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Kinetics of oxidation of hydroxylamine 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 NH₂OH quantitatively to N₂O in the pH range 3.00–7.30, themselves being reduced to Ag(I). Free ethylenebis(biguanide) was recovered in near-quantitative yield. The reactions are first-order in both [complex] and total hydroxylamine concentration. The reaction proceeds through three parallel paths: $[Ag(H_2L)]^{3+}$ –NH₂OH (k_1), $[Ag(HL)]^{2+}$ –NH₂OH (k_2) and $[AgL]^+$ –NH₂OH (k_3), where k_1 , k_2 and k_3 are 20.1, 12.5 and 4.35 dm³ mol⁻¹ s⁻¹, respectively, at 25.0 °C and I = 1.0 mol dm⁻³ (NaNO₃). No silver(I)-catalysed path was detected and the reactions appear to be inner-sphere in nature. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Silver; Hydroxylamine; Kinetics; Mechanism; Redox; Catalysis

1. Introduction

The hypervalent silver species [ethylenebis(biguanide)]silver(III) (Fig. 1) is one of the earliest known authentic [1,2] cationic complex of silver, strongly stabilised [3] by a square-planar acyclic tetraaza ligand. The in-plane ligand field stabilisation is so extensive that the complex behaves as a milder oxidant (0.43 V for the couple $[Ag(H_2L)]^{3+/2+}$ than Ag⁺ [4]. It is also stable in both strongly acidic and strongly alkaline media, a property unknown in other silver(III) complexes, and is freely soluble in aqueous media below pH approximately 4.5. Though to a limited extent, it is also soluble at least up to pH 8, if alkali is added, carefully avoiding local excesses. The study of reactivity of different silver(III) species connected through protic equilibria is thus possible because, in spite of this remarkable thermodynamic stability, the silver(III) complex oxidises [5-14] various organic and inorganic molecules with notable variation in the mechanistic pathways of electron transfer.

Hydroxylamine, the presently chosen reductant, is useful for probing reaction mechanisms of inorganic complexes, and the mechanistic versatility noted in its reactions is attractive in the way that it acts both as an oxidant or a reductant [15] and can co-ordinate through either the N- or the O- end [16].

We have now observed that hydroxylamine can reduce the title silver(III) complex at a moderately fast rate and report herein the kinetics of reactions of the parent complex and two of its conjugate bases in aqueous nitrate media and to our knowledge this is the first detailed investigation on the mechanistic pathways of electron-transfer between hydroxylamine and a silver(III) complex. However, it may be noted that $Ag(OH)_4^-$ oxidises NH₂OH and NH₂OCH₃ in basic media in a rather complicated manner [17].

2. Experimental

2.1. Materials

The silver(III) complex, abbreviated as $[Ag(H_2L)]^{3+}$ hereafter, was prepared according to the known procedure [18] with a slight modification in the crystallisation process [5]. Hydroxylamine nitrate was prepared in solution by double decomposition of hydroxylamine

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Fig. 1. Structure of $[Ag(enbbg)]^{3+}$. Bond lengths are in Å. \triangle is weakly bonded ClO_4^- ion at the axial site.

sulfate (G.R., E. Merck) with barium nitrate (G.R., E. Merck) and standardised by oxidation with KBrO₃ in presence of dilute H₂SO₄ [19]. We found this solution to be stable for at least 6 months when kept at low temperature (~5–10 °C) and in dark. Aqueous solutions of NaNO₃ (G.R., E. Merck) was standardised by passing 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 °C and I = 1.0 mol dm⁻³ (NaNO₃). All solutions were prepared in water which was deionised and then double distilled.

2.2. 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 was monitored in situ in the 'kinetic mode' of the instrument at 420 nm in the electrically controlled thermostated (25.0 ± 0.1 °C) cellhousing (CPS-240A). In this mode the change in absorbance is automatically and continuously recorded. Hydroxylamine solution (adjusted to the desired pH) was directly injected in to 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 ionic strength (I) was maintained at 1.0 mol dm⁻³ (NaNO₃). The solution pH values were adjusted with HClO₄ 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 [20].

