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Kinetics of the Oxidation of Quinol by Bis(2,2′-bipyridine)manganese(III) Ions in Aqueous Perchlorate Media

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Abstract

The kinetics of the oxidation of quinol by $Mn(bipy)_2{}^{3+}{}_{aq}$ ions have been investigated at 25 °C in aqueous perchlorate media using a high excess of H_2Q. The observed kinetic order in $[Mn(bipy)_2{}^{3+}]$ is unity and the linear plots of the reciprocal of the pseudo first order rate constant against $[H_2Q]^{-1}$ show that intermediate complexes are involved. From the manner in which the slopes of these latter plots vary with acidity, it is suggested that these reactive intermediate complexes are $Mn(bipy)_2HQ^{2+}{}_{aq}$ and $Mn(bipy)_2(OH)HQ^{+}{}_{aq}$. The mechanism of this reaction is compared with those suggested for the oxidation of quinol by aqua cations and by cations without a water molecule present in the inner sphere.

Introduction

Following our kinetic investigations of the oxidation of hydrogen peroxide [1], hydrazoic acid [2] and bromide ions [3] by bis(2,2′-bipyridine)manganese(III) ions in aqueous perchlorate media, we now report a kinetic investigation of the oxidation of quinol by this complex. Detailed kinetic studies have been made of the oxidation of quinol by aqua cations, such as $Fe^{III}{}_{aq}$ [4], $Mn^{III}{}_{aq}$ [5], $Ce^{IV}{}_{aq}$ [6], $V^{V}{}_{aq}$ [7], $Co^{III}{}_{aq}$ [8], $Tl^{III}{}_{aq}$ [9], $Np^{VI}{}_{aq}$ [10] and $Pu^{VI}{}_{aq}$ and $Pu^{IV}{}_{aq}$ [11], by cations complexed with other ligands, such as $Fe(phen)_3{}^{3+}$ [12], $[Ni^{III}\text{-cyclam}]^{3+}$ [13], $[Ni^{III}$bis(1,4,7-triazacyclonane)] [14] and $[Ni^{III}$tetraazamacrocycles] [15], and by anionic oxidants, such as $IrBr_6{}^{2-}$, $IrCl_6{}^{2-}$ and $[IrCl_5H_2O]^-$ [16], $Mo(CN)_8{}^{3-}$ and $Fe(CN)_6{}^{3-}$ [17] and 12-tungstocobaltate(III) [18]. In addition, the kinetics of the oxidation of quinol by an electrically neutral transition metal complex, $[IrCl_4(H_2O)_2$, have been investigated [16].

Experimental

Solutions of bis(2,2′-bipyridine)manganese(III) ions were prepared by the anodic oxidation of tris(2,2′-bipyridine)manganese(II) ions, as described previously [19]. Laboratory grade quinol was purified by sublimation under vacuum; all other materials were as described earlier [1–3].

Rates of decay of bis(2,2′-bipyridine)manganese(III) ions in the presence of quinol were followed at 490 nm using a Durrum-Gibson stopped flow spectrophotometer and reaction traces were photographed from the storage screen of a Telequipment DM 64 oscilloscope. Absorbances were measured using a Unicam SP 500 Series 2 spectrophotometer.

Results and Discussion

Stoichiometry

As quinol reacts with Fe^{III} ions [4], concentrations of $Mn(bipy)_2{}^{3+}$ were determined spectrophotometrically [19] at a wavelength where light absorbance from benzoquinone is not involved [4]. The reaction was investigated using an excess of $Mn(bipy)_2{}^{3+}$ over quinol H_2Q, estimating the concentration of the Mn^{III} complex before and after the oxidation using direct spectrophotometry at 490 nm with the extinction coefficient for the complex $\epsilon = 2.10 \times 10^2$ dm^3 mol^{-1} cm^{-1} [19]. Ionic strength was adjusted to 1.00 mol dm^{-3} by adding sodium perchlorate. Table 1 shows that the value for the consumption ratio $|\Delta[Mn^{III}]|/|\Delta[H_2Q]|$ is invariant with the concentration of perchloric acid, the mean value of this ratio in the range 0.4–1.00 mol dm^{-3} $HClO_4$ being 2.01 ± 0.04. We conclude that the stoichiometry is represented by eqn. (1) in agreement

$$2Mn^{III} + H_2Q \longrightarrow 2Mn^{II} + 2H^+ + \text{benzoquinone} \tag{1}$$

with the reactions of quinol with other oxidizing cations [5–18].

