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Kinetics of oxidation of pyruvic acid by [ethylenebis(biguanide)]silver(III) in aqueous acidic media

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Abstract

The oxidation of pyruvic acid by the title silver(III) complex in aqueous acidic (pH, 1.1–4.5) media is described. The reaction products are $MeCO_2H$ and CO_2, together with a colourless solution of the Ag^+ ion. The free ligand, ethylenebis(biguanide) is released in near-quantitative yield upon completion of the reduction. The parent complex, $[Ag(H_2L)]^{3+}$ and one of its conjugate bases, $[Ag(HL)]^{2+}$, participate in the reaction with both pyruvic acid (HPy) and the pyruvate anion (Py^-) as the reactive reducing species. Ag^+ was found to be catalytically inactive. At 25.0 °C, $I = 1.0$ mol dm^{-3}, rate constants for the reactions $[Ag(H_2L)]^{3+}$ + HPy (k_1), $[Ag(H_2L)]^{3+}$ + Py^- (k_2), $[Ag(HL)]^{2+}$ + HPy (k_3) and $[Ag(HL)]^{2+}$ + Py^- (k_4) are $k_1 = (94 \pm 6) \times 10^{-5}$ dm^3 mol^{-1} s^{-1}, $(k_2K_a + k_3K_{a1}) = (1.3 \pm 0.1) \times 10^{-5}$ s^{-1} and $k_4 = (58 \pm 4) \times 10^{-5}$ dm^3 mol^{-1} s^{-1}, respectively, where K_{a1} is the first acid dissociation constant of the $[Ag(H_2L)]^{3+}$ and K_a is for pyruvic acid. A comparison between the k_1 and k_4 values is indicative of the judgement that $k_2 \gg k_3$. A one-electron inner-sphere redox mechanism seems more justified than an outer-sphere electron-transfer between the redox partners.

Introduction

Solution studies of silver(III) have aroused a growing impact in recent years and genuine involvement of silver(III) in kinetics is now readily quite available [1–5]. This is true even in reactions where silver(III) entering the reaction mechanism through disproportionation of silver(II) [6, 7] to silver(III) and silver(I) although the disproportionation equilibrium lies far to the left [7–9]. Direct use of silver(III) complexes in kinetics involves silver(III) porphyrins [1], reactions of $Ag(OH)_4^-$ in alkaline media [2], reactions of periodato and tellurato complexes in alkaline media [3] and reactions of a notably stable ethylenebis(biguanide) complex of silver(III) occur in a wide acidity range [4, 5].

The mechanistic versatility of electron-transfer reactions in these complexes is intriguing. During recent years we have examined the redox kinetics of ethylenebis(biguanide)silver(III) ($[Ag(H_2L)]^{3+}$, Figure 1) in aqueous media over a wide acidity range. The title complex is a weak dibasic acid ($pKa_1 = 3.8 \pm 0.2$, $pKa_2 = 6.3 \pm 0.3$) and reactivity studies of the protolytic species of the title complex thus become possible. Also, it is noteworthy that, despite the mild oxidising nature [10] of the complexed silver(III), it oxidises a variety of substrates with widely differing acidities and redox potentials [4, 5]. Moreover, in some of its reactions, catalytic cycles involving $Ag^{I/II}$ [11] or $Ag^{I/0}$ [12, 13] were found to operate.

Recently, we found that the silver(III) complex oxidises pyruvic acid at a moderately fast rate. Pyruvic acid, one of the smallest biomolecules with the α-keto acid function, is of considerable interest as a reducing substrate as it involves in a major metabolic sequence (tricarboxylic acid cycle) in life systems, where in a series of reactions of the carbon atoms of pyruvic acid are oxidised one at a time to CO_2, with stepwise liberation of energy that is transferred to mechanical or chemical effectors by the generation of high energy phosphate bonds [14].