2.3. Stoichiometric measurements

The stoichiometry was measured under kinetic conditions by estimating excess hydroxylamine spectrophotometrically. Excess hydroxylamine was mixed with the complex in the pH range 4.0-6.0. After the reaction mixtures turned colourless indicating complete reduction of Ag(III) to Ag(I), pH of the mixtures were made to ~2. A solution of Fe₂(SO₄)₃ at pH ~2 was then added in each set and after a few minutes excess 2,2'-bipyridyl solution (at pH ~2) was added. The resulting red [Fe(bipy)₃]²⁺, generated by the quantitative reduction of excess Fe(III) by hydroxylamine was measured [21] at 523 nm ($\varepsilon = 8500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) after proper dilution.

3. Results and discussions

3.1. Preliminary observations

Within the time span of the reactions the autodecomposition [22] of the silver(III) complex is insignificant. No silver(I) catalysis was found in the reactions below $pH \sim 5.0$. Above this pH, addition of AgNO₃ in the reaction mixture produces a faint blackish suspension probably due to metallic silver and/or silver oxide and thus Ag⁺ catalysis, if any, was examined below pH ~ 5.0. No external buffer was used in the 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 0.05 units.

3.2. Stoichiometry and reaction products

Stoichiometric experiments under kinetic conditions indicate 1:1 reaction between the redox partners (Table 1). The principal conversion may then be represented by Eq. (1).

$$2Ag(III) + 2NH_2OH$$

$$\rightarrow 2Ag(I) + N_2O + H_2O + 4H^+$$
(1)

Immediately after completion of reaction (absorbance < 0.01 at 380 nm), all Ag⁺ was precipitated as AgCl and removed by filtration. From the filtrate, the free ligand, ethylenebis(biguanide), was quantitatively isolated [23] 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. The results showed that more than 95% of the free ligand (H₂L) was recovered.

The complicated redox chemistry of hydroxylamine in solution has been studied extensively [15]. It was observed that hydroxylamine is most commonly oxidised to N₂O [24–26]. Oxidation to N₂, NO₂⁻, NO₃⁻ and NO are relatively rare [16,24–26]. ESR spectroscopy has established the formation of the H₂NO[•] radical in the oxidation of NH₂OH with one-electron oxidants [27]. The ultimate oxidation product varies depending on the mode of decay (Eq. (3)) of H₂NO[•]

Table 1 Stoichiometric results for the oxidation of N(-I) by the silver (III) complex ^a

$[Ag(III)]_T \text{ (mmol dm}^{-3})$	$[N(-I)]_T \text{ (mmol dm}^{-3}\text{)}$	pH	$[N(-I)]_{left} \pmod{dm^{-3}}$	$\Delta[N(-I)]_T / \Delta[Ag(III)]_T$
0.15	0.30	3.8	0.17	0.87
	0.40	4.0	0.26	0.93
	0.50	4.9	0.34	1.07
0.30	0.80	5.0	0.48	1.07
	1.20	4.6	0.94	0.87
0.50	1.00	4.9	0.52	0.96
	1.50	3.9	1.05	0.90
				Average = 0.97 ± 0.10 .

^a T = 25.0 °C; I = 1.0 mol dm⁻³ (NaNO₃).

radical under different conditions [15]. Thus H₂NO[•] may decay to N₂ (Eq. (2)) or may be further oxidised (Eq. (3)) to HNO, which dimerises to *cis*- and *trans*-hyponitrous acid [28]. The *trans* form is more stable than the *cis*- form, decomposes into N₂O [29]. With strong oxidants such as $Mn^{3+}(aq)$ or $Ag^{2+}(aq)$, present in excess, the free radical is further oxidised to NO₃⁻ [30].

$$H_2 NO^{\bullet} \rightarrow 0.5N_2 + H_2 O \tag{2}$$

$$H_2NO^{\bullet} \rightarrow HNO + H^+ + e^-$$
 (3)

$$2HNO \rightarrow H_2N_2O_2 \rightarrow N_2O + H_2O \tag{4}$$

Thermodynamic oxidising strength of the title complex under investigation is moderate [4,11]. Hence N(III)or N(V) is not an expected oxidation product.

