Kinetics and Mechanism of the Multi-step Oxidation of Ethylenediaminetetraacetate by $[Ag(OH)_4]^-$ in Alkaline Media

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Alkaline solutions of $[Ag(OH)_4]^-$ oxidise ethylenediaminetetraacetate (edta) in a multistep sequence which produces iminodiacetate (ida), glycinate and glycolate ions, and eventually ammonia, formaldehyde, carbon dioxide and water. The reaction shows changing stoichiometry and product distribution. At $[edta]_0/[Ag(OH)_4^-]_0 = 1:1$, glycinate and ida are produced in similar amounts with detectable ammonia and formaldehyde. When $[edta]_0/[Ag(OH)_4^-]_0 = 200:1$, very little glycinate is produced with no ammonia or formaldehyde detected. The kinetics of the oxidation was studied by the stopped-flow method at high excesses of edta and 25 °C and $I = 1.2$ mol dm^{-3}. The overall rate is as in equation (i), where the coefficients, obtained by non-linear least-square analysis, are A =

$$k_{obs} = \frac{(A + B[OH^-])[edta^{4-}]}{[OH^-] + C[edta^{4-}]} \qquad (i)$$

4.38 ± 0.57 s^{-1}, $B = 34.8 \pm 1.1$ dm^3 mol^{-1} s^{-1} and $C = 26.3 \pm 2.1$. A multi-step electron-transfer mechanism is proposed involving initial C–N bond cleavage at the ethylenediamine group.

In contrast to its simple complexation stoichiometry, oxidations of ethylenediaminetetraacetic acid (H_4edta) and its anions are often rather complicated,[1–4] both in terms of stoichiometry and product distribution. The bond breaking which accompanies oxidation can be expected to take place at almost any C–N or C–C bond. In the presence of an excess of strong oxidant, the ultimate oxidation of edta requires 34 electrons as shown in reaction (1)†. Under milder conditions, a variety of intermediate organic species will be produced.

$$(HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)_2 + 34OH^- \longrightarrow 10CO_2 + 2NH_3 + 22H_2O + 34e^- \qquad (1)$$

At $[edta]/[Fe^{III}]$ ratios of 1.0 and 1.5:1 and a $[edta]/[Cu^{II}]$ ratio of 1.0:1, edta is oxidised to ethylenediaminetriacetic acid (H_3edtra) with no other products detected by NMR, GC or GC–mass spectrometry.[4] The iron(III)-catalysed oxidation of H_4edta by O_2 also yields H_3edtra in a two-electron transfer as shown in equation (2).

$$(HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)_2 + 2OH^- \longrightarrow CO_2 + HCHO + (HO_2CCH_2)NHCH_2CH_2N(CH_2CO_2H)_2 + H_2O + 2e^- \qquad (2)$$

The oxidation by lead(IV) oxide is more extensive.[2,5] It has been reported[5] that, at $[Pb^{IV}]/[H_4edta] = 0.085–0.53:1$, 3 mol of a suspension of PbO_2 in sulphuric acid oxidise 1 mol of edta to $C_4H_{10}N_2O_2$ (probably ethylenediaminemonoacetic acid, Hedma), formaldehyde and CO_2. When $[Pb^{IV}]/[H_4edta] = 4:1$, edta is oxidised to *N*-hydroxymethylethylenediamine according to reaction (3).

$$(HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)_2 + 4H_2O \longrightarrow 4CO_2 + 3HCHO + H_2NCH_2CH_2NHCH_2OH + 8H^+ + 8e^- \qquad (3)$$

