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

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## Abstract

The complex cation, [ethylenebis(biguanide)]silver(III),  $[Ag(H_2L)]^{3+}$ , and its conjugate bases,  $[Ag(HL)]^{2+}$  and  $[AgL]^+$  oxidise glyoxylic acid, CHOCO<sub>2</sub>H quantitatively to formic acid and carbon dioxide, themselves being reduced to  $Ag^+$ . Free ethylenebis(biguanide) was recovered in near-quantitative yield. In the investigated pH range (1.00-7.00), the reaction is first order in both [complex] and total glyoxylate,  $[HGX]_T$ . The reaction proceeds through four parallel paths:  $[Ag(H_2L)]^{3+} - HGX(k_1), [Ag(H_2L)]^{3+} - GX^-(k_2), [Ag(HL)]^{2+} - GX^-(k_3), and [AgL]^+ - GX^-(k_4)$ . The respective rate constants (in  $10^4 \text{ M}^{-1} \text{ s}^{-1}$ ) are, respectively, 7.34, 112, 40.7 and 19.2 at 25.0 °C and I = 1.0 M (NaNO<sub>3</sub>). Formation of adducts by the reducing species with the metal complex via hydrogen-bonding or electrostriction may be proposed for the low-energy pathway for electron-transfer. A substantial rate retardation in presence of the radical scavenger acrylonitrile suggests successive one-electron changes,  $Ag^{III} \rightarrow Ag^{I} \rightarrow Ag^{I}$ . © 2003 Elsevier Ltd. All rights reserved.

Keywords: Kinetics; Mechanism; Redox; Silver; Glyoxylic acid

# 1. Introduction

The trivalent silver species [ethylenebis(biguanide)]silver(III) (Fig. 1) is an authentic cationic complex of silver [1–3] stable in aqueous solution over a wide pH range against dechelation and intramolecular redox decomposition [4]. Stabilisation of the silver(III) center by the square-planar acyclic tetraaza ligand is so extensive  $(\log K = 52)$  [5] that the title complex behaves as a milder oxidant [6], more so than  $Ag^+$  [7]. The complex is freely soluble in aqueous media below pH ca. 4.5 but  $\sim 0.2$  mM complex can be made soluble up to pH at least 7.0 if alkali is added carefully with stirring to avoid local excesses. Moreover, the silver(III) retains its identity in strongly acidic and in strongly alkaline media, a property unknown in other higher valent silver complexes. In aqueous solutions the complex behaves as a mild dibasic acid ( $pK_{a1} = 3.8$ ,  $pK_{a2} = 6.3$ ) originating from ligandbased protic equilibria [8] and thus the reactivity studies

of different silver(III) species connected through protic equilibria is possible because, in spite of the remarkable thermodynamic stability, the silver(III) complex oxidises [9-20] various organic and inorganic species with a variety of electron transfer pathways – inner sphere for weakly reducing ligands [10,11,13,14,19,20], outer sphere for weakly basic but strongly reducing ligands [15,17] and even by Ag<sup>+</sup> catalysis [9,10,13].

We report herein the kinetics of oxidation of glyoxylic acid and its conjugate base by the title silver(III) complex. Detailed kinetic studies of the oxidation of glyoxylic acid, one of the smallest carboxylic acids, is of importance as in metabolic processes such as glycine catabolism [21] and in plant physiology [22], higher valent metal ions like manganese(III) complexes play an essential role. Glycine oxidation to CO<sub>2</sub> may occur via glyoxylic acid arising from oxidative deamination of glycine by the enzyme glycine oxidase [23]. The silver(III) species,  $[Ag(OH)_4]^-$  oxidises glycine [24] in strongly alkaline media to NH<sub>3</sub>, HCHO and CO<sub>2</sub>.  $[AuCl_4]^-$  also oxidises glycine [25] to NH<sub>3</sub>, HCO<sub>2</sub>H and CO<sub>2</sub> in weakly acidic media via the intermediate formation of glyoxylic acid. We observed that the title

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Fig. 1. Structure of [ethylenebis(biguanide)]silver(III) complex.

silver(III) complex reacts very slowly with glycine although it reacts with glyoxylic acid at a moderately fast rate. Under these perspectives it is important to understand the chemistry of Ag(III) – biomolecule interactions. Moreover, the ligand  $H_2L$  in  $[Ag(H_2L)]^{3+}$  is substitution inert so that  $Ag^{III}$  never is released in solution to open extra, complicating pathways in its reduction.

