Kinetics and Mechanism of Oxidation of Nitrogen(III) by [Ethylenebis(biguanide)]silver(III) Cation and its Conjugate Bases in Aqueous Perchlorate Media

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The complex cation [ethylenebis(biguanide)]silver(III), $[Ag(H_2L)]^{3+}$, oxidised N^{III} quantitatively to N^V, being reduced to Ag^I. Free ethylenebis(biguanide) was recovered in near-quantitative yield. In the investigated pH range (1–7.5) the reaction is first order in [complex] and $[N^{III}]_T$. The reaction proceeds through four parallel paths: $[Ag(H_2L)]^{3+}$–HNO_2 (k_1), $[Ag(H_2L)]^{3+}$–NO_2^- (k_2), $[Ag(HL)]^{2+}$–NO_2^- (k_3) and $[AgL]^+$–NO_2^- (k_4), where $[Ag(HL)]^{2+}$ and $[AgL]^+$ are two conjugate bases of $[Ag(H_2L)]^{3+}$. The respective rate constants ($10^2\,k$ dm^3 mol^{-1} s^{-1}) are $k_1 = 2.4$, $k_2 = 42.5$, $k_3 = 11.4$ and $k_4 = 4.4$ at 30 °C and $I = 1.0$ mol dm^{-3} ($NaClO_4$). The associated $\Delta H^\ddagger$ values are all moderately low and $\Delta S^\ddagger$ are significantly negative. Nitrogen(III) reduces the silver(III) complex much faster than do alcohols and hydrogen peroxide. No silver(I)-catalysed path was detected. The present reactions appear to be outer sphere in nature.

Nitrous acid and its conjugate base, nitrite ion, have a rich redox chemistry both as an oxidant and a reductant. They react in either or both of these capacities with several metallic and non-metallic reagents.[1–10] Rapid acid–base equilibria cause solutions of nitrous acid to contain HNO_2, NO_2^- and NO^+. Moreover, such solutions are unstable and significant quantities of NO and NO_3^-, along with other species, may quickly develop. Many of these components of nitrous acid are quite reactive in electron transfer, so that the study of nitrogen(III) chemistry remains a fertile endeavour. Nevertheless, the only known example of N^{III} reacting with higher-valent silver species is the reaction of the tellurato and periodato complexes of Ag^{III} with NO_2^- in strongly alkaline media.[11] The cation [ethylenebis(biguanide)]silver(III), $[Ag(H_2L)]^{3+}$ is a rare example of a fully characterised,[12–17] authentic complex of silver(III), strongly stabilised by an acyclic N-donor ligand.[18] The in-plane ligand-field stabilisation is so extensive that the complex behaves as a milder oxidising agent than Ag^+.[19] 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 *ca.* 4.5. Moreover, recently we have observed that it is also soluble, though to a limited extent, at least up to pH 8.0 if alkali is added, carefully avoiding local excesses. This observation enabled us to study the reactivity of different silver(III) species connected through protic equilibria because, in spite of its high thermodynamic stability,[12] $[Ag(H_2L)]^{3+}$ oxidises various organic and inorganic molecules.[18,20–23] We have now observed that it can also oxidise N^{III} at a moderately fast rate and report herein the kinetics of reactions of the parent complex, and two of its conjugate bases with N^{III} in aqueous perchlorate media.

Experimental

Materials.—Pure crystals of [ethylenebis(biguanide)]silver(III) nitrate, were prepared by the known method[24] with a slight alteration in the recrystallisation procedure.[20]

All chemicals were of reagent grade. Solutions were prepared in double distilled, freshly boiled water. Solid $NaNO_2$ (G. R., E. Merck), recrystallised from hot aqueous ethanol, was the source of nitrite. The stock nitrite solutions were standardised against $KMnO_4$[25] and also spectrophotometrically.[26] Both yielded similar results (within 4%). These solutions were spectrophotometrically found to be stable for more than 24 h at ≈30 °C and at pH > 6.0. Sodium perchlorate (G. R., E. Merck) solutions were standardised as described earlier.[20] For deoxygenation of solutions chromium(II)-scrubbed N_2 gas was used.