Mechanistic studies on pyruvate oxidation by higher-valent metals are not very common [15–19]. Silver(III) in the title complex is much stabilised by the acyclic tetraaza ligand and is inert to substitution (d^8). Yet, in some of its reactions it was proposed that the coordination by weakly acidic reducing agents to the axial (vacant) site of silver(III) precedes the electron-transfer and is a significant issue in its redox chemistry [5]. Though not strongly, there is sufficient evidence that pyruvic acid binds with metal ions [19, 20–22] leading to its deprotonation generating pyruvate anion [19]. Whether or not such a pre-equilibrium exists with the present silver(III) complex is of interest as X-ray photoelectron spectroscopic measurements clearly indicate the presence of a remarkable positive charge on the silver that makes the electron affinity of the silver(III) in the present complex quite high [23]. The title complex is a weak dibasic acid [24] and thus to uncover the reactivity of different protolytic species is also of significance. We, in this report, describe the kinetics

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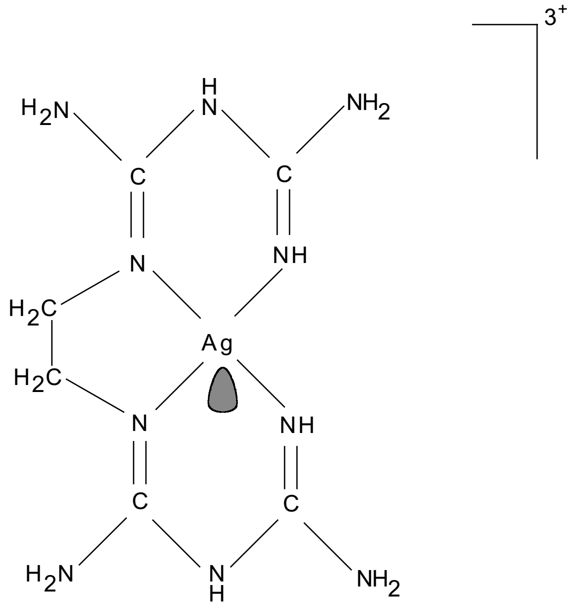

Fig. 1. Structure of [ethylenebis(biguanide)]silver(III) complex. ● represents axially bound anions.

and mechanism of pyruvate oxidation by the silver(III) complex under reference. We found kinetic evidence that the title complex oxidises glyoxylic acid by a two step one-electron transfer process [5], and thus we thought it worthwhile to oxidise pyruvic acid by the silver(III) complex to substantiate (or, compare) the mechanistic aspects of electron transfer as glyoxylic acid and pyruvic acid are in many ways kinetically comparable in their oxidations [15–17].

Experimental

Materials

The silver(III) complex, abbreviated $[Ag(H_2L)]^{3+}$ hereafter, was prepared according to a known procedure [25] with a slight modification in the crystallisation process [12]. Aqueous solutions of pyruvic acid were prepared from pyruvic acid (98%, Sigma) by dilution with water and standardised using a standard NaOH solution with phenolphthalein, or by converting pyruvic acid into its 2,4-dinitrophenylhydrazone derivative and measuring at 515 nm (reported [26] $\varepsilon = 1400$ dm^3 mol^{-1} cm^{-1}, found 1380 dm^3 mol^{-1} cm^{-1}). Both results agreed well (within 4%). We found that the pyruvic acid solutions (0.01–0.50 mol dm^{-3}) are stable for at least 1 week when kept at low temperature (*ca.* 5–10 °C) and in the dark. Aqueous solutions of $NaNO_3$ or $NaClO_4$ (both of E. Merck; G. R) were standardised by passage through a Dowex 50W X-8 strong cation exchange resin in the H^+ form and titrating the liberated acid with standard NaOH to a phenolphthalein end-point. All measurements were made at 25.0 °C and $I = 1.0$ mol dm^{-3} ($NaNO_3$ or $NaClO_4$). All solutions were prepared in water, which was deionised and then doubly distilled.