Unlike the simple stoichiometries shown above, the oxidation of edta by Ce^{IV} usually yields a mixture of products. When Ce^{IV} and edta are mixed in a 4:1 ratio in acid,[1,3,6] analysis by electrophoresis reveals a mixture of *N,N′*- and *N,N*-ethylenediaminediacetic acid (H_2edda), 2-oxopiperazine-1-acetic acid and small amounts of ethylenediamine and glycinate. The aerobic photodegradation of Fe^{III}–H_4edta gives H_3edtra, *N,N′*- and *N,N*-H_2edda, Hedma, iminodiacetic acid (H_2ida) and glycine.[7] Oxidation of edta by $[Fe(CN)_6]^{3-}$ (ref. 8) and H_2O_2[9] gives iminodiacetic acid and glyoxal (CHOCHO) or glycolic acid. Oxidation by *m*-chloroperbenzoic acid produces the *N,N′*-dioxide of the edta.[10]

The ion $[Ag(OH)_4]^-$ is a strong oxidising agent and its reactions exhibit interesting diversity and complexity.[11] In the reduction of Ag^{III} to Ag^I the two-electron transfer can be accomplished either in a single step, in two successive one-electron steps, or by oxygen-atom transfer. The ion $[Ag(OH)_4]^-$ oxidises glycinate ion to ammonia and carbon dioxide[12] and tri- and tetra-glycine[11b] to organic fragments. In this paper we report the oxidation of edta by $[Ag(OH)_4]^-$ in alkaline media. Kinetic and chromatographic results allow us to distinguish between the possible reaction paths.

Experimental

Reagents.—All stock solutions were made with doubly distilled water and reagent grade chemicals without further purification. Solutions of edta were made daily from reagent grade Na_2H_2edta (Fisher) and converted into $edta^{4-}$ with NaOH. The $NaClO_4$ solution was made from 50% low-carbonate NaOH and $HClO_4$ (Fisher). Solutions of $edta^{4-}$ used in kinetic experiments were prepared by dilution with 1.2 mol dm^{-3} NaOH and/or $NaClO_4$ to bring the ionic strength to 1.2 mol dm^{-3}. Solutions of $[Ag(OH)_4]^-$ were prepared by electrolysis of silver foil (Hardy and Harman) in 1.2 mol dm^{-3} NaOH.[13,14].

Dilute solutions (1×10^{-3} mol dm^{-3}) of glyoxal (MC & B], glycolic acid (Eastman), glyoxylic acid (Aldrich), ethylenediamine (MC & B), H_2edda (Aldrich), glycine (Fisher), iminodiacetic acid (Aldrich), formaldehyde (Fisher), formic

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† The abbreviation edta is used as a general term, and when more than one degree of protonation may occur.

Non-SI unit employed: in = 2.54×10^{-2} m.

acid (Allied Chemical) and ammonia (Mallinckrodt) were made by weight followed by dilution with the appropriate electrolyte.

Product Analysis.—In order to increase the concentration of products, the $[Ag(OH)_4]^-$ solutions were made to maximum attainable concentration (about 3×10^{-3} mol dm^{-3}) by keeping the electrolysis running for 3–4 h.

Jackson's modification of Nessler's reagent was used to test for ammonia.[15] Formaldehyde was identified by use of phenylhydrazine hydrochloride[15] and 2,4-dinitrophenylhydrazine.[16] Gas chromatography was used to search for other oxidation products. Prior to GC analysis, reaction mixtures were neutralised with 6 mol dm^{-3} HCl to pH 7, filtered and esterified with butanol–HCl and trifluoroacetic anhydride.[7,17] Analysis of the *N*-trifluoroacetyl butyl esters was performed on a 4 ft × $\frac{1}{8}$ in column of 3% SE-30 on Gas-Chrom-Q (100–200 mesh) using a gas chromatograph (Varian aerograph, Series 1400) with a flame ionisation detector and helium as carrier gas. The oven temperature was programmed from 110 to 260 °C at 10 °C min^{-1}, starting 2 min after injection. The injection temperature was 250 °C and the detector temperature 300 °C.