Physical Measurements and Kinetics.—Solution spectra and absorbances were obtained on a Shimadzu Graphicord (UV-240) spectrophotometer. Rate measurements were usually made at an ionic strength $I = 1.0$ mol dm^{-3} ($NaClO_4$) and over the acidity and temperature range shown in the Results and Discussion. Some measurements were also made at $I = 0.2, 0.5, 0.7$ and 1.5 mol dm^{-3}. The kinetics was studied in the presence of $[N^{III}]_T$ [total nitrogen(III) concentration] at least ten times that of $[Ag^{III}]_T$ to ensure pseudo-first-order conditions; some reactions were also studied in the presence of added ethylenebis(biguanide) or $AgClO_4$ or $NaNO_3$. Most experiments were monitored at 420 nm, some at 450 or 480 nm. At these wavelengths only the silver(III) complex absorbs. The solution pH was adjusted with $HClO_4$ or NaOH as described earlier.[27] Although the measured pH is usually defined in terms of the activity of the hydrogen ion, we used the hydrogen-ion concentration by calibrating the pH electrode with analytically prepared solutions. No external buffer was used in the entire study in order to avoid possible complexation with Ag^{III} and because the pH drift observed during the reaction is very small (within 0.05 unit).

Data Analyses.—Plots of the logarithm of the absorbance at time t, log A_t, *versus* time t were shown to be linear for more than three half-lives of the reactions. Their slopes provided values for the pseudo-first-order rate constants (k_{obs}), which were computed using the built-in linear least-squares procedure of a Casio (model fx 3600 P) calculator. After the k_{obs} values had been measured for each set of specified reaction conditions, individual rate constants for each step of the proposed mechanism were estimated using the Lotus 123 spreadsheet.[28] With this program it was very easy also graphically to demonstrate the fit of each set of estimates to all variations studied. The solid curve in Fig. 1 represents the calculated data on the basis of the fit.

Table 1 Stoichiometric results for the oxidation of N^{III} by the silver(III) complex[a]

$[Ag^{III}]$/ mmol dm^{-3}	$[N^{III}]$/ mmol dm^{-3}	pH	$[N^{III}]$ left/ mmol dm^{-3}	$[Ag^{III}]$ left/ mmol dm^{-3}	$[NO_3^-]$ produced/ mmol dm^{-3}	$\frac{\Delta[N^{III}]}{\Delta[Ag^{III}]}$	$\frac{\Delta[N^{V}]}{\Delta[Ag^{III}]}$
0.4	0.8	2.0	0.41	0.00	0.42	0.98	1.05
0.4	1.8	3.0	1.36	0.00	0.43	1.10	1.08
0.5	1.0	3.8	0.52	0.00	0.46	0.96	0.92[b]
0.5	1.8	6.0	1.33	0.00	0.49	1.06	0.98[b]
1.0	0.5	3.6	0.00	0.48	0.56	0.96	1.08
1.5	1.0	7.0	0.00	0.56	1.06	1.06	1.09
					Average	1.02 ± 0.08	1.03 ± 0.11

[a] At 25 °C. No external $NaClO_4$ added. [b] Reaction media purged with purified dinitrogen.

Table 2 First-order rate constants for the oxidation of N^{III} by the silver(III) complex at I = 1.0 mol dm^{-3} ($NaClO_4$)

pH	$[N^{III}]_T$/ mmol dm^{-3}	$10^4 k_{obs}/s^{-1}$ 20.0	30.0	40.0 °C
1.0	3.0	0.36	0.85	1.80
1.2	3.0	0.40	0.90	2.00
1.5	3.0	0.50	1.1	2.35
1.7	3.0	0.63	1.3	2.85
2.0	3.0	0.80	1.75	4.0
2.3	3.0	1.2	2.7	6.4
2.5	3.0	1.6	3.5	8.75
2.8	3.0	2.3	5.0	11.6
3.0	3.0	2.8	6.0	14.1
3.3	3.0	3.35	7.25	16.7
3.5	3.0	3.50	7.45	17.0
3.8	3.0	3.25	7.0	16.0
4.0	3.0	2.90	6.40	14.5
4.35	3.0	2.35	5.25	11.5
4.75	3.0	1.85	4.20	9.0
5.0	3.0	1.6	3.85	8.0
5.3	3.0	1.5	3.5	7.25
5.7	3.0	1.3	3.1	6.40
6.0	3.0	1.15	2.75	5.75
6.3	3.0	1.0	2.4	5.0
6.6	3.0	0.80	2.0	4.20
7.0	3.0	0.66	1.65	3.65
7.5	3.0	0.56	1.45	3.25
1.0	10	1.1	2.95	5.85
1.0	30	3.45	9.0[a]	17.0
1.0	50	5.6	14.6	30.0
1.0	100	10.8	31.5	—
3.0	1.5	1.40	2.85	7.0
3.0	4.5	4.4	8.75	20.5
3.0	6.0	5.5	11.2	29.0
3.0	9.0	8.2	16.6	42.5
4.0	1.5	1.5	3.15[b]	7.35
7.0	5.0	1.15	2.8	6.0
7.0	9.0	2.05	5.0	11.4
7.0	15	3.15	8.1	18.0
7.0	25	5.55	13.6	30.7