Physical measurements and kinetics

All absorbance *versus* time data were recorded on a Shimadzu (1601 PC) spectrophotometer using 1.00 cm quartz cells. The kinetics was monitored *in situ* in the 'kinetic mode' of the instrument at 420 nm in the electrically controlled thermostated (25.0 ± 0.1 °C) cell housing (CPS-240A). In this mode the change in absorbance is automatically and continuously recorded. In some runs pyruvic acid solutions (adjusted to the desired pH) were directly injected into the spectrophotometer cell containing other components of the reaction mixture, kept at the same pH, and immediate spectral changes, if any, were noted simultaneously. The desired concentration of the complex and reducing agent was achieved after mixing. The solution pH values were adjusted with HNO_3, $HClO_4$ or NaOH. Although the measured pH is usually defined in terms of the activity of hydrogen ions, we used the hydrogen ion concentration by calibrating the pH electrode with analytically prepared solutions as described earlier [27, 28]. Production of CO_2 as the gaseous reaction product was confirmed by g.c. analysis. The gaseous product formed during the reaction was collected over a saturated NaCl solution and analysed by gas chromatography as described earlier [29] using a Chemito (India) GCHT 8610 equipped with TCD, a Porapack Q and molecular sieve 13X column. A splitless mode injection of 500 μl of sample was used. The oven temperature, injector and detector temperature were kept at 50, 100 and 150 °C, respectively. The carrier hydrogen gas flow was adjusted to 30 cm^3 min^{-1}. The acid dissociation constant, K_a of the pyruvic acid was measured using a Titrino Autotitrator (Metrohm, 736 GP) at (25.0 ± 0.1) °C by titrating several aliquots with carbonate free deaerated NaOH solutions at 1.0 mol dm^{-3} $NaNO_3$.

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 a Ag/AgCl reference electrode. The potentials were referenced to a ferricyanide/ferrocyanide couple.

Stoichiometric measurements and product analysis

The stoichiometry of the reaction was determined under kinetic conditions by estimating the liberated CO_2 by g.c. analysis. Generation of acetic acid as another oxidation product of the title reaction was qualitatively assayed [30] by adding a drop each of 5% $La(NO_3)_3$, 0.01 (N) iodine solution and 1(N) ammonia to a drop of Ag^+ removed, (by adding an excess of NaCl and removing the AgCl) colourless reaction mixture (absorption < 0.01 at 420 nm). Appearance of a blue colour confirmed the presence of acetic acid in the product mixture. We verified that the released ligand, H_2L did not interfere in this detection. We also observed that more than 95% of the free ligand (H_2L) can be recovered at the end of the reaction. For this purpose concentrated (1.0–2.0 mmol dm^{-3}) solutions of the silver(III) complex were reacted with an excess of pyruvic acid. Immediately after completion of the reaction (absorbance < 0.01 at 420 nm), all Ag^{+} was precipitated as AgCl and removed by filtration. From the filtrate, the free ligand, ethylenebis(biguanide), was quantitatively isolated [31] as the sparingly soluble [ethylenebis(biguanide)]copper(II) sulfate, and the amount of copper (II) thus held was estimated iodometrically after decomposing the copper (II) complex.

Results and discussion

Preliminary observations

During the time-span of the reactions, the autodecomposition of the title silver(III) complex was insignificant (<5% of the first-order rate constants) and thus no correction for the autodecomposition was used in measuring the overall rates. Most of the kinetic runs were performed at 420 nm where other reaction components except Ag^{III} complex are transparent. No external buffer was used in kinetic measurements since buffering (by acetate, for example) affects the spectra of the complex, thus indicating a specific interaction of buffer with the complex. Even in the absence of an external buffer, the media pH before and after the reactions did not change by more than 0.10 units.

Equilibrium studies

Results of several determinations of pK_a of the pyruvic acid yielded a value 2.50 ± 0.10 at 25.0 °C and at $I = 1.0$ mol dm^{-3} (NaNO$_3$). We note here that although this value substantially differ from the reported [20] pK_a of 2.10 at 25.0 °C and at $I = 1.0$ mol dm^{-3} (NaCl), it is in agreement with the values [32] (25.0 °C) p$K_a = 2.55$ at $I = 0$ mol dm^{-3} and p$K_a = 2.45$ at $I = 2.0$ mol dm^{-3} maintained with NaClO$_4$. We, however, used the pK_a value 2.50 as measured by us for the computation of rate constants.

