | 2.9 | 4.2 |
| 3.00 | $2.4_5$ | 3.2 |

TABLE III. Effect of $Mn^{II}$ on the Reaction Rate $k_{obs}$ ($s^{-1}$); $[Mn^{III}] = 1.0 \times 10^{-4} M$; $[HClO_4] = 1.00$ M.

| $10^3 \times [H_2cat]$ mol $l^{-1}$ | $[Mn^{II}]$ mol $l^{-1}$ | | | |
|---|---|---|---|---|
| | 0.020 | 0.15 | 0.30 | 0.90 |
| 1.0 | 33 | 33 | 36 | 35 |
| 3.0 | 111 | 115 | 116 | 110 |

In the light of these experimental observations, the following reaction scheme can be advanced:

$$\begin{tikzcd}
Mn_{aq}^{3+} + H_2cat_{aq} \arrow[r, shift left, "\beta_1"] \arrow[d, shift left, "H^+ (4)"] & (Mn^{III}\text{–}H_2cat)_{aq}^{3+} \arrow[l, shift left, "(5)"] \arrow[d, shift left, "H^+ (7)"] \\
MnOH_{aq}^{2+} + H_2cat_{aq} \arrow[r, shift left, "\beta_2"] \arrow[u, shift left, "K_h"] & (Mn^{III}\text{–}Hcat)_{aq}^{2+} \arrow[l, shift left, "(6)"] \arrow[u, shift left, "K_H"]
\end{tikzcd}$$

$$(Mn^{III}\text{–}H_2cat)_{aq}^{3+} \xrightarrow{k} Mn_{aq}^{II} + Hcat\cdot_{aq} + H_{aq}^{+} \quad (8)$$

$$(Mn^{III}\text{–}Hcat)_{aq}^{2+} \xrightarrow{k'} Mn_{aq}^{II} + Hcat\cdot_{aq} \quad (9)$$

$$Mn_{aq}^{III} + Hcat\cdot_{aq} \xrightarrow{fast} Mn_{aq}^{II} + qno_{aq} + H_{aq}^{+} \quad (10)$$

This reaction sequence takes into account the two species of $Mn^{III}$ existing in solution under the present experimental conditions, and the reaction progress brings to the intermediate formation of species such as $(Mn^{III}\text{–}H_2cat)^{3+}$ and $(Mn^{III}\text{–}Hcat)^{2+}$ (this last being deprotonated or in the co-ordination sphere of the metal or in an hydroxy group of the substrate). These intermediate species give then rise to the redox steps (8) and (9), through the activation complexes $[^{3+}]^{\neq}$ and $[^{2+}]^{\neq}$.

No hypothesis can be advanced whether reactions 5 and 6 give outer-sphere ion pairs or inner-sphere weak species, and these equilibria can be assumed in both cases much faster than the observed overall rates as can be inferred from literature data on inner substitution of $Mn^{III}$.[9,10] In these instances the two possible rate determining steps in the oxidation are reactions 8 and 9 and the resulting semiquinone[1,2,3] is subsequently oxidized to *o*-quinone by another $Mn^{III}$ ion through reaction 10 which is very fast being both species highly reactive.

Under the above assumptions and taking into account that protolytic reactions 4 and 7 are very fast, the following expression for the overall reaction rate can be obtained:

$$-\frac{d[Mn^{III}]_{tot}}{dt} = \frac{2(k + k'K_H h)\beta_1[Mn^{III}]_{tot}[H_2cat]}{1 + K_h h + \beta_1[H_2cat](1 + K_H h)} \quad (11)$$

where $h = [H^+]^{-1}$

This expression agrees with the observed first order dependence on both $[Mn^{III}]$ and $[H_2cat]$ if $\beta_1[H_2cat](1 + K_H h) \ll 1$, in agreement with the failure of intermediate complex formation evidence, that is a small value of $\beta_1$, so that the pseudo-first order rate constant can be written as:

$$k_{obs} = k_0[H_2cat] = \frac{2(k + k'K_H h)\beta_1[H_2cat]}{1 + K_h h} \quad (12)$$

Figure 3 shows that the plots of $k_0(1 + K_h h) = k_0'$ against h, at the temperatures investigated, are linear with significant intercepts so that both paths 5–8 and 6–9 are responsible for the reaction progress.