[a] $10^4 k_{obs}$ = 11.5, 10.2, 9.5 and 8.2 s^{-1} at I = 0.2, 0.5, 0.7 and 1.5 mol dm^{-3} ($NaClO_4$) respectively. [b] $10^4 k_{obs}$ = 7.0, 5.15, 4.1 and 2.4 s^{-1} at I = 0.2, 0.5, 0.7 and 1.5 mol dm^{-3} ($NaClO_4$) respectively.

Stoichiometry Measurements.—The stoichiometry was measured under the kinetic conditions (excess of N^{III}) and also under the reverse condition (excess of Ag^{III}). Unspent N^{III} and the N^{V} produced in the reactions were quantified spectrophotometrically[26] after appropriate dilution, if necessary. The excess of Ag^{III} was measured spectrophotometrically at 350 nm (ε = 1160 dm^3 mol^{-1} cm^{-1} in 0.01 mol dm^{-3} $HClO_4$), where N^{V} does not interfere. The concentration of free H_2L was estimated as described earlier.[20]

Results and Discussion

Stoichiometry and Reaction Products.—Experiments both under the kinetic conditions and the reverse conditions indicated a 1:1 stoichiometry. More than 95% of free H_2L could be recovered and the formation of NO_3^- is quantitative over the entire pH range 1.0–7.5 (Table 1). The principal conversion may then be represented by equation (1).

$$[Ag(H_2L)]^{3+} + N^{III} \longrightarrow Ag^{I} + NO_3^- + H_2L \quad (1)$$

Kinetics.—No immediate spectral change is observed on mixing N^{III} with the silver(III) complex over the entire range of experimental pH and $[N^{III}]_T$ (1.5–100 mmol dm^{-3}). However, the absorbance at $\lambda \geqslant$ 420 nm, gradually decreases to less than 0.01. The pseudo-first-order rate constants, k_{obs}, defined by equation (2) were obtained as described before. Averages of the

$$-d[Ag^{III}]/dt = k_{obs}[Ag^{III}] \quad (2)$$

k_{obs} values from at least three runs were taken and individual runs were reproducible within 3%. Detailed data on the kinetics of the process were obtained as a function of pH, total nitrite ($[N^{III}]_T$), temperature (20–40 °C) and ionic strength (0.2–1.5 mol dm^{-3}). Some representative data are summarised in Table 2.

Over the entire pH range studied the reaction shows a clear first-order dependence on $[N^{III}]_T$ and there is no $[N^{III}]_T$-independent term. The following changes in the reaction conditions had, within the limits of experimental uncertainties, no influence on the values of k_{obs}: a five-fold variation in $[Ag^{III}]$ from 0.1 to 0.5 mmol dm^{-3}, addition of $AgClO_4$ (studied up to 0.01 mol dm^{-3}) and NO_3^- (up to 0.1 mol dm^{-3}), the presence or absence of dissolved oxygen and ambient light, and a variation in the monitoring wavelength in the range 420–480 nm.

No polymer is formed when 6% (v/v) acrylonitrile is added to the reaction mixture and the whole reaction course is EPR silent. There is thus no evidence for the formation of detectable amounts of free radicals or other paramagnetic species. However, one cannot conclude from this observation as to whether the reactions of Ag^{III} with N^{III} are one- or two-electron processes because NO_2, the likely one-electron transfer product, disproportionates at a nearly diffusion-controlled rate[29] and hence is not detectable.