3.3. Kinetics

No immediate spectral change was observed on mixing hydroxylamine with the Ag(III) complex over the entire range of experimental pH. However, the absorbance at $\lambda \ge 380$ nm gradually decreases to less than 0.01. Trace metal ions [31] in solution strongly catalyse the oxidation of hydroxylamine and affects both rate and the oxidation product. Ambient light sometime also plays a definite role [32]. We measured some k_0 values in presence of added ethylenebis(biguanide) $[1.0 \text{ mmol dm}^{-3}]$ and found to be identical with its absence within experimental uncertainties, and we observed no effect of diffused light in our system. The log_{10} (absorbance) versus time plots were found to be linear for more than 90% of reactions and the pseudo first-order rate constants, k_0 , defined by Eq. (5) were obtained from the least-squares slopes of these plots.

$$-d[Ag(III)]/dt = k_0[Ag(III)]$$
(5)

Any initial drop in absorbance for faster reactions can be computed from the time of mixing of solutions (~ 4 s) and the observed first-order rate constants. Averages of the 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 total NH₂OH (defined as $[N(-I)]_T$, which is $[NH_2OH] + [NH_3OH^+]$) and some representative data are summarised in Table 2. Over the entire pH range studied the reaction shows a clear first-order dependence on $[N(-I)]_T$ and there is no $[N(-I)]_T$ 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 mmol dm⁻³, addition of AgNO₃ (studied up to 0.01 mol dm⁻³), variation of ionic strength maintained by NaNO₃ or NaClO₄ in the range 0.1–1.0 mol dm⁻³, the occasional shaking of the spectrophotometer cell, presence or

Table 2 First-order rate constants for the oxidation of N(-I) by the Ag(III) complex ^a

pН	$[N(-I)]_T \text{ (mmol dm}^{-3})$	$10^4 k_0 (s^{-1})$
3.00	3.0	0.57
3.10		0.71
3.25		0.98
3.45		1.49
3.73		2.65
4.00		4.58
4.35		9.25
4.60		15.4
4.93		29.9
5.21		51.0
5.55		89.0
5.85		129
6.05		152
6.30		169
6.65		168
6.92		159
7.15		150
7.30		145
3.10	6.0	1.40
3.25	12.0	4.05
4.00	6.0	9.25
4.00	12.0	18.0
4.00	18.0	26.8
4.00	30.0	47.0
6.65	1.5	82.2

^a T = 25.0 °C, I = 1.0 mol dm⁻³; [complex] = 0.15 mmol dm⁻³.

absence of dissolved oxygen, and a variation in the monitoring wavelength in the range 380–480 nm.

No polymer is formed when 6% (v/v) acrylonitrile is added to the reaction mixture and whole reaction course is epr silent. There is thus no evidence for the formation of detectable amounts of free radicals or other paramagnetic species during the reaction. However, one can not conclude from these observations as to whether the reactions of Ag(III) with hydroxylamine are one or two electron processes, because the radicals produced from one-electron oxidation of hydroxylamine may react in a very fast manner with Ag(III) before they can escape into the bulk solvent, thus evading detection.