## 2. Experimental

#### 2.1. Materials

The silver(III) complex, abbreviated as  $[Ag(H_2L)]^{3+}$ hereafter, was prepared according to the known procedure [2,3] with a slight modification in the crystallisation process [9]. Aqueous solution of glyoxylic acid were prepared by dissolving solid glyoxylic acid monohydrate (98%, Lancaster) in water and standardised either by standard alkali using Weslow's indicator or spectrophotometrically [26] at 520 nm ( $\varepsilon = 17990 \text{ M}^{-1} \text{ cm}^{-1}$  as estimated by us, in agreement with the literature [26] value 17 870 M<sup>-1</sup> cm<sup>-1</sup>) after converting glyoxylic acid to 1,5-diphenylformazancarboxylic acid. Both the results agreed well (within 4%). We found that an aqueous solution of  $\sim 0.5$  M glyoxylic acid is stable for at least one week when kept at low temperature ( $\sim$ 5–10 °C) and in the dark. Aqueous solutions of NaNO<sub>3</sub> or NaClO<sub>4</sub> (both of G.R., E. Merk) were standardised by passing through a Dowex 50W X-8 strong cation exchange resin in the  $H^+$  from 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 M (NaNO<sub>3</sub> or NaClO<sub>4</sub>). All solutions were prepared in water, which was deionised and then doubly distilled.

## 2.2. Physical measurements and kinetics

The acid dissociation constant,  $K_a$  of the glyoxylic acid was determined by titrating several aliquots of different strengths with carbonate free deaerated NaOH

solution at 1.0 M NaNO<sub>3</sub> using a Titrino Autotitrator (Metrohm, 736 GP) at  $(25 \pm 0.1)$  °C. Production of CO<sub>2</sub> as the gaseous reaction product was qualitatively confirmed by GC analysis. The gaseous product formed during the reaction was collected over a saturated sodium chloride solution and analysed by gas chromatography as described earlier [27] using a Chemito (India) GCHT 8610 equipped with TCD, a Porapack Q and molecular sieve 13X column. Splitless mode injection of 500  $\mu$ L of sample was used. The oven temperature, injector and detector temperature were kept at 40, 55, and 100 °C, respectively. The carrier hydrogen gas flow was adjusted to 30 ml min<sup>-1</sup>. All absorbance versus time data were recorded with 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 ( $25.0 \pm 0.1$  °C) cell housing (CPS-240A). In this mode the change in absorbance is automatically and continuously recorded. For faster reactions glyoxylic acid solution (adjusted to desired pH) was directly injected into the spectrophotometer cell containing other components of the reaction mixture kept at the same pH. The desired concentration of the complex and reducing agent was achieved after mixing. The solution pH values were adjusted with HClO<sub>4</sub> 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 [28].

# 2.3. Stoichiometric measurements

The stoichiometry was measured both under kinetic and reverse condition by estimating glyoxylic acid spectrophotometrically and estimating unreacted Ag<sup>III</sup> in condition when initial [Ag<sup>III</sup>] is in excess over total glyoxylic acid,  $[HGX]_T$  (defined as  $[HGX] + [GX^-]$ ). Excess glyoxylic acid was mixed with the Ag<sup>III</sup> complex in the pH range 3.0-5.0. After the reaction mixture turned colourless indicating complete reduction of Ag(III) to Ag(I), excess NaCl was added to remove AgCl. Freshly prepared phenylhydrazine hydrochloride (1%) was added (3.0 ml) into each mixture. The resulting solutions were incubated at ~110 °C for 10 min and then cooled to room temperature ( $\sim 25$  °C) followed by successive addition of 2.5 ml each of concentrated HCl and 1% K<sub>3</sub>Fe(CN)<sub>6</sub>. The mixtures were allowed to stand for  $\sim 5$  min for the quantitative formation of pink coloured formazan derivative of glyoxylic acid [26] that was measured at 520 nm.

