Mechanistic Investigation of the Oxidation of Glyoxylic and Pyruvic Acids by Tris(biguanide)manganese(IV) in Weakly Acidic Aqueous Media

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In this study the kinetics of two electron transactions between the reducing substrates glyoxylic and pyruvic acids and the oxidising complex cation, tris(biguanide)manganese(IV) in aqueous acidic media have been examined. Under the experimental conditions (pH = 1.50–3.78) only the fully protonated form of the oxidant reacts with the anions of the substrates whereas the parent acids, viz. glyoxylic and pyruvic acids, were found to be unreactive. The second-order rate constants for the oxidations of glyoxylate and pyruvate by the title Mn^{IV} species are $(2.24 \pm 0.10) \times 10^{-1}$ and $(5.40 \pm 0.30) \times 10^{-2}$ $M^{-1}s^{-1}$, respectively, at 25.0 °C and at I = 1.0 M ($NaNO_3$ or $NaClO_4$). A rate-liming one-electron change between the redox partners seems justified.

Introduction

Tris(biguanide)manganese(IV) {Figure 1; $[Mn(LH_2)_3]^{4+}$ (LH_2 = biguanide, $C_2N_5H_7$)} is a rare example of a water-soluble mononuclear Mn^{IV} complex stable over a wide range of acidity levels (10^{-6} to 2 M).[1] In aqueous solutions the title Mn^{IV} complex behaves as a mild dibasic acid (pK_{a1} = 5.30 ± 0.20, pK_{a2} = 7.60 ± 0.30) and the deprotonations are believed to originate from the protons bound to the ligand sp^2 nitrogen atoms.[2] Though quite a few di-, tri- and tetranuclear Mn^{IV} complexes can be stabilised in aqueous solution[3] and have interesting solution chemistry,[4] the aqueous solution chemistry of mononuclear Mn^{IV} remained unexplored until recently when we reported[2] the oxidation of Fe^{2+} by Mn^{IV}. Parallel to our report, Gould et al.[5] observed that the oxidation of Fe^{2+} by this Mn^{IV} species is noticeably accelerated by chloride ions in what the authors viewed as the accelerating effect of the polarisable anion on the redox reaction between two positively charged metal centres.

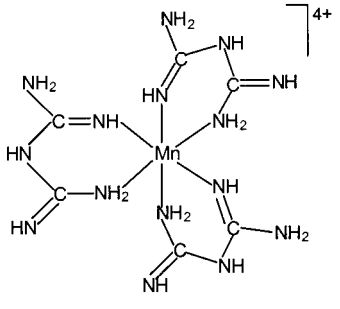

Figure 1. Structure of $[Mn(LH_2)_3]^{4+}$ drawn on the basis of its crystal structure

The present investigation deals with the kinetic and mechanistic aspects of the oxidation of two small carboxylic acids of biological relevance, viz. glyoxylic and pyruvic acid. Detailed kinetic studies of their oxidations are of importance because Mn^{III} species are involved in metabolic processes such as glycine catabolism[6a] and plant physiology,[6b] whereas the reducing substrate pyruvic acid is involved in a major metabolic sequence (TCA cycle) in living systems.[6c] Complete oxidation of these carboxylic acids with α-carbonyl groups ultimately leads to CO_2 with generation of energy in the metabolic processes. We also note that examples of oxidations of these substrates by higher valent oxidising species are only scarce in the literature.[7]

Results and Discussion

Equilibrium Studies and Preliminary Observations

Using a Metrohm 736 GP Titrino auto-titrator yielded pK_a values for glyoxylic and pyruvic acid from the pH-titration curves of 3.20 ± 0.10 and 2.50 ± 0.10, respectively, at 25.0 °C and at I = 1.0 M ($NaNO_3$ or $NaClO_4$). These values are in agreement with those previously reported.[7h,7i] Most of the kinetic runs were performed at 433 nm, i.e. the observed visible absorption maximum of the Mn^{IV} complex. At this wavelength, all other reaction components ex-

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cept Mn^{IV} are transparent. No additional buffer was used in the kinetic experiments since the pH drift was well within 0.05 units during the reaction. We observed no Mn^{2+} catalysis (studied up to 0.10 M) in the title reaction.