A plot of k_0 versus pH has a bell shape (Fig. 2). Such a pH dependence indicates the involvement of two or more acid-base equilibria [33]. Considering the values for the acid dissociation constants of the complex in aqueous solution [34] (K_{a_1} and K_{a_2} , which are 1.58×10^{-4} and 5.01×10^{-7} mol dm⁻³, respectively) and K_a (= 1.0×10^{-6} mol dm⁻³), the acid dissociation constant [35] of NH₃OH⁺, the scheme in Eqs. (3)–(8) provide a reasonable explanation for the kinetic observations.

$$[Ag(H_2L)]^{3+} \stackrel{\Lambda_{a_1}}{\rightleftharpoons} [Ag(HL)^{2+} + H^+$$
(6)

$$[Ag(HL)]^{2+} \stackrel{R_{a_2}}{\rightleftharpoons} [AgL]^+ + H^+$$
(7)

$$NH_3OH^+ \rightleftharpoons NH_2OH + H^+$$
 (8)

 $[Ag(H_2L)]^{3+} + NH_2OH \xrightarrow{k_1} Products$ (9)

 $\left[\operatorname{Ag}(\operatorname{HL})\right]^{2+} + \operatorname{NH}_{2}\operatorname{OH} \xrightarrow{k_{2}} \operatorname{Products}$ (10)

$$[AgL]^{+} + NH_{2}OH \xrightarrow{\kappa_{3}} Products$$
(11)

From these, expression (12) can be derived where the fraction of the complex present as $[Ag(H_2L)]^{3+}$ is given by Eq. (13) and the fraction of $[N(-I)]_T$ present as NH₂OH is given by Eq. (14).

$$k_0[{\rm H}^+]^2/([{\rm N}(-{\rm I})]_{\rm T}\alpha_1\alpha_2)$$

$$=k_{1}[\mathrm{H}^{+}]^{2}+k_{2}K_{\mathrm{a}_{1}}[\mathrm{H}^{+}]+k_{3}K_{\mathrm{a}_{1}}K_{\mathrm{a}_{2}}$$
(12)

$$\alpha_1 = [\mathrm{H}^+]^2 / ([\mathrm{H}^+]^2 + K_{\mathrm{a}_1}[\mathrm{H}^+] + K_{\mathrm{a}_2}K_{\mathrm{a}_2}$$
(13)



Fig. 2. Dependence of k_0 on pH at 25.0 °C, $[Ag(III)]_T = 0.15$ mmol dm⁻³, $[N(-I)]_T = 3.0$ mmol dm⁻³, I = 1.0 mol dm⁻³ (NaNO₃). The solid line represents the fit of Eq. (12).

$$\alpha_2 = K_a / (K_a + [H^+]) \tag{14}$$

Non-linear fitting of left-hand-side of Eq. (12) with $[H^+]$ yielded k_1 , $k_2K_{a_1}$ and $k_3K_{a_1}K_{a_2}$. Using known values of K_{a_1} and K_{a_2} , the rate constants k_2 and k_3 were evaluated. All these second-order rate constants are presented in Table 3 which reproduced all k_0 within 5%.

It may also be noted that in the pH interval 3.00-4.60, the second dissociation of the Ag(III) complex (K_{a_2}) can be neglected and Eqs. (9) and (10) are sufficient to represent the observed first-order rate constants. On the other hand, in the higher pH range 6.30-7.30 the first dissociation of the Ag(III) complex (K_{a_1}) can be neglected and only Eqs. (10) and (11) may account for the observed situation. The second-order rate constants evaluated in this manner agreed nicely with the values represented in Table 3 within 7%.

3.4. Mechanism

The observed sequence $k_1 > k_2 > k_3$ indicates that protonation of the oxidant increases its kinetic reactivity whereas the opposite is true for protonation of the reductant. Majority of the other known redox systems also follow a similar trend [36,37]. The trend was observed earlier for the oxidation [12] of N(III) with the title Ag(III) complex. In the present investigation we found that the conjugate acid NH_3OH^+ is kinetically inactive towards the Ag(III) complexes under investigation and its conjugate bases, whereas HNO₂ was active, though to a much lesser extent than NO_2^- towards the reduction of the Ag(III) complex. We anticipate that an unfavourable charge interaction between the cationic silver(III) complexes with NH₃OH⁺ makes the situation a different one. A molecule with a free electron pair should have a greater affinity for cation than would another positively charged ion.

