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Mechanism of Oxidation of Catechols by Mn(III) in Aqueous Acidic Perchlorate Media

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Introduction

The chemistry of Mn^{III} has been the object of several investigations reviewed by Davies,[1] and recently the same author proposed a substitution controlled mechanism in redox reactions involving $MnOH^{2+}_{aq}$.[2] In connection with previous investigations of the Mn^{III}_{aq} oxidation of 1,2-benzenediol[3] and some catecholamines,[4] the kinetics of oxidation of 4-methyl-1,2-benzenediol (later referred to as I) and 4-t-butyl-1,2-benzenediol (II) have been carried out.

Experimental

Reagents

Mn^{III} was prepared by anodic oxidation of Mn^{II} perchlorate in perchloric acid.[1,3] Solutions of I and II were prepared daily. Perchloric acid and sodium perchlorate were used for bringing the solutions to the proper acidity and ionic strength ($\mu = 2.0$ *M*). Twice distilled water was used. All the above products were reagent grade.

Procedure

Mn^{III} and Mn^{II} were estimated as previously described.[3] The reaction rates were followed at the wavelength of maximum absorption of the corresponding *o*-benzoquinones with a Durrum–Gibson stopped-flow spectrophotometer. The observed rate constants were calculated by a weighted least squares method.[6] The acidity range investigated was 0.50 - 2.00 *M* ($HClO_4$) and the kinetic runs were carried out with Mn^{III} in defect (1×10^{-4} *M*) and $[H_2cat] = 5 - 30 \times 10^{-4}$ *M*. A large excess of Mn^{II} in respect to Mn^{III} (> 100-fold) was present in order to avoid the disproportionation of Mn^{III}. The experiments were carried out at 25.0 °C.

Results

Stoichiometry

The stoichiometric measurements were carried out by adding a solution of Mn^{III} to an excess of reductant (H_2cat) and estimating the oxidation products (qno) spectrophotometrically; for I, $\epsilon_{390} = 1.3 \times 10^3$ and for II, $\epsilon_{400} = 1.3 \times 10^3$ l mol^{-1} cm^{-1}. The concentration ranges used were $[Mn^{III}] = 2 - 4 \times 10^{-4}$ *M*, $[H_2cat] = 2 - 20 \times 10^{-4}$ *M* and $[HClO_4] = 0.50 - 2.00$ *M*. The measurements indicate that the overall reaction which occurs is

$$2\,Mn^{III} + H_2cat \rightarrow 2\,Mn^{II} + qno + 2\,H^+ \qquad (1)$$

Kinetics

The reaction rates were first order with respect to both reagents. The observed second order rate constants k_0 at different acidities are collected in Table I. According to the previous findings[3,4] the following formal scheme can be suggested

$$\begin{tikzcd}
Mn^{3+}_{aq} + H_2cat \arrow[r, shift left, "\beta_1"] \arrow[dd, shift right, "K_h"'] & (Mn^{III}\text{–}H_2cat)^{3+} \arrow[l, shift left] \arrow[dr, "k"] & \\
 & & Mn^{II} + Hcat\cdot \arrow[d, "Mn^{III}"', "fast"] \\
MnOH^{2+}_{aq} + H_2cat \arrow[r, shift left, "\beta_2"] \arrow[uu, shift right, "H^+"'] & (Mn^{III}\text{–}H_2cat)^{2+} \arrow[l, shift left] \arrow[ur, "k'"] & Mn^{II} + qno
\end{tikzcd}$$

where β_1 and β_2 represent the formation constants of the precursor complexes (if an outer-sphere mechanism is operating β represent the constants of the fast equilibria between the reactants and a solvent-separated precursor) and K_h is the hydrolysis equilibrium constant of Mn^{3+}_{aq} (the value adopted was 0.93 mol l^{-1} according to previous work;[3,4] recently Rosseinsky determined a value of 1.05 ± 0.26).[7]

The reaction proceeds through the activation complexes $[^{3+}]^{\neq}$ and $[^{2+}]^{\neq}$. If it is assumed that steps (a) and (b) are rate-determining and that metal-substrate complexes are present in negligible concentrations then

$$-\frac{d[Mn^{III}]_t}{dt} = \frac{2(k\beta_1 + k'K_h\beta_2[H^+]^{-1})[Mn^{III}]_t[H_2cat]}{1 + K_h[H^+]^{-1}}$$

$$= k_0[Mn^{III}]_t[H_2cat] \qquad (2)$$

Hence

$$k_0(1 + K_h[H^+]^{-1}) = 2k\beta_1 + 2k'K_h\beta_2[H^+]^{-1} \qquad (3)$$

TABLE I. Values of Second Order Rate Constants, $10^{-4}k_0$ ($l\ mol^{-1}\ s^{-1}$) for the Reactions of I and II with Mn^{III} at Different Acidities ($\mu = 2.0$ *M*, 25.0 °C).