Stoichiometry and redox reaction

Stoichiometric determination and product analysis clearly indicate the occurrence of reaction (1) in the entire redox process:

$$\mathrm{Ag^{III} + MeCOCO_2H + H_2O \rightarrow Ag^{I} + MeCO_2H + CO_2 + 2H^{+}} \qquad (1)$$

Kinetics

No immediate spectral change was observed on mixing pyruvic acid with the silver(III) complex over the entire range of experimental pH and total pyruvic acid ([HPy]$_T$ = [HPy] + [Py$^-$]) concentration. However, the absorbance at $\lambda \geq 420$ nm gradually decreases to less than 0.01. We measured some k_0 values in the presence of added (1.0 mmol dm^{-3}) ethylenebis(biguanide) and found to be identical with its absence within experimental uncertainty, and we observed no effect of diffused light in our system. The log$_{10}$(absorbance) *versus* time plots at 420 nm were found to be linear for more than 85% completion of reactions, and the observed first-order rate constants, k_0, defined by Equation (2), were obtained from the least-squares slopes of these plots.

$$-\mathrm{d[Ag^{III}]}/\mathrm{d}t = k_0[\mathrm{Ag^{III}}] \qquad (2)$$

Any initial drop in absorbance for faster reactions can be computed from the time of mixing of reactants (~4 s) and the observed first-order rate constants. Averages of k_0 values from at least three runs were taken and individual runs were reproducible within 3%. Detailed data of the kinetics of the process were obtained as a function of pH and [HPy]$_T$ and some representative data are summarised in Table 1. Over the entire pH range studied, the reaction shows a clear first-order dependence in [HPy]$_T$ (Figure 2) and there is no [HPy]$_T$ independent term (*vide infra*, rate law). The following changes in the reaction conditions had, within the limits of experimental uncertainties, no influence on the values of k_0: a fivefold variation in [Ag^{III}] from 0.1 to 0.5 mmol dm^{-3}, occasional shaking of spectrophotometer cell, the presence or absence of dissolved oxygen and a variation in the monitoring wavelength in the 420–500 nm range.

The observed rate constants to some extent depend on the media ionic strength maintained by NaNO$_3$ or NaClO$_4$. Above pH > 2.5, the increase in k_0 with a decrease in ionic strength is substantial and indicates a reaction between oppositely charged ions, whereas at

Table 1. Some representative k_0 values for the oxidation of pyruvic acid by the silver(III) complex[a]

pH	[HPy]$_T$ (mol dm^{-3})	$10^5 k_0$ (s^{-1})
1.11	0.02	1.98
1.53		2.43
1.76		2.96
2.03		3.55
2.48		4.64
2.96		5.78
3.40		5.58
3.96		3.69[b]
4.52		2.40
1.10	0.04	3.71[c]
2.00	0.04	7.20
2.02	0.08	15.0
2.01	0.16	28.7
3.01	0.04	10.8
3.02	0.08	22.3
4.51	0.04	4.72

[a] [complex] = 0.20 mmol dm^{-3}, I = 1.0 mol dm^{-3} (NaNO$_3$), T = 25.0 °C.

[b] 10^5 k_0 = 4.90 s^{-1} at I = 0.1 (NaNO$_3$) mol dm^{-3}.

[c] 10^5 k_0 = 3.59 s^{-1} at I = 0.1 mol dm^{-3} (NaNO$_3$).

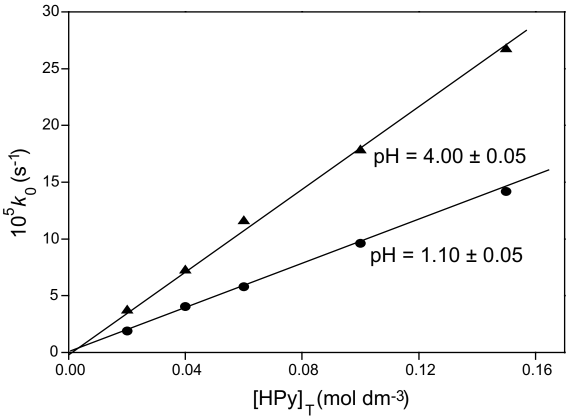

Fig. 2. Dependence of k_0 on $[\mathrm{HPy}]_\mathrm{T}$ at pH (1.10 ± 0.05) and at pH (4.00 ± 0.05).

pH ≤ 1.5, the reaction rate was found to be practically independent of the media ionic strength (Table 1) probably due to involvement of neutral pyruvic acid ($\mathrm{p}K_\mathrm{a} = 2.50$ as measured by us at 25.0 °C, $I = 1.0$ mol dm^{-3}) as the sole reducing agent.