A plot of k_{obs} *versus* pH has a bell shape (Fig. 1). Such a pH dependence indicates the involvement of two or more acid–base equilibria.[30] Considering the values for the acid dissociation constants of the complex in aqueous solution[31] (K_{a_1} and K_{a_2}) and K_a, the acid dissociation constant of HNO_2 (10^{-3} mol dm^{-3}),* the scheme in equations (3)–(9) provides a reasonable

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* This value was obtained by pH-metric titration of a 0.05 mol dm^{-3} $NaNO_2$ solution with $HClO_4$ in the presence of 1.0 mol dm^{-3} $NaClO_4$, and found to be independent of temperature in the range 20–40 °C and also of ionic strength 0.5–1.5 mol dm^{-3} ($NaClO_4$). The pK_a value (3.0 ± 0.1) agrees well with those reported under similar conditions. See, for example, refs. 32 and 33.

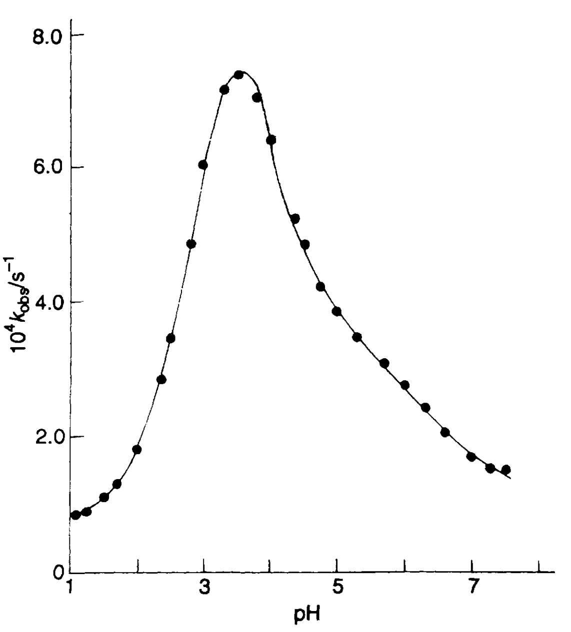

Fig. 1 Dependence of k_{obs} on pH. $[Ag^{III}]_T = 0.15$ mmol dm^{-3}, $[N^{III}]_T = 3.0$ mmol dm^{-3}, 30.0 °C, $I = 1.0$ mol dm^{-3}

Table 3 Second-order rate constants (in dm^3 mol^{-1} s^{-1}) and the corresponding activation parameters for the oxidation of N^{III} by the silver(III) complex *

T °C	10^2k_1	10^2k_2	10^2k_3	10^2k_4
20.0	1.0 ± 0.04	20.0 ± 0.5	4.9 ± 0.2	1.7 ± 0.05
30.0	2.4 ± 0.10	42.5 ± 1.8	11.4 ± 0.3	4.4 ± 0.1
40.0	5.0 ± 0.20	100 ± 3.5	23.2 ± 0.5	10.0 ± 0.3
$\Delta H^‡$/ kJ mol^{-1}	59 ± 4	59 ± 3	57 ± 5	65 ± 6
$\Delta S^‡$/ J K^{-1} mol^{-1}	−82 ± 8	−58 ± 6	−76 ± 9	−56 ± 7

* [complex] = 0.15 mmol dm^{-3}, $I = 1.0$ mol dm^{-3} ($NaClO_4$). The second-order rate constants were evaluated using pK_{a_1} = 3.8 and pK_{a_2} = 6.3 at all temperatures. See ref. 31.

$$[Ag(H_2L)]^{3+} \underset{}{\overset{K_{a_1}}{\rightleftharpoons}} [Ag(HL)]^{2+} + H^+ \qquad (3)$$