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TABLE 1. Consumption ratio for the oxidation of quinol by $Mn(bipy)_2{}^{3+}{}_{aq}$ at 20 ℃ and an ionic strength = 1.00 mol dm^{-3} with varying acidities and a constant total [bipy] = 1.13×10^{-3} mol dm^{-3}

$[H^+]$ (mol dm^{-3})	Initial $[Mn^{III}]$ (10^{-4} mol dm^{-3})	Initial $[H_2Q]$ (10^{-4} mol dm^{-3})	$\frac{\lvert\Delta[Mn^{III}]\rvert}{\lvert\Delta[H_2Q]\rvert}$
0.40	8.3	2.50	2.07
0.40	8.3	4.00	1.98
0.60	10.1	2.50	2.08
0.60	10.1	5.00	1.97
0.80	8.9	2.50	2.00
0.80	8.9	4.00	1.98
1.00	8.9	2.50	2.02
1.00	8.9	4.00	1.98

Kinetics at 25.4 ℃

Owing to the absorbance of light by benzoquinone at 400 nm, the wavelength used [1–3] in the investigations of the oxidations of other substrates by $Mn(bipy)_2{}^{3+}$, stopped-flow traces were measured at 490 nm. As the extinction coefficient for $Mn(bipy)_2{}^{3+}$ at 490 nm $\epsilon_{490} < \epsilon_{400}$, initial concentrations of $Mn(bipy)_2{}^{3+}$ were higher than those used in the investigations of the kinetics with other substrates. An initial $[Mn(bipy)_2{}^{3+}] \sim 6 \times 10^{-4}$ mol dm^{-3} was used and this resulted in the use of a more limited range of $[HClO_4]$ than before.

The decay of $Mn(bipy)_2{}^{3+}$ at $[HClO_4] = 0.40$ mol dm^{-3} with an ionic strength = 1.00 mol dm^{-3} adjusted by the addition of sodium perchlorate was first order for $[H_2Q] = 0.01$–0.10 mol dm^{-3}. A plot of the pseudo first order rate constant k_o against $[H_2Q]$ is a curve, but a plot of $k_o{}^{-1}$ against $[H_2Q]^{-1}$ is linear with an intercept on the $k_o{}^{-1}$ axis (Fig. 1). The values for k_o are collected in Table 2 and these show that k_o is unchanged when the sodium perchlorate used to adjust the ionic strength to 1.00 mol dm^{-3} is replaced by lithium perchlorate.

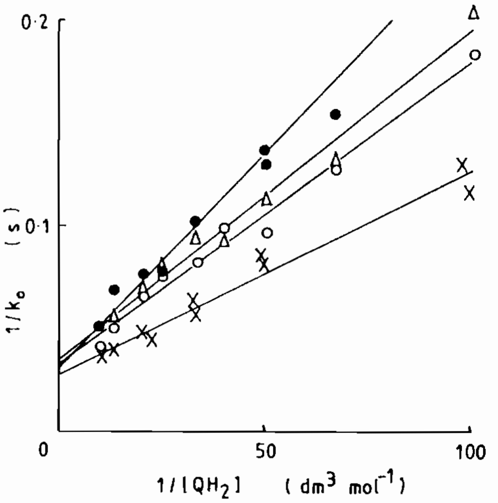

Fig. 1. Plots of $k_o{}^{-1}$ against $[H_2Q]^{-1}$ for the oxidation of quinol by $Mn(bipy)_2{}^{3+}{}_{aq}$ at an ionic strength = 1.00 mol dm^{-3} and at 25.4 ℃ with $[HClO_4]$ (mol dm^{-3}) varying as follows: ×, 0.40; ○, 0.60; △, 0.80; ●, 1.00.

Similar linear plots for $\log[Mn(bipy)_2{}^{3+}]$ against time were obtained at $[HClO_4] = 0.60, 0.80$ and 1.00 mol dm^{-3} and plots of $k_o{}^{-1}$ against $[H_2Q]^{-1}$ were linear for constant acidity (Fig. 1). All the values for k_o are given in Table 2. This Table shows that increasing the added concentration of 2,2′-bipyridine at 1.00 mol dm^{-3} $HClO_4$ has no effect on the rate constant.