Reactions carried out in the presence of 6% (v/v) acrylonitrile showed the formation of dense polymer – more prominent at the lower pH region. Formation of polymerisation initiating radicals, *viz.* HPy^{+} and $\mathrm{Py}^{\cdot}$, are thus indicated and possibly tells us that a one-electron transfer leads to the formation and quick decay of $\mathrm{Ag}^{\mathrm{II}}$.

A plot of k_0 *versus* pH is bell-shaped at a particular $[\mathrm{HPy}]_\mathrm{T}$ (Figure 3). Such a pH dependence indicates the involvement of two or more acid–base equilibria [33] in the title reaction. Considering the values for the acid dissociation constants of the $\mathrm{Ag}^{\mathrm{III}}$ complex in aqueous solution ($K_{\mathrm{a}1}$ and $K_{\mathrm{a}2}$, which are 1.58×10^{-4} and 5.01×10^{-7} mol dm^{-3}, respectively) [24] and K_a (= 3.16×10^{-3} mol dm^{-3}), the measured acid dissociation constant of pyruvic acid under experimental conditions, the Scheme 1 in Equations (3)–(8) provides a reasonable explanation for the kinetic observations.

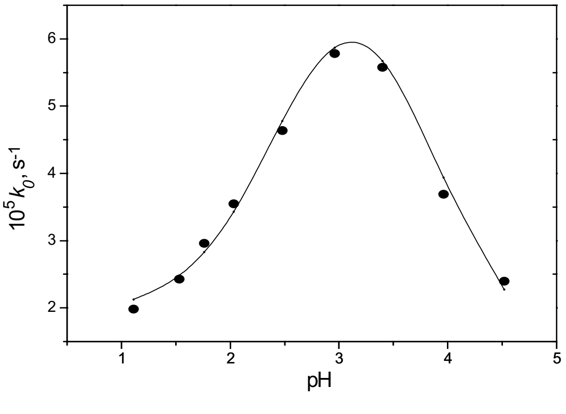

Fig. 3. Dependence of k_0 on pH at $T = 25.0$ °C, $[\mathrm{Ag(III)}]_\mathrm{T} = 0.2$ mmol dm^{-3}, $[\mathrm{HPy}]_\mathrm{T} = 0.02$ mol dm^{-3}, $I = 1.0$ mol dm^{-3} ($\mathrm{NaNO_3}$). The solid line represents the fit of Equation (9).

$$[\mathrm{Ag(H_2L)}]^{3+} \overset{K_{\mathrm{a}_1}}{\rightleftharpoons} [\mathrm{Ag(HL)}]^{2+} + \mathrm{H}^+ \tag{3}$$

$$\mathrm{HPy} \overset{K_\mathrm{a}}{\rightleftharpoons} \mathrm{H}^+ + \mathrm{Py}^- \tag{4}$$

$$[\mathrm{Ag(H_2L)}]^{3+} + \mathrm{HPy} \xrightarrow{k_1} \mathrm{Products} \tag{5}$$

$$[\mathrm{Ag(H_2L)}]^{3+} + \mathrm{Py}^- \xrightarrow{k_2} \mathrm{Products} \tag{6}$$

$$[\mathrm{Ag(HL)}]^{2+} + \mathrm{HPy} \xrightarrow{k_3} \mathrm{Products} \tag{7}$$

$$[\mathrm{Ag(HL)}]^{2+} + \mathrm{Py}^- \xrightarrow{k_4} \mathrm{Products} \tag{8}$$

Scheme 1.