Paper chromatographic analysis was carried out on Whatman 1 Chroma paper for separating and testing carboxylic acids possibly produced as another group of edta oxidation products. Chromatograms were run in a solvent containing *tert*-pentyl alcohol–formic acid–water (80:10:40) by the descending technique for about 10 h. Then the chromatograms were dried at room temperature, dipped in 1.1% ammonium thiocyanate in acetone, dried at 20–30 °C, and finally dipped in 0.03% anhydrous iron(III) chloride in acetone.[18] In order to increase the chromatographic sensitivity, the solution was added to the same spot repeatedly after each drop was dry.

Stoichiometry.—The stoichiometry under conditions where all of the Ag^{III} was consumed was measured by determining the remaining edta by complexometric titration. Various volumes of 0.05 mol dm^{-3} H_4edta solution were mixed with 25 cm^3 of $[Ag(OH)_4]^-$ solution [$(1-2) \times 10^{-3}$ mol dm^{-3}]; the mixtures were allowed to react for a few minutes and neutralised to pH 10.0 with 2 mol dm^{-3} HCl solution. After filtration and addition of ammonia–ammonium chloride buffer (pH 10), solutions were titrated with Mg^{2+} to an eriochrome black-T end-point. Blank titrations with edda, ida and glycine were carried out and the results showed that the presence of significant amounts of those compounds (up to three times the edta concentrations) would not interfere with the edta titration.

Kinetics.—All kinetic data were accumulated by an Aminco-Morrow stopped-flow assembly interfaced to a IBM compatible personal computer and processed with the Kinfit program (OLIS, Jefferson, GA). A large excess of reductant was maintained throughout the experiments in order to obtain pseudo-first-order behaviour. The temperature was kept at 25.0 ± 0.1 °C and the ionic strength at 1.2 mol dm^{-3}. The decrease of $[Ag(OH)_4]^-$ was normally monitored at 300 nm, which is near its absorbance maximum (267 nm).[14] All reactions were found to be first order in $[Ag(OH)_4{}^-]$ for at least four half-lives. The observed rate constants were independent of monitoring wavelength.

Results

Products and Stoichiometry.—When mixed with less than a 20-fold excess of edta, 10^{-3} mol dm^{-3} $[Ag(OH)_4]^-$ solutions rapidly become colourless and then cloudy with a black precipitate forming after a few seconds. The black precipitate could not be dissolved completely in acid, indicating that it contained silver metal. The acidified solution formed a white precipitate with chloride, indicating the presence of Ag^I. However, under kinetic conditions $\{[Ag(OH)_4{}^-] \approx 5 \times 10^{-5}$ mol dm^{-3} and $[edta^{4-}] = (0.5-5) \times 10^{-2}$ mol dm$^{-3}\}$ no precipitates (Ag^I or Ag) were observed.

Table 1 Product analysis (%)

	$[edta]_0/[Ag(OH)_4{}^-]_0$	
Product	1:1	200:1
ida*	40	95
Glycinate*	60	5
HCHO	Yes	No
Glycolate	Yes	Yes
NH_3	Yes	No

* The percentages are the relative amounts of ida to glycinate.

When the suggested amount[15] of Nessler's reagent was added to the filtered reaction solutions from 10^{-3} mol dm^{-3} $[Ag(OH)_4]^-$ and 10^{-3} mol dm^{-3} edta^{4-}, there was no indication of any colouring, but excess of Nessler's reagent gave a reddish brown colour, indicating the presence of ammonia. The failure to detect ammonia at lower ratios may be due to the complexation of mercury(II) ion in Nessler's reagent by edta. Similar phenomena occurred after oxidation of excess of cyanide by Ag^{III}.[19] The reaction of 10^{-3} mol dm^{-3} $[Ag(OH)_4]^-$ with 0.2 mol dm^{-3} edta did not yield ammonia.

At $[edta]_0/[Ag(OH)_4{}^-]_0 = 1.0:1$ the presence of formaldehyde was confirmed by the phenylhydrazine hydrochloride method and by the melting point of the 2,4-dinitrophenylhydrazone precipitate (167 °C).[16,20] When the ratio equalled 200:1 no formaldehyde was detected.