Stoichiometry and Reaction Products

Results of the stoichiometry experiments yielded $\Delta[Mn^{IV}]/\Delta[\text{Reductant}] = 0.98 \pm 0.10$ for glyoxylic oxidation and 1.07 ± 0.05 for pyruvic acid oxidation. The presence of the oxidation product formic acid in the oxidation of glyoxylic acid was tested for by the addition of chromotropic acid which gave a violet colour.[8] Acetic acid was detected in the pyruvate oxidation by the addition of lanthanum nitrate and iodine which produced a deep blue precipitate.[8] We verified that the reaction products, Mn^{2+} or the released biguanide did not interfere with these qualitative experiments. The generation of gaseous CO_2 in both the reactions was confirmed by GC analysis as described earlier.[9] The overall redox processes for glyoxylic acid and pyruvic acid are thus described by Equation (1) and (2), respectively.

$$Mn^{IV} + CHOCOOH + H_2O \rightarrow Mn^{2+} + HCO_2H + CO_2 + 2\,H^+ \quad (1)$$

$$Mn^{IV} + CH_3COCOOH + H_2O \rightarrow Mn^{2+} + CH_3CO_2H + CO_2 + 2\,H^+ \quad (2)$$

The small amounts of evolved gas in these reactions did not interfere with the kinetic measurements. Iodometric determination of copper in the cupric biguanide which precipitated[10] from the solution indicated release of more than 90% biguanide.

Kinetics

No immediate spectroscopic change was observed on mixing either glyoxylic or pyruvic acid with the Mn^{IV} complex over the entire range of experimental pH values examined (1.50−3.78). The whole reaction course follows first-order kinetics and the $\log(A_t - A_\infty)$ versus time plots were found to be linear to more than three half-lives. In all the kinetic runs, A_∞ values were less than 0.01. The first-order rate constants, k_o, as described by Equation (3), were obtained from least-squares slopes of these plots and are presented in Table 1. Moreover, a tenfold variation in the initial $[Mn^{IV}]$ value (0.02−0.20 mM) resulted in no change in the k_o values within experimental uncertainty (± 5%).

$$-d[Mn^{IV}]/dt = k_o[Mn^{IV}] \quad (3)$$

Table 1. Some representative first-order rate constants for oxidation of glyoxylic and pyruvic acid by $[Mn(LH_2)_3]^{4+}$ at $T = 25.0$ °C, $I = 1.0$ M ($NaNO_3$), $\lambda = 433$ nm [concentration of complex used 0.10 mM; the k_o values calculated using Equation (7a) are given in parentheses]

pH	RCOCOOH [M]	$10^4 k_o$ (R = H) [s^{-1}]	$10^4 k_o$ (R = CH_3) [s^{-1}]
1.46	0.02	0.8 (0.79)	0.8 (0.79)
1.70		1.4 (1.37)	1.4 (1.30)
1.96		2.4 (2.43)	2.2 (2.16)
2.20		4.1 (4.06)	3.3 (3.28)
2.37		5.8 (5.76)[a]	4.3 (4.23)[b]
2.80		13 (12.7)[c]	6.8 (6.85)[c]
3.03		18 (18.1)	8.0 (8.06)
3.02		18 (18.1)[d]	8.2 (8.05)[d]
3.25		23 (23.7)[e]	8.9 (8.96)[e]
3.50		30 (30.3)	9.6 (9.66)
3.78		35 (35.4)	10 (10.2)
2.37	0.01	2.8 (2.88)	2.1 (2.11)
	0.03	8.7 (8.64)	6.3 (6.34)
	0.05	15 (14.4)	11 (10.6)