In the above scheme for the overall reaction, we did not consider the second dissociation of the silver(III) complex, as under the pH interval chosen (1.1–4.5) for our study. The maximum achievable concentration of the species $[\mathrm{AgL}]^+$ is only *ca.* 1.3% of the total silver(III), and also with anticipation that the reactivity of the doubly deprotonated species $[\mathrm{AgL}]^+$ would be at best very small, smaller than $[\mathrm{Ag(HL)}]^{2+}$. A substantial lowering in reactivity of the deprotonated oxidants is well established for the title silver(III) complex [4, 5, 34, 35] and in general for many metal centre oxidants [36, 37] where such protonation equilibria are possible.

Scheme 1 leads to the rate law

$$k_0(K_{\mathrm{a}1} + [\mathrm{H}^+])(K_\mathrm{a} + [\mathrm{H}^+])/[\mathrm{HPy}]_\mathrm{T} = k_1[\mathrm{H}^+]^2 + (k_2K_\mathrm{a} + k_3K_{\mathrm{a}1})[\mathrm{H}^+] + k_4K_{\mathrm{a}1}K_\mathrm{a} \tag{9}$$

A plot of the left hand side of Equation (9) *versus* $[\mathrm{H}^+]$ yielded a good second-order polynomial fit in $[\mathrm{H}^+]$ ($r > 0.98$), whence k_1, $(k_2K_\mathrm{a} + k_3K_{\mathrm{a}1})$ and $k_4K_{\mathrm{a}1}K_\mathrm{a}$ were evaluated. These values thus found to be respectively $(94 \pm 6) \times 10^{-5}$ dm^3 mol^{-1} s^{-1} ($=k_1$), $(1.3 \pm 0.1) \times 10^{-5}$ s^{-1} [$=(k_2K_\mathrm{a} + k_3K_{\mathrm{a}1})$] and $(2.90 \pm 0.2) \times 10^{-10}$ dm^3 mol^{-1} s^{-1} ($=k_4K_{\mathrm{a}1}K_\mathrm{a}$). The constant coefficient $k_4K_{\mathrm{a}1}K_\mathrm{a}$ yielded k_4 equals to $(58 \pm 4) \times 10^{-5}$ dm^3 mol^{-1} s^{-1}. We are at a loss to directly determine the individual values of k_2 and k_3 as these paths are proton ambiguous to each other. The k_1 and k_4 values (Table 2) are similar – the decreased reactivity of the silver(III) species, $[\mathrm{Ag(HL)}]^{2+}$ in the k_4 path over $[\mathrm{Ag(H_2L)}]^{3+}$ in the k_1 path is found to be partly compensated by the increased reactivity of the deprotonated reductant, Py^- in the k_4 step; it substantiates a general view that deprotonated reductants react faster [38–40] in comparison with protonated reductants. Also, bearing in mind that the protonated oxidants react quicker, one can anticipate a much higher reactivity of $[\mathrm{Ag(H_2L)}]^{3+}$ towards Py^- (k_2 step) than $[\mathrm{Ag(HL)}]^{2+}$ with HPy (k_3 step). A probable guess that k_2 should be much higher than k_3 and in turn, k_3 should be lower than k_1 is thus justified. The coefficient of the first power of $[\mathrm{H}^+]$ as found by the polynomial fit of

Table 2. Ag^{III} oxidation of glyoxylic acid and pyruvic acid[a]

Reaction	10^4Rate constant ($dm^3\ mol^{-1}\ s^{-1}$)	Ref.
$[Ag(H_2L)]^{3+}$ + HGX[b]	7.34 ± 0.5	[5]
$[Ag(H_2L)]^{3+}$ + HPy	9.40 ± 0.6	This work
$[Ag(H_2L)]^{3+}$ + GX^{-b}	112 ± 7	[5]
$[Ag(H_2L)]^{3+}$ + Py^-	41 ± 1	This work
$[Ag(HL)]^{2+}$ + GX^{-b}	40.7 ± 3	[5]
$[Ag(HL)]^{2+}$ + Py^-	5.8 ± 0.4	This work

[a] [complex] = 0.20 mmol dm^{-3}, I = 1.0 mol dm^{-3} ($NaNO_3$), T = 25.0 °C.
[b] HGX = glyoxylic acid, GX^- = glyoxylate anion.