Gas chromatography showed a changing product spectrum. At all the $[edta]_0/[Ag(OH)_4{}^-]_0$ ratios used, glycinate and iminodiacetate were the only two iminocarboxylic acid products, but their ratio changed with the ratio $[edta]_0/[Ag(OH)_4{}^-]_0$. At a high excess of edta $\{[edta]_0/[Ag(OH)_4{}^-]_0 = 200:1$, such as under kinetic conditions$\}$ the product was almost exclusively iminodiacetate ion, while at low excess $\{[edta]_0/[Ag(OH)_4{}^-]_0 = 1:1\}$ the yields of ida and glycinate ion were similar. No peaks due to edtra, edda and edma were observed. The identifications of iminodiacetate and glycinate ions as products and the absence of the other three acids in the reaction mixture clearly indicates the oxidation path (see next section).

Paper chromatographic analysis showed that glycolic acid was also an oxidation product. The chromatogram run in *tert*-pentyl alcohol–formic acid–water solution showed a yellow zone and a white zone after developing in 1.1% ammonium thiocyanate–acetone solution and 0.03% anhydrous iron(II) chloride–acetone solution; the yellow zone indicated the presence of glycolic acid and the cream white zone may be due to glycinate.[18] The results of the product analysis are summarised in Table 1.

Although the measurements by edta titration clearly indicate a change in stoichiometry in the range $[edta]_0/[Ag(OH)_4{}^-]_0 = 0.14-7.9:1$, the observed numbers of $[Ag(OH)_4]^-$ consumed by each edta were higher than expected when compared to the product analysis and kinetic results (see below). These results could have a large error due to competition from the spontaneous decomposition of Ag^{III} during the course of the experiments. It is this self-decomposition that precludes extending the range of the kinetic experiments to lower $[edta^{4-}]$. Since all silver(III) is lost during the analysis it is impossible to account for the relative amount involved in each process (spontaneous decomposition or reduction by edta). On the basis of the product analysis, however, we would predict a ratio of slightly more than 2:1 for a 200-fold excess of edta and much higher values for equal concentrations of reactants.

From a mechanistic point of view, the product analysis points to a reaction pathway in which C–N bond cleavage occurs