[a] $10^4\,k_o$ (R = H) [s^{-1}] values are 8.3 and 11 at $I = 0.5$ and 0.2 M ($NaNO_3$), respectively. [b] $10^4\,k_o$ (R = CH_3) [s^{-1}] values are 6.5 and 8.2 at $I = 0.5$ and 0.2 M ($NaNO_3$), respectively. [c] $10^4\,k_o$ [s^{-1}] values are 16 and 8.8 for glyoxylic and pyruvic acid, respectively, at $I = 1.0$ M ($LiClO_4$). [d] Reactions carried out in the presence of externally added 1.00 m M biguanide. [e] $10^4\,k_o$ [s^{-1}] values are 23 and 9.0 for glyoxylic and pyruvic acid, respectively, at $I = 1.0$ M (NaCl).

For both the reducing agents, the k_o values were found to increase significantly with the pH of the reaction medium (Table 1). The title Mn^{IV} complex is a weak acid ($pK_{a1} = 5.30$) and thus its deprotonation may be disregarded, whereas the concentration of both the neutral and anionic forms of the reducing agents are substantial under the pH interval studied (1.46−3.78).

The observed rate constants depend remarkably on the ionic strength of the reaction medium maintained by $NaNO_3$ or $NaClO_4$ (Table 1). A considerable increase in the reaction rate over the entire pH range for both the reductants with a decrease in ionic strength indicates a reaction between oppositely charged ions. The rate constants were also found to increase substantially when $LiClO_4$ was used instead of Na^+ salts for maintaining the ionic strength of the reaction mixture. As the redox partners of the title reactions are oppositely charged, conventional metal ion catalysis can be ruled out.[11] We also verified that the reactions are not accelerated by addition of chloride. A possible reason for the rate enhancement in the presence of Li^+ may be explained by the very high approximate hydration number of Li^+ (25.3), as estimated by transference data,[12] compared with that of Na^+ (16.6). This results in a major lowering of the effective concentration of solvent water which in turn increases the activity of the redox partners.[7h]

Reactions studied in the presence of 6% (v/v) acrylonitrile showed slow polymerisation after consumption of ca. 40−50% of the initial Mn^{IV} amount. The $\log(A_t - A_\infty)$ versus time plots under these conditions showed a definite up-

ward curvature after ca. 50% completion of the reaction, probably due to heterogeneity in the reaction media. Polymerisation of acrylonitrile is more prominent in the case of glyoxylic acid than in that of pyruvic acid.

Scheme 1 provides a reasonable explanation for the kinetic observations considering the acid dissociation constants of the complex in aqueous solution (K_{a1} and K_{a2} are 5.01×10^{-6} and 2.50×10^{-8} M, respectively) and K_a values (i.e. the measured acid dissociation constants of glyoxylic and pyruvic acid under experimental condition, 6.31×10^{-4} M for glyoxylic and 3.16×10^{-3} M for pyruvic acid).

$$RCOCOOH \overset{K_a}{\rightleftharpoons} RCOCOO^- + H^+ \quad (4)$$

$$[Mn(LH_2)_3]^{4+} + RCOCOOH \xrightarrow{k_1} Products \quad (5)$$

$$[Mn(LH_2)_3]^{4+} + RCOCOO^- \xrightarrow{k_2} Products \quad (6)$$

(R = H for glyoxylic and CH_3 for pyruvic acid)

Scheme 1

Scheme 1 leads to the rate law of Equation (7), where $T_R = [RCOCOOH] + [RCOCOO^-]$.

$$k_o(K_a + [H^+])/T_R = k_1[H^+] + k_2K_a \quad (7)$$

The left-hand-side values of Equation (7) were found to be nearly a constant within allowable uncertainty in the entire pH range studied, both for glyoxylic [$(1.40 \pm 0.02) \times 10^{-4}$ s^{-1}] and pyruvic acid [$(1.60 \pm 0.06) \times 10^{-4}$ s^{-1}]. We thus found no contribution from k_1 for both the reducing agents to the overall rates. Equation (7) can thus be simplified to Equation (8).