Mechanism of the Oxidation

The linearity of the plots of $k_o{}^{-1}$ against $[H_2Q]^{-1}$ in Fig. 1 shows that intermediate complexes are involved in the oxidation. It is assumed that these involve only a ratio of $Mn^{III}:H_2Q = 1.0$ and the various possibilities for the pre-equilibria are given in eqns. (2)–(8).

$$Mn(bipy)_2{}^{3+}{}_{aq} \overset{K_h}{\rightleftharpoons} Mn(bipy)_2OH^{2+}{}_{aq} + H^+{}_{aq} \quad (2)$$

$$Mn(bipy)_2{}^{3+}{}_{aq} + H_2Q_{aq} \overset{\beta_1}{\rightleftharpoons} Mn(bipy)_2H_2Q^{3+}{}_{aq} \quad (3)$$

$$Mn(bipy)_2{}^{3+}H_2Q_{aq} \overset{K_1}{\rightleftharpoons} Mn(bipy)_2HQ^{2+}{}_{aq} + H^+{}_{aq} \quad (4)$$

$$Mn(bipy)_2\,HQ^{2+}{}_{aq} \overset{K_2}{\rightleftharpoons} Mn(bipy)_2(OH)HQ^+{}_{aq} + H^+{}_{aq} \quad (5)$$

$$Mn(bipy)_2OH^{2+}{}_{aq} + H_2Q_{aq} \overset{\beta'}{\rightleftharpoons} Mn(bipy)_2(OH)H_2Q^{2+}{}_{aq} \quad (6)$$

$$Mn(bipy)_2(OH)H_2Q_{aq} \overset{K_3}{\rightleftharpoons} Mn(bipy)_2(OH)HQ^+{}_{aq} + H^+{}_{aq} \quad (7)$$

$$Mn(bipy)_2OH^{2+}{}_{aq} + H_2Q_{aq} \overset{\beta''_1}{\rightleftharpoons} Mn(bipy)_2HQ^{2+}{}_{aq} \quad (8)$$

TABLE 2. Pseudo first order rate constants k_o for the oxidation of quinol by $Mn(bipy)_2{}^{3+}{}_{aq}$ with varying $[HClO_4]$ at 25.4 °C and an ionic strength = 1.00 mol dm^{-3} adjusted with additions of $NaClO_4$ and at a constant total [bipy] = 1.13 × 10^{-3} mol dm^{-3} for an initial $[Mn^{III}]$ ~ 6 × 10^{-4} mol dm^{-3}

$[H^+]$ (mol dm^{-3})	$[H_2Q]$ (10^{-2} mol dm^{-3})	k_o (s^{-1})
0.40	1.00	8.6
0.40	1.02	7.7[a]
0.40	2.00	12.4
0.40	2.04	11.6[a]
0.40	3.00	17.5
0.40	3.06	15.7[a]
0.40	4.00	22.2
0.40	4.90	20.8
0.40	7.4	25.6
0.40	9.8	27.8
0.40	9.91	28.0[a]
0.60	0.95	5.5
0.60	1.49	6.7
0.60	1.99	10.3
0.60	2.46	10.1
0.60	2.99	12.2
0.60	3.98	13.3
0.60	4.93	15.2
0.60	7.4	20.0
0.60	9.8	24.4
0.80	0.95	4.9
0.80	1.49	7.6
0.80	1.99	8.9
0.80	2.46	10.9
0.80	3.00	10.8
0.80	4.00	12.4
0.80	4.93	14.5
0.80	7.4	18.1
1.00	0.95	4.1
1.00	1.00	3.9
1.00	1.00	4.2[b]
1.00	1.49	6.5
1.00	2.00	7.8
1.00	2.00	7.3[b]
1.00	3.00	9.8
1.00	4.00	13.0
1.00	4.90	13.0[b]
1.00	7.4	14.5
1.00	9.8	19.6

[a] Ionic strength adjusted to 1.00 mol dm^{-3} with the addition of $LiClO_4$. [b] Total added [bipy] = 5.13 × 10^{-3} mol dm^{-3}.

Some of these combinations of pre-equilibria are mutually indistinguishable: (3) + (4) and (2) + (8); (3) + (4) + (5), (2) + (6) + (7) and (2) + (8) + (5). Possible rate determining redox steps are (9)–(12)

$$Mn(bipy)_2H_2Q^{3+}{}_{aq} \xrightarrow{k_1} Mn^{II}{}_{aq} + HQ\cdot_{aq} + H^+{}_{aq} + 2bipy_{aq} \qquad (9)$$

$$Mn(bipy)_2HQ^{2+}{}_{aq} \xrightarrow{k_2} Mn^{II}{}_{aq} + HQ\cdot_{aq} + 2bipy_{aq} \qquad (10)$$

$$Mn(bipy)_2(OH)H_2Q^{2+}{}_{aq} \xrightarrow{k_3} Mn^{II}{}_{aq} + HQ\cdot_{aq} + 2bipy_{aq} \qquad (11)$$

$$Mn(bipy)_2(OH)HQ^{+}{}_{aq} \xrightarrow{k_4} Mn^{II}{}_{aq} + HQ\cdot_{aq} + 2bipy_{aq} \qquad (12)$$

which, in turn, will be followed by the rapid conversion of the semiquinone HQ· to benzoquinone via (13) [4–18]

$$Mn^{III} + HQ\cdot \xrightarrow{\text{fast}} Mn^{II} + \text{benzoquinone} + H^+ \qquad (13)$$