Reaction mixtures containing excess  $Ag^{III}$  over glyoxylic acid were used to measure the unreacted [ $Ag^{III}$ ]. After completion of reactions (as indicated by no further change in absorbance), measured volumes of dilute HNO<sub>3</sub> were added to reach a final pH within 1.0–2.0

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Table 1 Stochiometric results for the oxidation of glyoxylic acid (HGX) by the silver(III) complex at I = 1.0 M (NaNO<sub>3</sub>) and T = 25 °C

[Ag(III)] <sub>T</sub> (mM)	[HGX] <sub>T</sub> (mM)	pН	[HGX] <sub>left</sub> (mM)	[Ag(III)] <sub>left</sub> (mM)	$\Delta[HGX]_T/\Delta[Ag(III)]_T$
0.15	0.30	3.1	0.16		0.94
	0.40	4.2	0.24		1.07
	0.60	4.9	0.47		0.87
0.20	0.80	5.3	0.61		0.95
	1.00	4.6	0.79		1.05
0.30	1.00	4.4	0.71		0.97
	1.20	3.9	0.88		1.07
0.45	0.30	3.5		0.13	0.94
1.00	0.50	3.7		0.46	0.93
					$Average = 0.98 \pm 0.10$

and the remaining  $[Ag^{III}]$  was estimated at 380 nm ( $\varepsilon = 1175 \text{ M}^{-1} \text{ cm}^{-1}$ ) [8]. Both experiments, whether in kinetic or in reverse condition resulted a 1:1 stoichiometry between the redox partners (Table 1).

## 2.4. Product analysis

Generation of formic acid as one of the oxidation products of the title reaction was tested by the addition of chromotropic acid [29] in the product mixture after removing  $Ag^+$  as AgCl. Formation of  $CO_2$  as the gaseous product was qualitatively confirmed by GC analvsis. We also observed that at the end of the reaction, more than 90% of the free ligand (H<sub>2</sub>L) can be recovered. For this purpose concentrated (1.0-2.0 mM) solutions of the Ag<sup>III</sup> complex were reacted with stoichiometric excess glyoxylic acid. Immediately after completion of reaction (absorbance <0.01 at 420 nm), all Ag<sup>+</sup> was precipitated as AgCl and removed by filtration. From the filtrate, the free ligand, ethylenebis(biguanide) was quantitatively isolated [30] as the sparingly soluble [ethylenebis(biguanide)]copper(II) sulfate, and the amount of Cu(II) thus held was estimated iodometrically after decomposing the Cu(II) complex.

## 3. Results and discussion

#### 3.1. Equilibrium studies and preliminary observations

The  $pK_a$  of the glyoxylic acid was found to be  $3.20 \pm 0.10$  at 25.0 °C and at I = 1.0 M (NaNO<sub>3</sub>). Though this value to some extent differs from the reported [31] value (2.91) under similar condition of temperature and ionic strength, we used the value 3.20 for  $pK_a$  for the calculation of rate constants. Most of the kinetic runs were performed at 420 nm where all other reaction components except Ag<sup>III</sup> are transparent. Within the time span of the reactions, autodecomposion of the silver(III) complex was insignificant at the ex-

perimental temperature. No external buffer was used in kinetic measurements since buffering (by acetate, for example) affects the spectra of the complex; specific interaction of buffer with the complex was thus indicated. 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.

# 3.2. Stoichiometry and the redox reaction

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

$$Ag^{III} + CHOCO_2H + H_2O$$
  

$$\rightarrow Ag^I + HCO_2H + CO_2 + 2H^+$$
(1)

# 3.3. Kinetics

No immediate spectrophotometric change was observed on mixing glyoxylic acid with the silver(III) complex over the entire range of experimental pH and total glyoxylate ([HGX]<sub>T</sub>). However, the absorbance at  $\lambda \ge 420$  nm gradually decreases to less than 0.01. We measured some  $k_0$  values in the presence of added (1.0 mM) ethylenebis(biguanide) and found to be identical with experiments in its absence within reasonable uncertainties, and we observed no effect of diffused light in our system. The log<sub>10</sub> (absorbance) versus time plots were found to be linear for more than 90% completion of reactions and the pseudo-first-order rate constants,  $k_0$ , defined by Eq. (2) were obtained from the leastsquares slopes of these plots

$$-d[Ag(III)]/dt = k_0[Ag(III)].$$
<sup>(2)</sup>

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 [HGX]<sub>T</sub> and some representative data are summarised in Table 2. Over the entire pH range studied the reaction shows a clear firstorder dependence on [HGX]<sub>T</sub> and there is no [HGX]<sub>T</sub> independent term. 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 mM, occasional shaking of spectrophotometer cell, presence or absence of dissolved oxygen and a variation in the monitoring wavelength in the range 420–500 nm.