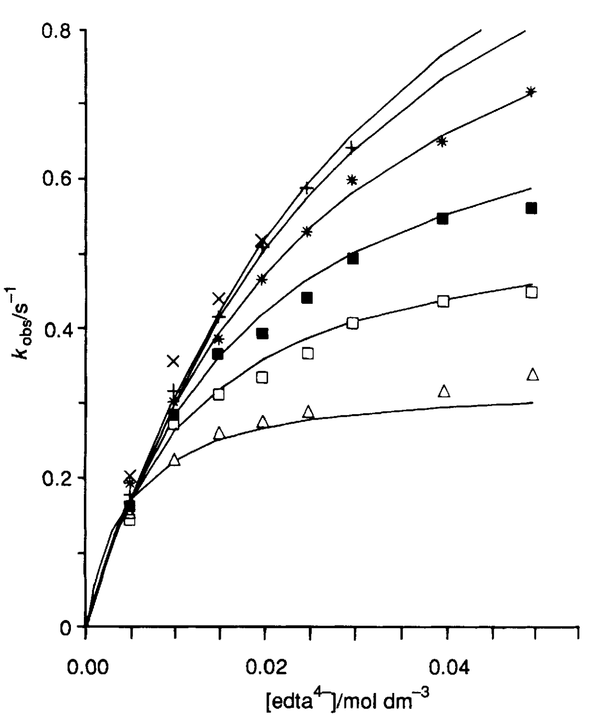
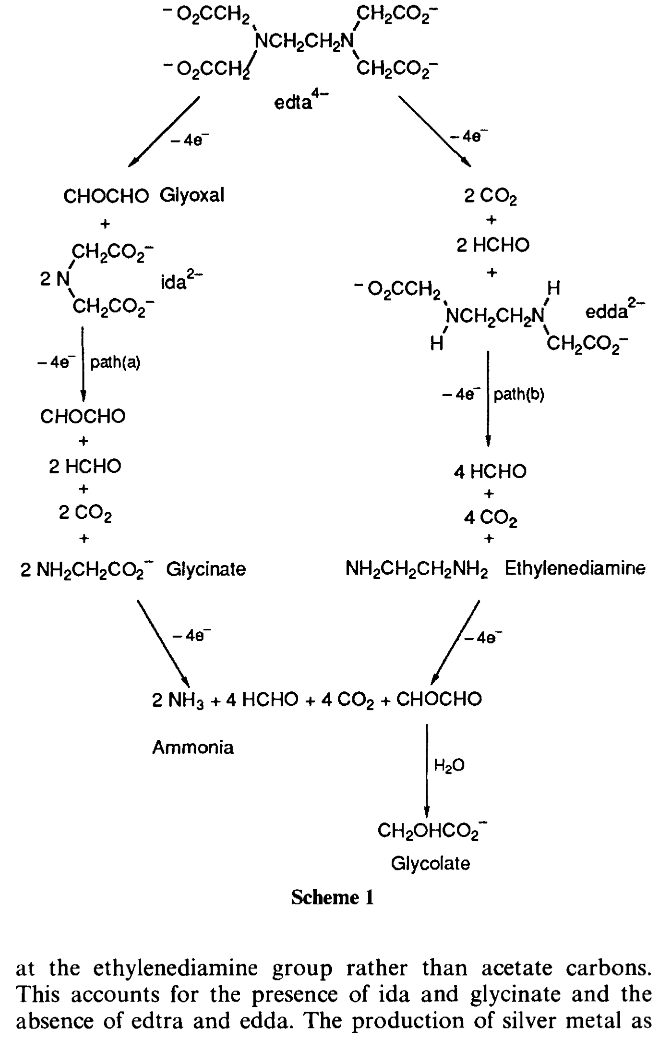


Fig. 1 Dependence on $[edta^{4-}]$ of pseudo-first-order rate constants at 25 °C and $I = 1.2$ mol dm^{-3}. $[OH^-] = 1.0$ (×), 0.9 (+), 0.7 (✱), 0.48 (■), 0.3 (□) and 0.12 mol dm^{-3} (△). The curves drawn were calculated from equation (5)



Scheme 1

at the ethylenediamine group rather than acetate carbons. This accounts for the presence of ida and glycinate and the absence of edtra and edda. The production of silver metal as well as the overall mechanism will be discussed in the next section.

Kinetics.—The oxidation of edta^{4-} is first order in $[Ag^{III}]$ at excess of edta^{4-}. Values of k_{obs} are listed in Table 2 and plotted in Fig. 1. A non-linear least-square analysis (weighed by $1/k_{obs}$) of the data gives the experimental rate law shown in equation (5) with the empirical parameters $A = 4.38 \pm 0.57$ s^{-1}, $B = 34.8 \pm 1.1$ dm^3 mol^{-1} s^{-1} and $C = 26.3 \pm 2.1$.

$$k_{obs} = \frac{A + B[OH^-]}{[OH^-] + C[edta^{4-}]}[edta^{4-}] \qquad (5)$$

Oxidations of Related Compounds.—For comparison, the oxidations of a series of potential intermediates and products were also studied. In each case the concentration was 1×10^{-3} mol dm^{-3}. All reactions were pseudo-first order in $[Ag(OH)_4^-]$. Rate data for these reactions are listed in Table 3.