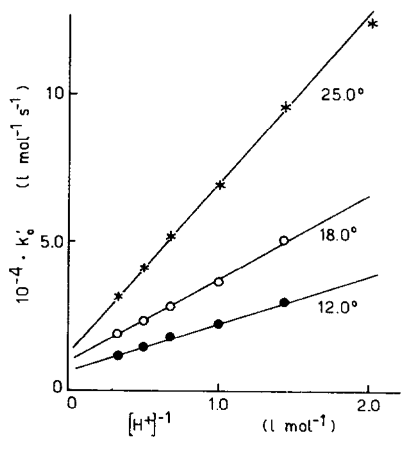

Figure 3. Plots of $k_0'$ as a function of $[H^+]^{-1}$, at different temperatures for $Mn^{III}$ oxidation of catechol.

Table IV collects the computed rate constants together with the activation parameters.

The reaction between $Mn^{III}$ and catechol has many features in common with systems previously studied. In particular it is worthy of comparison with the literature data on the behaviour of quinol with $Mn^{III}$.[9,11]

According to the first paper,[9] an increase in absorption at 470 nm takes place by mixing the reactants. This has been interpreted as a fast complex formation; then the absorbance decays with first order kinetics on both reactants. The hydrogen ion dependence (linear rate decrease with increasing acidity) was explained as indication that a complex between $MnOH^{2+}$ and quinol is the exclusive reactant ($k'K_H\beta_1 = 4.3 \times 10^4$ at 25.8 °C); no evidence has been found by the authors for an acid-independent path. In the second paper,[11] no evidence is given for intermediate complex formation so that the oxidation is, from the start, of simple second order, first order on both reactants. The acidity dependence indicates both $Mn^{3+}$ and $MnOH^{2+}$ to be effective oxidants with second order rate constants at 25 °C, $k = (4.8 \pm 1.2) \times 10^3$ for $Mn^{3+}$ and $k' = (3.28 \pm 0.43) \times 10^4$ l mol$^{-1}$s$^{-1}$ for $MnOH^{2+}$.

The general findings of the latter investigation and in particular the dependence on reagents concentration as well as on acidity recall the present results: also the data concerning k and k' can be compared; unfortunately no comparison can be made on the basis of activation parameters (Davies and Kustin studied $Mn^{III}$–quinol at 25 °C).

In many other instances ($H_2O_2$,[12] $HNO_2$,[12] hydroxylamine,[12] hydrazine,[12] $Fe^{II}$ [13]) the oxidation by $Mn^{III}$ takes place through a path independent and a path dependent on $[H^+]^{-1}$, the ratio between the rates of the two paths being $R = k/k' < 1$ (with the exception of $H_2O_2$), and this has been taken as an evidence[11] that in these reactions, the redox step does not take place through a simple electron transfer, but mainly through H atom transfers, thus differentiating $Mn^{3+}$ from $MnOH^{2+}$; and this can be the case of the present reaction (R = 0.22).

In all cases it seems impossible to distinguish between a mechanism involving proton release in the intermediate complexes formation and a mechanism involving $Mn^{3+}$ and $MnOH^{2+}$ in the rate determining step. In this last case $\beta_1$ and $\beta_2$ represent the outer-sphere ion

TABLE IV. Values of $k\beta_1$ (l mol$^{-1}$ s$^{-1}$), $k'K_H\beta_1$ (l mol$^{-1}$ s$^{-1}$), $\Delta H^{\ddagger}$ (kcal mol$^{-1}$), $\Delta S^{\ddagger}$ (e.u.) for the Reactions of $Mn^{III}$ with Catechol.

| | 25.0 °C | 18.0 °C | 12.0 °C | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ |
|---|---|---|---|---|---|
| $10^{-3} \times k\beta_1$ | 6.5 ± 0.6 | 4.7 ± 0.5 | 3.2 ± 0.4 | 10 ± 1 | −12 ± 3 |
| $10^{-4} \times k'K_H\beta_1$ | 2.9 ± 0.3 | 1.4 ± 0.2 | 0.9 ± 0.1 | 15 ± 1 | +10 ± 3 |

pair formation constants (~1 l $mol^{-1}$ at 25°C and I = 3.0*M*, as computed with Fuoss eq.[14]).

Additional kinetic data concerning the oxidation in the presence of an excess of $Mn^{III}$ could give valuable information on the reaction mechanism.[4] Unfortunately, in these conditions the absorbance of excess $Mn^{III}$ is too high as compared to that of quinone formed so that no reliable data on the progress of reaction can be obtained by spectrophotometric way.

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