$$T_R/k_o = 1/k_2 + [H^+]/(k_2K_a) \quad (8)$$

Plots of T_R/k_o versus $[H^+]$ yielded straight lines (Figure 2) with intercepts yielding k_2 values of $(2.24 \pm 0.10) \times 10^{-1}$ and $(5.40 \pm 0.30) \times 10^{-2}$ M^{-1}s^{-1} for glyoxylic and pyruvic acid, respectively. From the slopes, using such k_2 values, K_a values could be determined. These kinetically evaluated K_a values agree well (within 10%) with the literature values supporting the proposed reaction scheme.

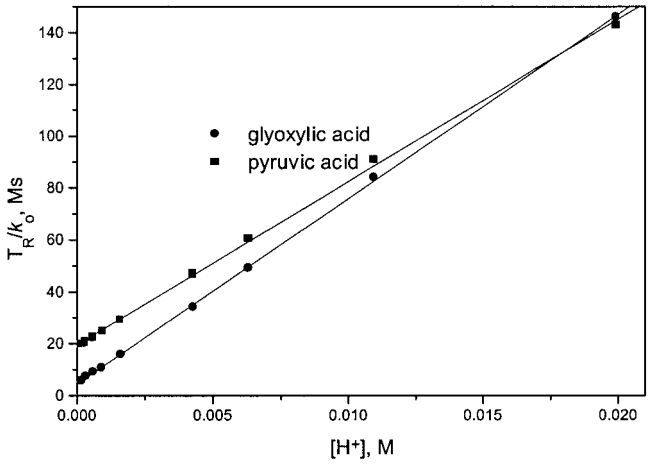

Figure 2. Plot of T_R/k_o versus $[H^+]$; [complex] = 0.10 mM, T_R = 0.02 M, I = 1.0 M ($NaNO_3$), T = 25.0 °C

Mechanism

The reducing anions glyoxylate and pyruvate have been found to be the only reactive species and this result supports the well-accepted concept that deprotonated reductants are more effective than their conjugate acids in reducing higher valent metal centres.[2,7h,9,13] However, we were astonished at the extent of this behaviour since we recently observed that both glyoxylic and pyruvic acids are reactive in reducing ethylenebis(biguanide)silver(III).[7h,7j] (One of the referees of this article commented that these reducing agents have inherent equilibria between the gem-diol and carbonyl forms in aqueous solution. Literature reports also support this.[7c] The reactivity of glyoxylate and pyruvate anions as found in this investigation is thus the combined reactivities of their gem-diol and carbonyl forms.)

The reduction of Mn^{IV} to Mn^{II} and the oxidation of the reductants chosen in this study are both net two-electron transactions. Nevertheless, it is extremely unlikely that the Mn^{IV} reduction proceeds in a single step. Moreover, polymerisation experiments also lend support to single-electron steps which generate polymerisation initiating radicals. Generation of these substrate radicals by one-electron oxidation has been well established by EPR spectroscopy.[14]

Pyruvate oxidation by the Mn^{IV} complex was found to be slower than glyoxylate oxidation. The increase in reaction rate may originate from the weaker C−C bond energy in glyoxylic acid compared with that in pyruvic acid due to the presence of an electron-donating methyl group in pyruvic acid which increases the electron density at the carbonyl carbon atom. The weakening of the C−C bond in glyoxylic acid may be a driving force for a faster initial electron transfer leading to a quicker overall oxidation of glyoxylic acid.[7g] A similar explanation was also offered for the oxidation of these reducing agents by Cr^{VI} [7g] and ethylenebis(biguanide)silver(III).[7h,7j] Moreover, the presence of a strongly reducing aldehyde function in glyoxylic acid may also be another explanation, at least in part, for obtaining a higher rate.