$$[Ag(HL)]^{2+} \overset{K_{a_2}}{\rightleftharpoons} [AgL]^+ + H^+ \qquad (4)$$

$$HNO_2 \overset{K_a}{\rightleftharpoons} NO_2^- + H^+ \qquad (5)$$

$$[Ag(H_2L)]^{3+} + HNO_2 \xrightarrow{k_1} \text{Products} \qquad (6)$$

$$[Ag(H_2L)]^{3+} + NO_2^- \xrightarrow{k_2} \text{Products} \qquad (7)$$

$$[Ag(HL)]^{2+} + NO_2^- \xrightarrow{k_3} \text{Products} \qquad (8)$$

$$[AgL]^+ + NO_2^- \xrightarrow{k_4} \text{Products} \qquad (9)$$

explanation for the kinetic observations. From these, expression (10) can be derived where the fraction of the complex present as $[Ag(H_2L)]^{3+}$ is given by equation (11) and the fraction of $[N^{III}]_T$ present as HNO_2 is given by (12). Equation (10) can be

$$k_{obs}/[N^{III}]_T = (k_1 + k_2K_a/[H^+])\alpha_1\alpha_2 + \\ (k_3 + K_{a_2}k_4/[H^+])(K_{a_1}K_a\alpha_1\alpha_2/[H^+]^2) \qquad (10)$$

$$\alpha_1 = \frac{[H^+]^2}{[H^+]^2 + K_{a_1}[H^+] + K_{a_1}K_{a_2}} \qquad (11)$$

$$\alpha_2 = [H^+]/(K_a + [H^+]) \qquad (12)$$

rearranged to the form $y = ax_1 + bx_2 + cx_3 + \ldots$, *etc.* and thus solved for a, b, $c \ldots$ with the help of the Lotus 123 spreadsheet. The kinetic parameters listed in Table 3 were calculated from a, b, $c \ldots$, *etc. i.e.* the coefficients of the dependent variables x_1, x_2, $x_3 \ldots$, *etc.* They reproduce all k_{obs} values within 5%.

Kinetic Evaluation of K_{a_2}.—For pH > 5.5, assuming $[N^{III}]_T \approx [NO_2^-]$ and that the k_1 and k_2 paths are absent, equation (10) reduces to (13). At every pH point > 5.5 and every

$$k_{obs}[H^+] = k_3[H^+][N^{III}]_T + K_{a_2}k_4[N^{III}]_T - k_{obs}K_{a_2} \qquad (13)$$

$[N^{III}]_T$ equations similar to (13) can be derived comprising the unknowns k_3, $K_{a_2}k_4$ and K_{a_2}. This group of simultaneous equations was then reduced to three normal equations using Gauss's method[34] (giving equal weights to all equations) and solved by a matrix or iteration method. The values of k_3, k_4 and K_{a_2} thus obtained at 20 °C are 5.10 × 10^{-2} dm^3 mol^{-1} s^{-1}, 1.60 × 10^{-2} dm^3 mol^{-1} s^{-1} and 5.43 × 10^{-7} mol dm^{-3} respectively. The excellent agreement of the kinetically determined value of K_{a_2} with its spectrophotometric value supports the proposed scheme.

Mechanism.—The observed sequence $k_1 < k_2 > k_3 > k_4$ indicates that protonation of the oxidant increases its reactivity whereas the opposite is true for protonation of the reductant. The vast majority of other known redox systems also follow a similar trend.[35,36] The trend $k_1 < k_2$ was observed earlier for alcohols (ROH, R = Et, Pr^i or $PhCH_2$)[22] and hydrogen peroxide,[21] all being kinetically less active than their corresponding conjugate bases, *viz.* RO^- and HO_2^-, towards $[Ag(H_2L)]^{3+}$.

We have not considered reactions of HNO_2 with $[Ag(HL)]^{2+}$ and $[AgL]^+$ in the proposed scheme because the concentrations of both complexes are very small in the pH range where $[HNO_2]$ is significant and we presume that HNO_2 is kinetically less active than NO_2^- not only towards $[Ag(H_2L)]^{3+}$ but also towards $[Ag(HL)]^{2+}$ and $[AgL]^+$.