Discussion

The oxidation of edta usually results in C–N bond cleavage and can begin either within the ethylenediamine group [path (a)] or at an acetate group [path (b)] as shown in Scheme 1. Path (a) has been suggested by Lambert and Jones[8] in the oxidation of edta by $[Fe(CN)_6]^{3-}$ and by Alary and Coeur[9] in the oxidation by H_2O_2. In both reactions edta lost four electrons and was oxidised to ida and glyoxal without the build-up of any two-electron-transfer intermediate products. The time-scale of subsequent processes in the $[Fe(CN)_6]^{3-}$ reaction was such that the stoichiometry remained at 4:1 through six half-lives. Although the above-mentioned oxidations of edta are obviously multistep processes, the possible identification and properties of reaction intermediates (two- or even one-electron-transfer intermediates) were not reported in either of the two works. Path (b) seems to operate in the reactions of edta with Ce^{IV} (refs. 1 and 3) in acidic media and with Fe^{III}.[4] In this path the carboxylate groups are removed one by one and each step requires the transfer of two electrons. In the reactions of edta with excess of Ce^{IV} in $HClO_4$[3a] and H_2SO_4[3b] media an average of 4.2 mol of Ce^{IV} per mol of edta were consumed 'almost instantaneously', with the successive reactions being slow. Eventually, 14 electrons were transferred per edta reacting. On the other hand, paths (a) and (b) both seem operative in the photodegradation of Fe^{III}–edta. The relative importance of each path depends on the reaction conditions. Under acidic conditions (pH 4.5) the iron(III) reaction goes by path (b) while in basic media (pH 6.9–8.5) both paths operate.

In the edta–$[Ag(OH)_4]^-$ system in strongly alkaline media the product analysis indicates that path (a) is that by which edta is oxidised to organic products. This is consistent with the fact that high pH favours the production of ida and glycinate.[17] Nevertheless, ida and glyoxal are four-electron-transfer products while $[Ag(OH)_4]^-$ is a two-electron oxidant, and hence the oxidation to ida and glyoxal is likely to be a two-step process. In the first step edta^{4-} reacts with one $[Ag(OH)_4]^-$ to give ida and an intermediate. Such an intermediate has never been observed experimentally, probably because of its high instability. The intermediate then reacts rapidly with a second $[Ag(OH)_4]^-$ to give glyoxal and a second ida. If sufficient $[Ag(OH)_4]^-$ is available the ida undergoes oxidative decarboxylation to glycinate, which can be further oxidised to formaldehyde and ammonia.[12]

Ethylenediaminetetracetate is a strong multidentate complexing agent. Although we did not see spectroscopic evidence for the formation of an edta–Ag^{III} complex, the kinetic data suggest replacement of one of the bound hydroxyls from the square-planar $[Ag(OH)_4]^-$. For the hydroxide range employed in the study ($0.12 \leqslant [OH^-] \leqslant 1.2$ mol dm^{-3}) edta exists almost exclusively as the tetraanion edta^{4-} (the dissociation constant of the last proton of edta is 6.8 ×

Table 2 Pseudo-first-order rate constants for oxidation of edta

$[OH^-]$/ mol dm^{-3}	$10^2[edta^{4-}]$/ mol dm^{-3}	k_{obs}/s^{-1}	k_{calc}*/s^{-1}
1.0	0.5	0.202	0.173
	1.0	0.357	0.301
	1.5	0.441	0.421
	2.0	0.520	0.513
0.9	0.5	0.177	0.173
	1.0	0.316	0.307
	1.5	0.415	0.414
	2.0	0.508	0.501
	2.5	0.626	0.573
	3.0	0.640	0.634
0.7	0.5	0.194	0.173
	1.0	0.302	0.298
	1.5	0.384	0.394
	2.0	0.465	0.469
	2.5	0.528	0.529
	3.0	0.597	0.579
	4.0	0.677	0.656
	5.0	0.715	0.713
0.48	0.5	0.150	0.172
	1.0	0.283	0.283
	1.5	0.367	0.362
0.48	2.0	0.393	0.419
	2.5	0.439	0.463
	3.0	0.451	0.498
	4.0	0.544	0.550
	5.0	0.558	0.587
0.3	0.5	0.142	0.172
	1.0	0.272	0.263
	1.5	0.329	0.320
	2.0	0.334	0.359
	2.5	0.364	0.387
	3.0	0.404	0.408
	4.0	0.402	0.438
	5.0	0.444	0.459
0.12	0.5	0.147	0.170
	1.0	0.243	0.223
	1.5	0.252	0.249
	2.0	0.277	0.265
	2.5	0.289	0.275
	3.0	—	0.282
	4.0	0.313	0.292
	5.0	0.335	0.298

* Calculated from equation (5).