As $K_h h^{-1} \gg 1$ ($h = [H^+]$) [19], the rate of decay of all species of $Mn(bipy)_2{}^{3+}$ will be given by (14)

$$-(d[Mn^{III}]_{total}/dt) = \{2(k_1\beta_1 + k_2\beta_1K_1h^{-1} + k_4\beta_1K_1K_2h^{-2})[Mn^{III}]_{total}[H_2Q]\}/\{K_hh^{-1} + \beta_1(1 + K_1h^{-1} + K_1K_2h^{-2})[H_2Q]\} \qquad (14)$$

bearing in mind the indistinguishable sets of pre-equilibria and that (11) is also indistinguishable kinetically from (10). The pseudo first order rate constant k_o is then given by (15) and the slopes S

$$\frac{1}{k_o} = \frac{K_hh}{2\beta_1(k_1h^2 + k_2K_1h + k_4K_1K_2)[H_2Q]} + \frac{h^2 + K_1h + K_1K_2}{2(k_1h^2 + k_2K_1h + k_4K_1K_2)} \qquad (15)$$

of the linear plots of k_o^{-1} versus $[H_2Q]^{-1}$ will be given by (16)

$$S^{-1} = \frac{2\beta_1(k_1h + k_2K_1 + k_4K_1K_2h^{-1})}{K_h} \qquad (16)$$

Values for the slopes of the lines in Fig. 1 are collected in Table 3 and Fig. 2 shows that S^{-1} against h^{-1} gives a linear plot with an intercept on the S^{-1} axis. For (16) to apply to this plot, $k_1h \ll (k_2K_1 + k_4K_1K_2h^{-1})$. This will give values of $k_2\beta_1K_1K_h{}^{-1} = 75 \pm 40$ s^{-1} and $k_4\beta_1K_1K_2K_h{}^{-1} = 170 \pm 30$ dm^3 mol^{-1} s^{-1} at 25.4 °C.

TABLE 3. Values of the slopes S with standard errors determined by the least-squares procedure of the plots of $k_o{}^{-1}$ vs. $[H_2Q]^{-1}$ for the oxidation of quinol by $Mn(bipy)_2{}^{3+}{}_{aq}$ at 25.4 °C with ionic strength = 1.00 mol dm^{-3}

$[H^+]$ (mol dm^{-3})	S (10^{-3} dm^{-3} mol s)
0.40	1.00 ± 0.06
0.60	1.48 ± 0.07
0.80	1.61 ± 0.10
1.00	2.11 ± 0.08

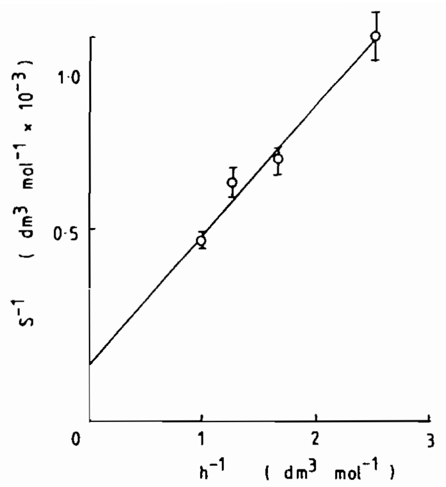

Fig. 2. Plot of the variation of the reciprocal of the slope (S) of the plots of k_o^{-1} against $[H_2Q]^{-1}$ with the reciprocal of the hydrogen ion concentration (h) for an ionic strength = 1.00 mol dm^{-3} and 25.4 °C.