The observed rate constants remarkably depend on the media ionic strength maintained by NaNO<sub>3</sub> or Na-ClO<sub>4</sub> (Table 2). A considerable increase in reaction rate at pH > 3.0 with decrease in the ionic strength indicates reaction between oppositely charged ions. <sup>1</sup> However at pH  $\leq 2.0$  the reaction rate was found to be practically independent on the media ionic strength probably due to involvement of neutral species glyoxylic acid as the sole reducing component.

Reactions studied in the presence of 6% (v/v) acrylonitrile showed slow polymerisation after ca. 60%consumption of initial Ag<sup>III</sup>. The log<sub>10</sub> (absorbance) versus time plots in this condition showed a definite upward curvature after ca. 50% completion of reactions probably due to heterogeneity in the reaction media. However, the first-order rate constants computed from the initial linear portions of these curves clearly demonstrate much slower reactions in presence of radical scavengers like acrylonitrile.

A plot of  $k_0$  versus pH has a bell shape (Fig. 2) at a particular [HGX]<sub>T</sub>. Such a pH dependence indicates the involvement of two or more acid–base equilibria [32]. Considering the values for the acid dissociation

#### Table 2

Some representative first-order rate constants for oxidation of glyoxylic acid by the silver(III) complex<sup>a</sup>

pН	[HGX] <sub>T</sub> (M)	$10^4 k_0 \ (\mathrm{s}^{-1})$
1.00	0.10	$0.80\pm0.02$
1.40		$0.96\pm0.03$
2.00		$1.40\pm0.03$
2.26		$1.77\pm0.06$
2.50		$2.20\pm0.05$
2.85		$3.71\pm0.06$
3.00		$4.40\pm0.09$
3.50		$6.09^{\mathrm{b}}\pm0.08$
4.00		$6.00\pm0.08$
4.35		$5.30\pm0.09$
4.50		$4.90\pm0.10$
5.01		$4.20\pm0.11$
5.62		$3.72\pm0.10$
6.00		$3.34\pm0.06$
6.30		$3.00\pm0.06$
6.51		$2.80\pm0.07$
6.77		$2.46\pm0.07$
7.00		$2.30\pm0.07$
2.02	0.20	$2.67\pm0.08$
2.01	0.40	$5.70\pm0.12$
2.03	0.80	$11.0 \pm 0.22$
3.55	0.20	$13.0\pm0.27$
3.52	0.40	$25.2\pm0.35$
6.00	0.20	$6.55\pm0.12$
5.98	0.40	$13.4\pm0.20$

<sup>a</sup> T = 25.0 °C, I = 1.0 M (NaNO<sub>3</sub>), [complex] = 0.15 mM.

<sup>b</sup> 10<sup>4</sup>  $k_0$  (s<sup>-1</sup>) values are 9.25, 14.0 and 19.0 at I = 0.5, 0.2 and 0.1 M (NaNO<sub>3</sub>), respectively.



Fig. 2. Dependence of  $k_0$  on pH at T = 25.0 °C,  $[Ag(III)]_T = 0.15$  mM,  $[HGX]_T = 0.10$  M, I = 1.0 M (NaNO<sub>3</sub>). The solid line represents the fit of Eq. (10).

constants of the complex in aqueous solution [8]  $(K_{a1} \text{ and } K_{a2}, \text{ which are } 1.58 \times 10^{-4} \text{ and } 5.01 \times 10^{-7} \text{ M},$  respectively) and  $K_a$  (=6.31 × 10<sup>-4</sup> M), the measured acid dissociation constant of glyoxylic acid under experimental conditions, Scheme 1 in Eqs. (3)–(9) provides a reasonable explanation for the kinetic observations.