Compound	$[HClO_4]$, *M*				
	0.50	0.70	1.00	1.40	2.00
I	3.3±0.3	3.1±0.3	2.9±0.2	2.8±0.2	2.5±0.2
II	2.8±0.2	2.5±0.2	2.4±0.2	2.2±0.2	$2.1 \pm 0.1_5$

TABLE II. Values of the Specific Rate Constants $k\beta_1$ and $k'\beta_2$ ($l\ mol^{-1}\ s^{-1}$) and Overall ΔG° ($kcal\ mol^{-1}$) of Reaction for the Oxidation of Catechols with Mn^{III} ($\mu = 2.0$ *M*, 25.0 °C).

	$10^{-3}k\beta_1$	$10^{-4}k'\beta_2$	$-\Delta G^\circ$	Ref.
Catechol[a]	6.5	3.2	35.3	3
Adrenaline[b]	2.7	2.0	34.3	4
L-Dopa[c]	3.7	1.8	34.9	4
I	10.5±1.0	2.0±0.2	37.9	This Work
II	8.3±0.8	$1.7 \pm 0.1_5$	37.1	This Work

[a] $\mu = 3.0$ *M*. [b] Extrapolated to 25.0 °C. [c] Extrapolated to 25.0 °C assuming the activation parameters of Adrenaline.

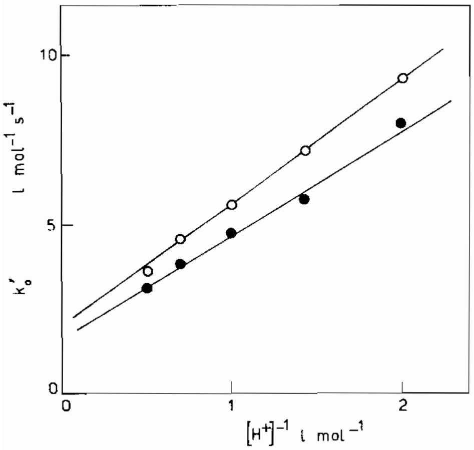

Fig. 1. Plots according to eq. (3) of $k_0(1 + K_h[H^+]^{-1})$ (*i.e.* k'_0) against $[H^+]^{-1}$, for the reaction of I (○) and II (●) with Mn^{III} (25.0 °C, $\mu = 2.0$ *M*).

Figure 1 shows the plots obtained according to eq (3), and Table II reports the rate constants $k\beta_1$ and $k'\beta_2$ for the investigated systems together with those for other catechols for comparison.

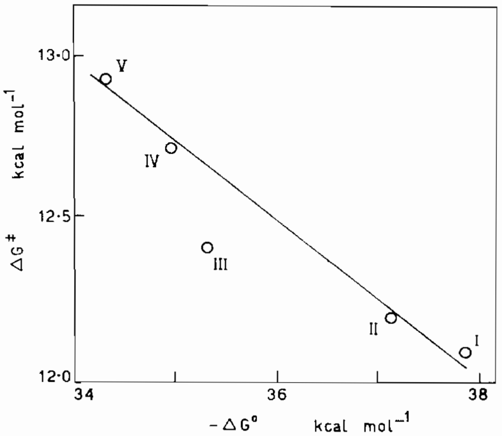

Fig. 2. Relation between $\Delta G^{\neq}$ of rate determining step and the overall standard free energy change (referred to eq. (1)) at 25.0 °C and $\mu = 2.0$ *M*: I, 4-methyl-1,2-benzenediol; II, 4-t-butyl-1,2-benzenediol; III, 1,2-benzenediol (at μ = 3.0 *M*); IV, L-Dopa; V, Adrenaline.

Discussion

The assignment of the mechanism in the redox reactions of metal ions has been the object of several investigations. A recent review by Bodek and Davies[5] summarizes the mechanistic features in such reactions. In the present case, the lability of the species Mn^{3+}_{aq} and $MnOH^{2+}_{aq}$ makes the assignment of the mechanism of reaction quite difficult.