Comparison with Other Oxidants

The linearity of the plots of k_o^{-1} versus $[H_2Q]^{-1}$ shows that at least one intermediate complex is involved in the oxidation by $Mn(bipy)_2{}^{3+}{}_{aq}$ and k_o is decreased by increasing acidity. This can be compared with the results for a series of aqua cations. No intermediate complexes were detected for $Fe^{III}{}_{aq}$ [4], $Np^{VI}{}_{aq}$ [10], $Pu^{VI}{}_{aq}$ [11], $Pu^{IV}{}_{aq}$ [11], $[IrCl_5H_2O]^-$ [16] and $[IrCl_4(H_2O)_2$ [16]; oscilloscope traces suggest that they may be involved with $Mn^{III}{}_{aq}$ [5] and $Co^{III}{}_{aq}$ [8] and the kinetics show that they are involved for $V^V{}_{aq}$ [7], $Ce^{IV}{}_{aq}$ [6] and $Tl^{III}{}_{aq}$ [9]. Where the effect of changes in the hydrogen ion concentration h on the rate constant has been investigated, a wide spectrum of effects is observed. The rate constant increases with decreasing h for $Fe^{III}{}_{aq}$ [4], $Mn^{III}{}_{aq}$ [5], $Tl^{III}{}_{aq}$ [9] and $Pu^{VI}{}_{aq}$ [11], increases with increasing h for $V^V{}_{aq}$ [7], is independent of h for $Ce^{IV}{}_{aq}$ [6], $Np^{VI}{}_{aq}$ [10] and $Pu^{IV}{}_{aq}$ [11] and varies differently with h for $Co^{III}{}_{aq}$ according to the conditions [8]. For ions possessing at least one water molecule in the first coordination sphere reacting with acidic substrates, ambiguities of interpretation of variations of rate with h exist: the h variation can be ascribed either to the hydrolysis of the metal ion or to the acid dissociation of the substrate, or to a combination of both. However, as the acid dissociation constant for $H_2Q \rightleftharpoons HQ^- + H^+$ is low ($K_a = 1.22 \times 10^{-10}$ at 28.2 °C) [4], the participation of the species HQ^- in high acidities has been questioned. Indeed, for the small retardations with increasing h observed with $[Ni^{III}(cyclam)]$ [13], [Nitetraazamacrocycles] [15] and $[Ni^{III}bis(1,4,7$-triazacyclononane] [14] as oxidants, the participation of the protonation equilibrium (17) is proposed.

$$H^+{}_{aq} + H_2Q_{aq} \overset{K_c}{\rightleftharpoons} H_3Q^+{}_{aq} \qquad (17)$$

Thus, with aqua cations as oxidants, a combination of equilibrium (17) for the substrate and the hydrolytic equilibrium of the cation would be invoked, similar to the situation found in the oxidation of alcohols by $Mn^{III}{}_{aq}$ [20] and $Co^{III}{}_{aq}$ [21]. However, against this proposed participation of equilibrium (17) in the oxidation of quinol is the unexpected absence of any variation of rate with h found with the oxidants $Fe(phen)_3{}^{3+}$ [12], 12-tungstocobaltate(III) [18] and $IrCl_6{}^{2-}$ [16] and the low value of $K_c \lesssim 0.01$ dm^3 mol^{-1} for quinol deduced [22] by comparison with the equilibrium measurements made on other organic hydroxy compounds: this experimental estimate for $K_c \lesssim 0.01$ dm^3 mol^{-1} has recently been confirmed [23] and contrasts with $K_c = 0.22$–0.24 dm^3 mol^{-1} calculated [13, 14] from the kinetic variations. However, as found in the present oxidation and in those involving similar acidic substrates, the presence of H_2Q in either an inner or outer sphere complex can increase K_a by stabilizing HQ^- in proximity to the cation, so that this anion can participate in the mechanism. Intermediate complexes were also detected in the oxidations of Br^- [3], H_2O_2 [1] and HN_3 [2] by $Mn(bipy)_2{}^{3+}{}_{aq}$, and in the last two cases [1, 2] the acid dissociation of the substrate ligand is facilitated by its juxtaposition with the Mn^{3+} ion. Moreover, in the oxidation of HN_3 by $Ni(bipy)_3{}^{3+}$, where the intermediate involvement of $N_3{}^-$ is shown by the kinetic dependence on h, K_a for HN_3 must be increased by its presence in an outer sphere complex with $Ni(bipy)_3{}^{3+}$ [24]; the involvement of outer sphere complexes with $Ni(bipy)_3{}^{3+}$ was established kinetically for the oxidation of chloride ions by $Ni(bipy)_3{}^{3+}$ [25]. Therefore, in the oxidations of H_2Q by cations M^{n+}, discussed above, an increase, a decrease or an independence of rate constant with h could result from the formation of intermediate complexes, inner or outer sphere, in which K_a for H_2Q in the complex is increased, with the individual dependency on h arising from the particular balance between the kinetic and thermodynamic stabilities of $M^{n+}H_2Q$ and $M^{n+}HQ^-$ with that cation M^{n+}.

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