<sup>&</sup>lt;sup>1</sup> One of the referees suggested that the rate constants might have been changed if LiClO<sub>4</sub> is used instead of Na<sup>+</sup> salts for maintaining the ionic strength of the reaction medium. We performed several experiments in presence of varying amount of  $LiClO_4$  keeping I = 1.0 M. The first-order rate constants thus obtained were found to be substantially higher (15-25%, depending on pH of reaction) than those measured using NaNO3 or NaClO4. The redox partners of the title reaction are oppositely charged and thus conventional metal ion catalysis (M. Gupta, S.K. Saha, P. Banerjee, J. Chem. Soc., Perkin Trans. II (1988) 1781) can be ruled out. A possible reason for the rate enhancement in presence of Li<sup>+</sup> ion may be explained by very high approximate hydration number as estimated by transference data (F.A. Cotton, G. Wilkinson, C.A. Murillo and M. Bochmann, Advanced Inorganic Chemistry (Ch. 3), 6th ed., Wiley, New York, 1999, p. 102) of Li<sup>+</sup> (25.3) than Na<sup>+</sup> (16.6) that results in a major lowering of the effective concentration of solvent water which in turn increases the activity of the redox partners. A similar situation has also been verified with the oxidation of azide by the title silver(III) complex. We also note that the effect of LiClO<sub>4</sub> for the rate enhancement is marginal when the reactive form of the reducing agent is uncharged. We will explore in future the finer details of these effects.

$$\left[\operatorname{Ag}(\operatorname{H}_{2}\operatorname{L})\right]^{3+} \stackrel{\kappa_{a1}}{\rightleftharpoons} \left[\operatorname{Ag}(\operatorname{HL})\right]^{2+} + \operatorname{H}^{+}$$
(3)

$$\left[\operatorname{Ag}([\operatorname{HL})\right]^{2+} \stackrel{\kappa_{a2}}{\rightleftharpoons} \left[\operatorname{AgL}\right]^{+} + \operatorname{H}^{+}$$
(4)

$$\mathrm{HGX} \stackrel{\mathrm{A}_{a}}{\rightleftharpoons} \mathrm{H}^{+} + \mathrm{GX}^{-} \tag{5}$$

 $\left[\operatorname{Ag}(\operatorname{H}_{2}\operatorname{L})\right]^{3+} + \operatorname{HGX} \xrightarrow{k_{1}} \operatorname{Products}$ (6)

 $\left[Ag(H_2L)\right]^{3+} + GX^{-\frac{k_2}{2}} Products$ (7)

 $\left[\operatorname{Ag}(\operatorname{HL})\right]^{2+} + \operatorname{GX}^{-\frac{k_3}{\rightarrow}}\operatorname{Products}$ (8)

$$[AgL]^{+} + GX^{-} \xrightarrow{k_{4}} Products \tag{9}$$

Scheme 1 leads to the rate law

$$k_{0}[\mathrm{H}^{+}]^{3}/([\mathrm{HGX}]_{T}\alpha_{1}\alpha_{2})$$
  
=  $k_{1}[\mathrm{H}^{+}]^{3} + k_{2}K_{a}[\mathrm{H}^{+}]^{2} + k_{3}K_{a1}K_{a}[\mathrm{H}^{+}] + k_{4}K_{a1}K_{a2}K_{a},$   
(10)

where  $\alpha_1 = [H^+]^2/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})$  is the fraction of the silver(III) complex present as  $[Ag(H_2L)]^{3+}$  and  $\alpha_2 = [H^+]/(K_a + [H^+])$  is the fraction of glyoxylic acid present as HGX.

In the lower pH range (up to pH 2.5), the second dissociation of the dibasic complex may be neglected and reactions (8) and (9) are unnecessary to reproduce the observed  $k_0$  values. On the other hand at pH  $\ge 6.0$  we can assume only  $[Ag(HL)]^{2+}$  and  $[AgL]^+$  as the contributing silver species reacting with GX<sup>-</sup>. The rate-laws in these extremes are, respectively,

$$k_0(K_a + [H^+]) / [HGX]_T = k_1[H^+] + k_2 K_a,$$
(11)

$$k_0(K_{a2} + [H^+])/[HGX]_T = k_3[H^+] + k_4K_{a2}.$$
 (12)

The second-order rate constants (in  $10^4 \text{ M}^{-1} \text{ s}^{-1}$ ) evaluated from these linear plots (left-hand sides of Eqs. (11) and (12) versus [H<sup>+</sup>]) are, respectively,  $k_1 = 7.34$ ,  $k_2 = 112$ ,  $k_3 = 40.7$  and  $k_4 = 19.2$ . They reproduce the observed first-order rate constants satisfactorily (within 10%) using Eq. (10). We also tried to construct a global fit of the left-hand side of Eq. (10) with  $[H^+]$ ; a thirdorder polynomial fit of the left-hand side of Eq. (10) with [H<sup>+</sup>] resulted a very close (within 2%) value of  $k_1$  as found by Eq. (11) and less close agreement for the  $k_2$ value. However, the constant term  $k_4K_{a1}K_{a2}K_a$  yielded a negative value that could not be made positive even varying  $k_1$  and  $k_2$  values by more than 50%. We thus used a constant value of the term  $k_4K_{a1}K_{a2}K_a$  (using the  $k_4$  values as obtained from Eq. (12) and known  $K_{a1}$ ,  $K_{a2}$ and  $K_a$  values) and  $k_1$ , and then started iteration to obtain the best values of the coefficients of the  $[H^+]^2$  and