The Mn^{IV} centre in the title complex is coordinatively saturated and thus replacement of the strong field chelating biguanide ligand by the substrate anions seems to be unlikely. The estimated maximum value for the pre-equilibrium formation of a 1:1 adduct between Mn^{IV} and $RCOCOO^-$ (R = H for glyoxylate and CH_3 for pyruvate) lies between 1 and 10 and this does not confirm a strong inner-sphere attachment. However, we note that among the three s^2 metal-ion centres studied for the reduction of Mn^{IV}, only the reaction of In^I with $[Mn(LH_2)_3]^{4+}$ is subject to kinetic saturation for which an association constant of 6×10^3 M^{-1} for the formation of this adduct (believed to be due to strong hydrogen bonding) was estimated by Gould et al.[5] The estimated low value for the formation of adducts in the present study may be due to electrostriction[15] or a

process aided by hydrogen bonding[16] involving the reductants and the NH or NH_2 fragments of the ligand biguanide moiety of the title complex. The presence of a strong chelating ligand can be expected to stabilise Mn^{IV} to a great extent and render the complex a mild oxidant. Cyclic voltammetric studies of an aqueous solution (deoxygenated by purging with nitrogen) of the Mn^{IV} complex (0.10 mM) in the presence of 0.1 M Et_4NClO_4 as a supporting electrolyte revealed a single irreversible wave corresponding to Mn^{IV}/Mn^{III} reduction at ca. 0.4 V versus Ag/AgCl (ΔE_p = 400 ± 50 mV depending on scan rate, 50−300 mV s^{-1}). A direct outer-sphere oxidation by this weakly oxidising Mn^{IV} may thus be eliminated. We observed that more than 90% of the biguanide ligand is released at the end of the reaction (tested using an ammoniacal $CuSO_4$ solution)[10] and the high protonation constants of biguanide[17] encourages the overall reactions to completion.

Experimental Section

Materials: The complex salt $[Mn(C_2N_5H_7)_3]_2SO_4(NO_3)_6{\cdot}3H_2O$ was prepared by a known procedure. The crystals obtained were sufficiently pure as indicated by satisfactory C, H, N analyses: $C_{12}H_{48}Mn_2N_{36}O_{25}S$ (1238): calcd. C 11.63, H 3.88, N 40.71; found C 11.3, H 3.9, N 39.9. Biguanide sulfate $[C_2N_5H_7{\cdot}H_2SO_4]$ was prepared by a known method reported previously.[10b] An aqueous solution of glyoxylic acid was prepared by dissolving solid glyoxylic acid monohydrate (98%, Lancaster) in water and this was standardised either with standard alkali using Weslow's indicator or by spectrophotometry[18] at 520 nm (ε = 17990 $M^{-1}cm^{-1}$ as estimated by us, in agreement with the literature value of 17870 $M^{-1}cm^{-1}$)[18] after converting glyoxylic acid to 1,5-diphenylformazancarboxylic acid. Both results agree well with each other (within 4%). We found that an aqueous solution of ca. 0.5 M glyoxylic acid is stable for at least one weak when kept at low temperature (ca. 5−10 °C) and in the dark. Pyruvic acid (98%, Sigma) was used and standardised using spectrophotometry[19] at 515 nm (ε = 1400 $M^{-1}{\cdot}cm^{-1}$). An aqueous solution of $NaNO_3$ or $NaClO_4$ (G. R., E. Merck) was standardised by passing through a Dowex 50 W X-8 strong cation exchange resin in the H^+ from and titrating the liberated acid with standard NaOH to a phenolphthalein end point. All other chemicals were of reagent grade. Most of the kinetic measurements were carried out at I = 1.0 M ($NaNO_3$ or $NaClO_4$ resulted in almost the same k_o values). All solutions were prepared in water which had been deionised and doubly distilled.