Table 3 Oxidations of related compounds[a]

Compound	Acid form	k_{obs}/s^{-1}	pK_a[b]
ida	$\overset{+}{N}H_2(CH_2CO_2H)_2$	3.4×10^{-1}	1.82 2.84 9.79
Glyoxylic acid	$CHOCO_2H$	3.0×10^{-1}	2.98
Ethylenediamine	$\overset{+}{N}H_3CH_2CH_2\overset{+}{N}H_3$	2.5×10^{-1}	6.85 9.93
Glycine	$\overset{+}{N}H_3CH_2CO_2H$	1.8×10^{-1}	2.33 9.60
N,N'-H$_2$edda	$(\text{-}CH_2NH_2CH_2CO_2H)_2$	1.0×10^{-1}	6.48 9.57
Formaldehyde	HCHO	1.0×10^{-1}	—
Glyoxal	CHOCHO	2.4×10^{-2}	—
Glycolic acid	CH_2OHCO_2H	2.1×10^{-2}	3.62
Formic acid	HCO_2H	1.7×10^{-2}	3.75
Ammonia	$\overset{+}{N}H_4$	1.1×10^{-2}	9.24

[a] $[OH^-] = 1.2$ mol dm^{-3}, 25 °C, $I = 1.2$ mol dm^{-3}, $[L] = 1 \times 10^{-3}$ mol dm^{-3}. [b] Taken from Ref. 21.

10^{-11} mol dm^{-3}).[21] The dependence of the reaction rate on hydroxide is not expected to be related to the fractions of edta^{4-} and Hedta^{3-} anions unless the latter were much more reactive than the former anion. In that case, however, the increase in hydroxide concentration would cause a decrease (not increase, as observed) in the rate. The proposed mechanism is given by reactions (6)–(8). The corresponding rate law

$$[Ag(OH)_4]^- + edta^{4-} \xrightleftharpoons{K} [Ag(OH)_3(edta)]^{4-} + OH^- \quad (6)$$

$$[Ag(OH)_3(edta)]^{4-} \xrightarrow{k_1} Ag^I + \text{organic products} \quad (7)$$

$$[Ag(OH)_4]^- + edta^{4-} \xrightarrow{k_2} Ag^I + \text{organic products} \quad (8)$$

is as in equation (9). Comparison with the empirical rate law

$$k_{obs} = \frac{k_1K + k_2[OH^-]}{[OH^-] + K[edta^{4-}]}[edta^{4-}] \quad (9)$$

gives $K = C = 26.3 \pm 2.1$, $k_2 = B = 34.8 \pm 1.1$ dm^3 mol^{-1} s^{-1}, $k_1K = A = 4.38 \pm 0.57$ dm^3 mol^{-1} s^{-1} and $k_1 = A/C = 0.174 \pm 0.022$ s^{-1}.

In light of the probability (see above) that the two-electron intermediate is rapidly oxidised by a second $[Ag(OH)_4]^-$, we can write the sequence (7′), (8′) and (10) to account for the

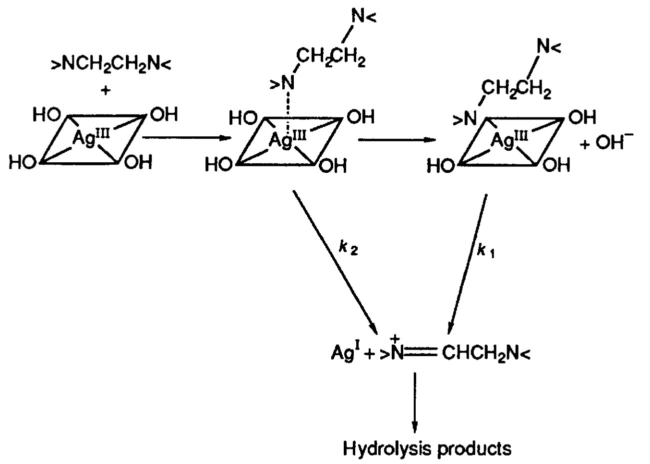
$$[Ag(OH)_3(edta)]^{4-} \xrightarrow{k_1'} Ag^I + \text{intermediate} + ida^{2-} \quad (7')$$