Equation (9) with $[H^+]$ is 1.3×10^{-5} $(k_2K_a + k_3K_{a1})$. With the anticipated order $k_2 \gg k_3$, $(k_2)_{max}$ will be *ca.* 4.1×10^{-3} $dm^3\ mol^{-1}\ s^{-1}$ if k_3 is assumed to be very small or nearly non-contributing (practically zero) to the overall rate. It could well be anticipated that in the range $k_1 - k_4$, k_3 would be the lowest as this path describes a redox process between the highest degree of both the deprotonated oxidant and protonated reductant. Moreover, as the acid dissociation constants of $[Ag(H_2L)]^{3+}$ and HPy are quite distant, simultaneous generation of appreciable concentrations of $[Ag(HL)]^{2+}$ and Hpy are at best very poor. We thus, assume, $k_2 \geq 10k_3$ and to numerically resolve the k_2 and k_3 from their composite in Equation (9), we started the iteration with the initialisation $k_2 = 10k_3$ and $k_3 = 5 \times 10^{-4}$ $dm^3\ mol^{-1}\ s^{-1}$ (*ca.* half of k_1) and by fixing k_1 and k_4 to their values as found directly by the second-order polynomial fit [Equation (9)]. At the end of each iteration, the k_0 values are recalculated and compared with their observed magnitudes until the agreement is acceptably good (within 5%). The k_2 found in this way is $(4.10 \pm 0.01) \times 10^{-3}$ $dm^3\ mol^{-1}\ s^{-1}$ and there becomes no lower limit for k_3 with a justification that $k_4 > k_3$ and $k_1 > k_3$.

Mechanism

The observed order for the rate constants: $k_2 > k_4$ and $k_2 > k_1$, clearly demonstrates the increased reactivity of protonated oxidants [34–37] and deprotonated reductants [38–40] over their conjugate bases and acids. This trend is normally followed in a majority of known redox reactions that are mechanistically well studied [34–40]. The trend was earlier observed for the oxidation of quite a few reducing agents with the title silver(III) complex [4, 5, 34, 35]. Only in the redox couple having anionic oxidants, where pyruvic acid was found to be more reactive than its anion, may possibly be due to a repulsive charge effect [18].

The title silver(III) complex is a weak oxidant, its one-electron potential ($[Ag(H_2L)]^{3+}/[Ag(H_2L)]^{2+}$) is 0.43 V *versus* NHE [10(b), 41]. A survey of the literature reveals no redox as well as self-exchange rate data for the one-electron oxidation of pyruvic acid or pyruvate anion. Cyclic voltammetric studies of pyruvic acid (1.0 mmol dm^{-3}) at pH ~ 0.7 in a N_2 atmosphere and in the presence of 1.0 mol dm^{-3} $NaNO_3$ serving as supporting electrolyte reveals a single quasi-reversible wave[1] [42] corresponding to oxidation at −0.32 V *versus* Ag/AgCl with $\Delta E_P = (130 \pm 20)$ mV at a scan rate of 100 mV s^{-1}. One may estimate the self-exchange rate for Hpy/HPy^+ using −0.10 V as its one-electron potential (corrected for NHE) and the known self-exchange rate for $[Ag(H_2L)]^{3+}/[Ag(H_2L)]^{2+}$ ($10^{6.6}$ $dm^3\ mol^{-1}\ s^{-1}$) [43] by the simplified Marcus cross relation, $k_{12} = (k_{11}k_{22}K_{12})^{1/2}$ [44] where k_{12} is taken as 94×10^{-5} $dm^3\ mol^{-1}\ s^{-1}$. The estimated self-exchange rate thus obtained is found to be very low, around 10^{-18} $dm^3\ mol^{-1}\ s^{-1}$, indicating for pyruvic acid perhaps a very poor outer-sphere reducing agent. However, one cannot conclusively eliminate the possibility of a one-electron outer-sphere oxidation of pyruvic acid by the silver(III) complex, despite the record low self exchange rate for HPy/HPy^+ thus estimated.