One may use Marcus cross relation [38], $k_{12} = (k_{11}k_{22}K)^{1/2}$ to identify the nature of electron transfer. The equilibrium constant *K* of the one-electron transfer between $[Ag(H_2L)]^{3+}$ and NH₂OH may be calculated from the known redox potentials of $[Ag(H_2L)]^{3+/2+}$ couple (0.43 V) [4,11] and NH₂OH–NH₂OH⁺ (-0.42 V) [39]. The self-exchange rate constant for the couple NH₂OH–NH₂OH⁺ is 5×10^{-13} dm³ mol⁻¹ s⁻¹ [39] and the maximum possible self-exchange rate for

Table 3

Second-order rate constants (in dm³ mol⁻¹ s⁻¹) for the oxidation of N(–I) by the Ag(III) complex ^a

Reaction	Rate constant
$\frac{[Ag(H_2L)]^{3+} + NH_2OH}{[Ag(HL)]^{2+} + NH_2OH}$ $[AgL]^{+} + NH_2OH$	$k_1 = 20.1 \pm 1.0 k_2 = 12.5 \pm 0.60 k_3 = 4.35 \pm 0.50$

^a [Complex] = 0.15 mmol dm⁻³, I = 1.0 mol dm⁻³ (NaNO₃), T = 25.0 °C.

 $[Ag(H_2L)]^{3+/2+}$ couple is $10^{6.6}$ [13]. Using these values, the calculated maximum value of k_{12} becomes ~ 1.7×10^{-3} dm³ mol⁻¹ s⁻¹, much lower than the experimentally observed value (20.1 dm³ mol⁻¹ s⁻¹), which refutes one-electron outer sphere pathway as the ratedetermining step. This is not unexpected in light of the remarkably low NH₂OH–NH₂OH⁺ self-exchange rate coupled with a near zero E° value for the one electron reaction.

It is well documented that hydroxylamine (NH₂OH) can co-ordinate to higher valent metal ions [40–42]. The electron affinity of the Ag(III) in the present complex is high [43] as established by X-ray photoelectron spectroscopic measurements that the Ag(III) centre has a high degree of positive charge and it is known from structural [44–46] and kinetic [6,7] studies that the complex undergoes axial co-ordination with alcohols, H₂O₂, SO₄²⁻, NO₃⁻ or even ClO₄⁻. We thus anticipate a similar co-ordination of NH₂OH to the Ag(III) centre and subsequent electron transfer.

4. Conclusions

Reduction of the complex cation $[Ag(H_2L)]^{3+}$ may proceed via a Ag⁺- catalysed path and/or an uncatalysed path depending on the nature of the reductant. Only the uncatalysed path is detectable in the oxidation of N(-I), N(III) [12], alcohols [6], ascorbic acid [10] and $Fe^{2+}(aq)$ [11] by this complex. The catalysed path involves a $Ag^+ - Ag^0$ cycle (for HCO₂H [5], N₂H₅⁺ [8] and H_3PO_2 [9]) or a Ag(I)-Ag(II) cycle (for H_2O_2 [7]). Predominance of the uncatalysed or catalysed path depends on a critical balance of thermodynamic and also on kinetic factors, but grossly speaking when the reductant is powerful [47] like HCO₂H, $N_2H_5^+$ or H₃PO₂ or a good ligand for Ag(III), then catalysed path dominates. We observed that below $pH \sim 5.0$ hydroxylamine does not react with Ag⁺ over a long period and we observed no Ag⁺ catalysis in our reactions. Below pH 3.0, hydroxylamine was found to be kinetically inactive towards the reduction of the title complex which indicates absence of any possible $[Ag(H_2L)]^{3+}-NH_3OH^+$ path. We found that NH_3OH^+ is kinetically inactive but the conjugate base, NH₂OH, a neutral species reacts with the charged Ag(III) complexes. An indirect outcome of these types of reacting species may be the innocent influence of media ionic strength on the rate of reactions. All the reaction paths k_1 , k_2 and k_3 possibly involve innersphere processes. It cannot be concluded at this stage whether the reaction involves one- or two-electron changes.

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