$$[Ag(OH)_4]^- + edta^{4-} \xrightarrow{k_2'} Ag^I + \text{intermediate} + ida^{2-} \quad (8')$$

$$[Ag(OH)_4]^- + \text{intermediate} \xrightarrow{\text{fast}} Ag^I + ida^{2-} + CHOCHO \quad (10)$$

production of glyoxal and 2 mol of ida. This treatment introduces a stoichiometric factor of 2 into the rate measurements,[22] so that $k_1' = \frac{1}{2}k$, and $k_2' = \frac{1}{2}k_2$.

Reaction (10) appears to be sufficiently fast that a constant stoichiometry is maintained throughout the range of the kinetic study. On the other hand, the reactions of $[Ag(OH)_4]^-$ with ida



Scheme 2

and other potential products must be sufficiently slow that these compounds will not be oxidised significantly under the kinetic conditions. In the experiments done with potential products and intermediates the concentrations were at least an order-of-magnitude higher than could be expected from the Ag^{III}–edta reaction. The observed rate constants (Table 3) indicate that, under kinetic conditions where edta was in at least one-hundred-fold excess, none of these compounds would be competitive.

Using the experimentally observed rate constants and assuming first-order behaviour in reductant concentration, numerical simulation (using the personal computer version of GEAR[23]) by path (a) confirms that, under kinetic conditions, essentially all of the nitrogen-containing product is ida with no production of either formaldehyde or ammonia. On the other hand, when $[edta]_0/[Ag(OH)_4^-]_0 = 1:1$, the calculated ida/glycinate production is in reasonable agreement with experiment (Table 1); small amounts of formaldehyde and ammonia are also predicted. The predicted number of $[Ag(OH)_4]^-$ ions consumed by each edta ranges from 6 to 2.2 when $[edta]_0/[Ag(OH)_4^-]_0$ changes from 0.14 to 7.9:1. By the time the ratio equals 50:1 (kinetic condition), each edta consumes 2 $[Ag(OH)_4]^-$; the simulated $[Ag(OH)_4]^-$ disappearance is strictly first order, and the simulated rate constants are close to those observed experimentally.

Since $[Ag(OH)_4]^-$ has square-planar geometry, like the analogous complexes of low-spin Cu^{III},[24] Au^{III},[25] Pt^{II} and Pd^{II},[26] the axial position is available for nucleophilic attack with the formation of a five-co-ordinated intermediate.[27] In the edta oxidation, the $edta^{4-}$ ion apparently interacts with the positive silver(III) centre. The fact that bond cleavage takes place at the ethylenediamine group rather than a carboxylate is an indication that co-ordination is at nitrogen rather than at oxygen as shown in Scheme 2. Electron transfer from a bound carboxylate would result in formaldehyde and CO_2 as shown in path (b) (Scheme 1). The charged Schiff base hydrolyses readily to amine and aldehyde,[28] followed by reaction with a second Ag^{III}.

During the oxidation of edta a fraction of $[Ag(OH)_4]^-$ was reduced to silver metal. Silver(I) does not readily oxidise edta, or its primary oxidation products (ida or glycinate), but it can react with aldehydes as in the Tollen's test. Silver metal has been detected after the oxidation of glycinate[12] and mandelic acid[29] by silver(III). The former gives ammonia and formaldehyde as products and the latter benzaldehyde. Metallic silver is also produced after the oxidation of ethylenediamine (to aminoacetaldehyde) at low excess of reductant.[30]

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