[H<sup>+</sup>] terms, viz.  $k_2K_a$  and  $k_3K_{a1}K_a$  respectively, until  $\chi^2$  for the fitting becomes acceptably small (of the order of 10<sup>-16</sup>). The rate constants  $k_2$  and  $k_3$  evaluated in this way agree quite well (within 5%) with the values obtained from Eqs. (11) and (12). This is another support for the proposed scheme of reactions.

# 3.4. Mechanism

The observed sequence of rate constants  $k_1 < k_2 > k_3 > k_4$  clearly demonstrates superior kinetic reactivity of protonated oxidants and deprotonated reductant over their counterparts – a trend normally followed in majority of redox reactions [16–19,33–37]. Among the rate constants evaluated  $(k_1-k_4)$ , we find  $k_1$  is the smallest indicating negligible reactivity of HGX towards the title Ag<sup>III</sup> complex. We therefore did not include in the scheme the reaction between [Ag(HL)]<sup>2+</sup> and HGX. Moreover, the acid dissociation constants of [Ag(H\_2L)]<sup>3+</sup> and HGX are quite distant and simultaneous equilibrium generation of both [Ag(HL)]<sup>2+</sup> and HGX is not appreciable.

The title silver(III) complex is a weak oxidant  $(E_{1/2})$  $Ag^{III}/Ag^{II} = 0.05$  V) versus saturated calomel electrode (SCE) [6,38] but the thermodynamics of two electron oxidation of glyoxylic acid is much favourable, estimated to be around 0.3 V versus NHE.<sup>2</sup> Rate retardation in presence of acrylonitrile indicates generation of Ag<sup>II</sup> and polymerisation initiating radicals, viz.  $HGX^+$  and  $GX^-$ . A competitive decay of glyoxylate radicals occurs via fast consumption by Ag<sup>II</sup> leading to products and initiation of acrylonitrile polymerisation it explains lowering in reaction rate in presence of acrylonitrile. Generation of glyoxylate radicals by oneelectron oxidation of glyoxylic acid is well-established by EPR spectroscopy [39]. However, we observed that the whole reaction course was EPR silent. We infer that the radicals produced from one-electron oxidation of glyoxylic acid react in a fast manner with Ag<sup>II</sup> before they can escape into bulk solvent, thus evading detection. Unfortunately one electron potential data for HGX/HGX<sup>+</sup> couple as well as its self-exchange rate is unavailable. Thus we are unable to conclude the nature of electron transfer, inner or outer sphere.

Up to pH 2.5, where only  $[Ag(H_2L)]^{3+}$  is the kinetically reactive oxidant, preequilibrium formation of any adducts between  $[Ag(H_2L)]^{3+}$  and HGX or GX<sup>-</sup> is at best poor, estimated to be within a maximum of the order of  $10^{-1}$  M<sup>-1</sup>. Such a low value does not confirm a

<sup>&</sup>lt;sup>2</sup> Private communication with Dr. Philip N. Ross, Senior Scientist, Lawrence Berkeley National Laboratory. Glyoxylic acid can thermodynamically be considered as half formic acid and half oxalic acid. The redox potential should therefore be exactly half way between that of formic acid (0.14 V) and oxalic acid (0.49 V).

strong inner sphere attachment of glyoxylic acid with the metal center. Formation of a strong inner sphere adduct by glyoxylate with  $[Mn(pd)_2(H_2O)_2]^+$  (Hpd = pentane 2,4 dione) has been proposed [40] and the formation constants of glyoxylate complexes of tripositive rare-earth-metal cations are also high [41]. The in-plane coordinatively saturated Ag<sup>III</sup> in the title complex makes the situation a different one in aqueous solution where the replaceable water molecules attach only weakly with the axial positions of the AgIII center. Replacement of water molecule by glyoxylate is thus expected to be weak at best. The estimated low value for the formation of adducts in the present study may be assigned to electrostriction [42-45] or any kind of it aided by hydrogen bonding [46,47] in the adducts.