Recently, a substitution-controlled mechanism has been advanced[2] for the reaction paths involving $MnOH^{2+}_{aq}$ by comparing the rate constants and the activation parameters assessed for the reaction of $MnOH^{2+}_{aq}$ with a series of thioureas[8] and a 1,2-benzenediol.[3] According to the data in Table II, the reaction rates of path (a) increase as the estimated overall free energy changes become more negative. A plot of $\Delta G^{\neq}$ *vs.* ΔG° (where ΔG° is the free energy involved in the stoichiometric eq. (1)) shows a good linearity with a slope of *ca.* 0.25 (see Figure 2), as predicted by the rearrangement of the Marcus cross relation for these reactions.[9,10] The slight deviation for catechol may be explained by taking into account the different ionic strength (in the similar reaction of catechol with Co^{III} an increase of ionic strength increases the reaction rate[9]).

The rate-determining step in the reaction with Mn^{3+}_{aq} appears to be electron transfer rather than complex formation; moreover, because similar free energy relationships have been found to operate in some inner-sphere mechanisms,[11] and the present reactions are slower than that of water exchange in Mn^{3+}_{aq} coordination shell,[1,12] no definite assignment to an outer-sphere mechanism can be made.

On the other hand, the specific rate constants for path (b) exhibit a narrow range of values (1.8 - 3.2×10^4 l mol^{-1} s^{-1}) and a substitution-controlled mechanism can be advanced for $MnOH^{2+}_{aq}$. As mentioned above, Davies suggested a similar mechanism by comparing the reactions with thioureas and 1,2-benzenediol. Besides, it is worth pointing out that the specific rate constants for 1,4-benzenediol (3.28×10^4 l mol^{-1} s^{-1})[13] and 4,4'-biphenyldiol (2.63×10^4 l mol^{-1} s^{-1})[14] are consistent with this suggestion, particularly when the differences in ionic strength are taken into account ($\mu = 3.9$ and 4.0 *M* for quinol and 4,4'-biphenyldiol respectively). $\Delta H^{\neq}_b$ and $\Delta S^{\neq}_b$ for the latter compound are also in agreement with the findings concerning the other reductants.

The formal similarity of the present findings with the behavior of Co^{III} in the oxidation of catechols should also be noted. The path involving Co^{3+}_{aq} has been found to show a dependence of $\Delta G^{\neq}$ on ΔG° similar to that assessed for Mn^{3+}_{aq}, while the rate constants for $CoOH^{2+}_{aq}$ are almost invariant for different organic substrates. In these latter reactions the rapidity of the reaction rates relative to that for water substitution suggests that both paths are outer-sphere; for $CoOH^{2+}_{aq}$ the independence of reaction rate on the nature of the substrates was attributed to a *limiting* outer-sphere mechanism.[5]

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References

1 G. Davies, *Coord. Chem. Rev., 4,* 199 (1969).
2 G. Davies, *Inorg. Chim. Acta,* in press.
3 E. Mentasti, E. Pelizzetti, E. Pramauro and G. Giraudi, *Inorg. Chim. Acta, 12,* 61 (1975).
4 E. Mentasti, E. Pelizzetti and E. Pramauro, *Gazzetta,* in press.
5 I. Bodek and G. Davies, *Coord. Chem. Rev., 14,* 269 (1974).
6 G. Giraudi, E. Mentasti and E. Pelizzetti, *Atti Accad. Sci. Torino, 108,* 825 (1974).
7 D. R. Rosseinsky, M. J. Nicol, K. Kite and R. J. Hill, *J. Chem. Soc. Faraday I,* 2232 (1974).
8 G. Davies, *Inorg. Chem., 11,* 2488 (1972).
9 R. A. Marcus, *J. Phys. Chem., 72,* 891 (1968) and references therein.
10 E. Pelizzetti, E. Mentasti and E. Pramauro, *J. Chem. Soc. Dalton,* in press.
11 J. E. Earley, *Prog. Inorg. Chem., 13,* 243 (1970).
12 A. McAuley and J. Hill, *Quart. Rev., 23,* 18 (1969).
13 G. Davies and K. Kustin, *Trans. Faraday Soc., 65,* 1630 (1969).
14 E. Pelizzetti, E. Mentasti and C. Baiocchi, *J. Inorg. Nucl. Chem.,* in press.