Equilibrium Measurements: The acid dissociation constants, K_a, of both the glyoxylic[7h] and pyruvic acids were determined by titrating several aliquots of different strengths with carbonate-free deoxygenated NaOH solution at 1.0 M $NaNO_3$ using a Titrino Autotitrator (Metrohm, 736 GP) at (25.0 ± 0.1) °C.

Physical Measurements and Kinetics: All absorbance versus time data were recorded with a Shimadzu (1601 PC) spectrophotometer using 1.00-cm quartz cells. The kinetics were monitored in situ in the "kinetic mode" of the instrument at 433 nm which is one of the absorption peaks of the Mn^{IV} complex. An electrically controlled thermostat (25 ± 0.1) °C cell housing (CPS-240) was employed. For faster reactions, the reductant solution (adjusted to the desired pH) was injected directly into the spectrophotometer cell containing other components of the reaction mixture kept at the same pH. The desired concentrations of the complex and the reducing agent were achieved after mixing. The solution pH values were adjusted with HNO_3 or NaOH. Solution pH values ranged from 1.52 to 3.78 and were measured with an Ag/AgCl combined glass electrode attached to a Metrohm 736 GP Titrino autotitrator. The electrode calibration was carried out as reported previously.[20] Production of CO_2 as the gaseous reaction product was qualitatively confirmed by GC analysis. The gaseous product formed during the reaction was analysed by gas chromatography using a Chemito (India) GCHT 8610 instrument equipped with TCD (a Porapak Q and molecular sieves 13X column). A splitless mode of injection of 500 μL of the sample was used. The oven, injector, and detector temperatures were kept at 50, 100 and 150 °C, respectively. The carrier hydrogen gas flow was adjusted to 30 mL·min^{-1}. Cyclic voltammetric studies were performed with an Electrochemical Analyser (Model 600A, CH Instruments, USA) using a three-component electrode system consisting of Pt wire working and auxiliary electrodes and an Ag/AgCl reference electrode.

Stoichiometry and Reaction Products: The stoichiometries were evaluated by estimating unchanged glyoxylic or pyruvic acid spectrophotometrically. Reaction mixtures containing an excess of 4−6 equiv. of glyoxylic or pyruvic acid relative to the title complex were allowed to react under nitrogen until the solutions turned colourless. To estimate the unspent glyoxylic acid[18] freshly prepared phenylhydrazine hydrochloride (1%) solution was added (3.0 mL) into the reaction mixture. The resultant solution was incubated at ca. 110 °C for 10 min and then cooled to room temperature (ca. 25 °C) followed by successive addition of 2.5-mL aliquots of concentrated HCl and 1% $K_3Fe(CN)_6$. The reaction mixtures were allowed to stand for ca. 5 min for the quantitative formation of a pink formazan derivative of glyoxylic acid which was analysed at 520 nm (ε = 17990 $M^{-1}cm^{-1}$).[18] To estimate unchanged pyruvic acid[19] freshly prepared 2,4-dinitrophenylhydrazine solution in MeOH (1 mL, 1%) and 0.1 M HCl (1 mL) were added to the reaction mixture along with K-phosphate (K_2HPO_4) buffer (0.1 M) of pH = 7.5. The resultant solution was incubated at ca. 80 °C for 10 min and then cooled in an ice box for 10 min. A 50% KOH solution (5 mL) was then added to the solution which was again incubated at room temperature for 10 min. The red colour of the 2,4-dinitrophenylhydrazone pyruvate derivative was then analysed at 515 nm (1400 $M^{-1}{\cdot}cm^{-1}$).[19] The biguanide ligand in the product solution was isolated as $[Cu(LH_2)_2]SO_4$ by the addition of Cu^{II} sulfate. The amount of Cu^{II} thus consumed was determined iodometrically after decomposing the copper complex.[10]

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