A kinetically indistinguishable scheme where the adducts formed by electrostriction or aided by hydrogen bonding on the basal plane may be proposed. However, this proposition enforces a large separation between the oxidant and the reductant species that inhibits electron transfer within the adduct due to incorrect approach, as it were. Occurrence of electron transfer rather is justified when the reductant approaches the metal center along the axial site of the latter. A comparatively strong adduct formation between the complex and the oxalic acid or bioxalate ion [18] in comparison to glyoxylate indicate a much stronger binding with the more potentially complexing oxalate species inherited by their bidentacy.

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### Appendix A. Derivation of Eq. (10)

The acid dissociation constants for the title silver(III) complex are

$$K_{a1} = [Ag(HL)^{2+}][H^{+}]/[Ag(H_{2}L)^{3+}],$$
(A.1)

$$K_{a2} = [AgL^+][H^+]/[Ag(HL)^{2+}].$$
 (A.2)

The analytical concentration of the silver(III) complex,  $T_{\rm c}$ , may be written as

$$T_{\rm c} = [{\rm Ag}({\rm H}_2{\rm L})^{3+}] + [{\rm Ag}({\rm HL})^{2+}] + [{\rm Ag}{\rm L}^+],$$

Substituting  $[Ag(HL)^{2+}]$  and  $[AgL^{+}]$  in terms of  $[Ag(H_2L)^{3+}]$  and rearranging, it results

$$T_{\rm c} = [{\rm Ag}({\rm H}_{2}{\rm L})^{3+}](1 + K_{\rm a1}/[{\rm H}^{+}] + K_{\rm a1}K_{\rm a2}/[{\rm H}^{+}]^{2}),$$
  
whence we may write

whence we may write,

$$[Ag(H_2L)^{3+}]/T_c$$
  
= fraction of the silver(III)complex  
present as  $[Ag(H_2L)^{3+}]$   
=  $[H^+]^2/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})$   
=  $\alpha_1$  (say).

Thus, using (A.1) and (A.2) it yields

 $[Ag(H_2L)^{3+}] = \alpha_1 T_c; [Ag(HL)^{2+}] = K_{a1}\alpha_1 T_c$ and

$$[\mathrm{AgL}^+] = K_{\mathrm{a}1}K_{\mathrm{a}2}\alpha_1 T_{\mathrm{c}}/[\mathrm{H}^+]^2$$

From the glyoxylic acid dissociation equilibrium  $K_{\rm a} = [{\rm GX}^-][{\rm H}^+]/[{\rm HGX}],$ 

it appears

$$[\mathrm{HGX}]/([\mathrm{HGX}] + [\mathrm{GX}^{-}])$$

= fraction of glyoxylic acid present as

$$[HGX] = [H^+]/(K_a + [H^+]) = \alpha_2$$
 (say).

Thus,

$$HGX] = \alpha_2[HGX]_T$$

and

$$[\mathbf{G}\mathbf{X}^{-}] = K_{\mathbf{a}}\alpha_{2}[\mathbf{H}\mathbf{G}\mathbf{X}]_{\mathrm{T}}/[\mathbf{H}^{+}].$$

Now, for the proposed scheme (see text), rate of the reaction becomes

$$Rate = k_1 \alpha_1 \alpha_2 T_c [HGX]_T + k_2 K_a \alpha_1 \alpha_2 T_c [HGX]_T / [H^+]$$
$$+ k_2 K_a K_{a1} \alpha_1 \alpha_2 T_c [HGX]_T / [H^+]^2$$
$$+ k_4 K_a K_{a1} K_{a2} \alpha_1 \alpha_2 [HGX]_T / [H^+]^3,$$

whence, it becomes,

$$k_0[\mathrm{H}^+]^3 / ([\mathrm{H}\mathrm{G}\mathrm{X}]_{\mathrm{T}}\alpha_1\alpha_2) = k_1[\mathrm{H}^+]^3 + k_2K_{\mathrm{a}}[\mathrm{H}^+]^2 + k_3K_{\mathrm{a}1}K_{\mathrm{a}}[\mathrm{H}^+] + k_4K_{\mathrm{a}1}K_{\mathrm{a}2}K_{\mathrm{a}}.$$

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