The electron affinity of the metal centre, silver(III) in the present complex is high as estimated by X-ray photoelectron spectroscopic measurements that the silver(III) centre has a high degree of positive charge [23] and it is also known from structural [45–47] and kinetic studies [5, 48] that the complex undergoes axial co-ordination with alcohols, H_2O_2, $SO_4{}^{2-}$, $NO_3{}^-$, or even $ClO_4{}^-$. An anticipated co-ordination of pyruvic acid or pyruvate anion to silver(III) and subsequent electron transfer is thus possible. An inner-sphere binding of pyruvic acid with trivalent [19, 21] as well as with divalent [20, 22] metal centres is well documented in the literature, with formation constants lying in the range 10^1–10^2. The linear dependence of k_0 on $[Hpy]_T$ requires a maximum value around 1 for any possible preequilibrium adduct formation between $[Ag(H_2L)]^{3+}$ and Hpy as estimated from rate data at the lowest experimental pH. Initial decarboxylation of pyruvic acid generating acetaldehyde, which on subsequent oxidation forms acetic acid, seems unlikely here because it is known that acetaldehyde on oxidation by metal ions in mineral acid produces both formic and acetic acids [49, 50] and also the fact that the title silver(III) complex reacts only very slowly with acetaldehyde in concentrations comparable to that of the silver(III) complex.

Conclusions

Reductions of the complex cation $[Ag(H_2L)]^{3+}$ may proceed *via* an uncatalysed path or a Ag^+-catalysed path, or both, depending on the nature of the reducing agent. Grossly speaking, predominance of the uncatalysed or catalysed path depends on a critical balance between thermodynamic and/or kinetic factors but when the reductant is powerful like HCO_2H [13], $N_2H_5{}^+$ [12]

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[1] A reversible electron-transfer is characterised by a separation of cathodic and anodic CV peak potentials by 57/*n* mV or slightly higher, quasi-reversibility is characterised by cathodic and anodic peak potentials separated by substantially higher than 57/*n* mV, *n* = number of electrons.

or H_3PO_2 [14] or a good ligand for silver(III), the catalysed path dominates. We observed that within the experimental pH range, pyruvic acid does not react with Ag^+ over a long period and no Ag^+ catalysis was observed in the title reaction. In an attempt to estimate the redox potential of pyruvic acid by CV, it results in a quasi-reversible one-electron oxidation at −0.10 V *versus* NHE. Using the Marcus relation with the known one-electron self-exchange and redox potential of the title silver(III) complex, an approximate value for the self-exchange rate of HPy/HPy^+ was estimated to be very low, of the order of 10^{-18} dm^3 mol^{-1} s^{-1}. However, the so far known structural and kinetic features of the silver(III) complex along with the potential ligating character of pyruvic acid towards metal ions provokes one to tilt towards an inner-sphere nature for the electron transfer. Following the observation on the polymerisation experiment, an initial one-electron redox is associated with a moderately high equilibrium constant (as estimated by the HPy/HPy^+ and $[Ag(H_2L)]^{3+}/[Ag(H_2L)]^{2+}$ potential) and the very high protonation constants of the ligand [52] H_2L drag the overall reaction to completion in acidic media. An initial one-electron transfer from azide to the silver(III) complex [4], instead requires a very high thermodynamic price that was proposed to compensated by inner-sphere attachment of N_3^- to the silver(III) centre leading to one-electron rate limiting transfer and the very high values for the protonation constants of the released ligand, H_2L. We noted that the pyruvate oxidation is slower than the glyoxylate oxidation by the silver(III) complex (Table 2), the increase in reaction rate may originate from the weaker C—C bond energy in glyoxylic acid than in pyruvic acid due to the presence of an electron-donating methyl group in pyruvic acid that increases the electron density at the carbonyl carbon. The weakening of the C—C bond energy in glyoxylic acid compared to pyruvic acid may be a driving force for a faster initial act of electron transfer leading to a quicker overall oxidation of glyoxylic acid. Moreover, the presence of a strongly reducing aldehyde function in glyoxylic acid may also be another answer, at least in part, for obtaining a higher rate. Glyoxylic acid is also found to reduce tris(biguanide)manganese(IV) quicker than pyruvic acid. A mechanistic study of the reaction is in progress.

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