It might be mentioned here that H_3PO_3 reduces $[Ag(H_2L)]^{3+}$ only very slowly[18] in spite of the higher thermodynamic reducing power of P^{III} than of N^{III}.[37] Probably, slow tautomerisation[38] of normal $OPH(OH)_2$ to the active three-co-ordinated $\dot{P}(OH)_3$ is the bottleneck in the reaction of H_3PO_3 with $[Ag(H_2L)]^{3+}$. The reaction of H_3PO_3 with $[Ag(OH)_4]^-$ is also slow.[39] However, there is no indication of any reaction of $[Ag(OH)_4]^-$ with NO_2^- even at $[NO_2^-] = 1.0$ mol dm^{-3}.[39] The thermodynamic oxidising strength[40] of $[Ag(OH)_4]^-$ is greater than that of $[Ag(H_2L)]^{3+}$. Its failure to oxidise NO_2^- may be due to the unfavourable charge interaction between $[Ag(OH)_4]^-$ and NO_2^-. Since N^{III} has no vacant acceptor orbital, an oxygen-atom-transfer path is equally unlikely for $[Ag(OH)_4]^-$ and $[Ag(H_2L)]^{3+}$. The reaction of $[Ag(H_2L)]^{3+}$ with NO_2^- and even HNO_2 is also faster than those of the stronger reductants[37] H_2O_2 and alcohols. This is unexpected if N^{III}, H_2O_2 and alcohols all follow a similar mechanism. The inner-sphere path, earlier established for H_2O_2 and alcohols, therefore seems unlikely for N^{III}.

In reactions of N^{III} in acidic media NO might be produced and has sometimes been considered as a reductant.[7,41,42] However, we could not detect any reaction path involving NO which would require a $[HNO_2]^2$ term in the rate law. The equilibrium constant of reaction (14) is small (6.0×10^{-6}),[43]

$$2\,HNO_2 \rightleftharpoons NO + NO_2 + H_2O \qquad (14)$$

and under the reaction conditions adopted in this investigation the maximum [NO] is *ca.* 10^{-4} mol dm^{-3} and such low [NO] might be a major reason why any possible NO path evaded its detection. Also, it is known that NO_2 disproportionates in aqueous solution almost at a diffusion-controlled rate (1.0×10^8 dm^3 mol^{-1} s^{-1})[29] and hence cannot directly reduce Ag^{III}.

No reducing action of NO^+ is known to our knowledge, though it is a well known oxidant[43–46] generated through equation (15) having a small equilibrium constant (3.0×10^{-7}

$$HNO_2 + H^+ \rightleftharpoons NO^+ + H_2O \qquad (15)$$

dm^3 mol^{-1}).[47] In the present case also the absence of a third-order term $[Ag(H_2L)]^{3+}[HNO_2][H^+]$ in the rate law rules out NO^+ as a reducing agent.

The Question of Diazotisation.—Some arylbiguanides[48,49] and acid-stable biguanide complexes[50,51] of Pt^{II}, Pd^{II} and Au^{I} are known to react with HNO_2 in strongly acidic media plausibly *via* NO^+, NO, N_2O_3, *etc.* No such reactions occur here as evidenced from the lack of an immediate spectral change and the almost complete recovery of the ligand at the end of the reactions. Species responsible for diazotisation occur at very low concentrations under the present reaction conditions and plausibly no such reactions could occur.

Significance of $\Delta H^‡$ *and* $\Delta S^‡$.—All the reaction paths k_1 to k_4 are associated with moderately low $\Delta H^‡$ and significantly negative $\Delta S^‡$ which might indicate that only moderate work is necessary to bring the reactants to within reacting distance and that a fairly compact transition state is formed by charge interaction and/or hydrogen bonding.

Oxidation reactions of $[Ag(H_2L)]^{3+}$ with HCO_2H,[20] $N_2H_5^+$[23] and H_3PO_3[18] were found to be strongly catalysed by Ag^+ through Ag^+–Ag^0 catalytic cycles. No such catalysis is observed here because N^{III} cannot reduce Ag^+ to Ag^0 due to the high thermodynamic requirements and no efficient inner-sphere path is available since specific covalent bonding is at best weak in the $Ag^{I}\cdot N^{III}$ adduct.

The first-order rate constants, k_{obs}, increase with decreasing ionic strength as might be expected for reactions between oppositely charged species. The effect is minimum at pH 1 (see footnote *a* to Table 2) where the $[Ag(H_2L)]^{3+}$–HNO_2 (k_1) path is dominant.

Conclusion

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^{III}, alcohols, ascorbic acid and Fe^{2+}(aq)[52] by this complex. The catalysed path involves a Ag^+–Ag^0 cycle (for HCO_2H, $N_2H_5^+$ and H_3PO_3) or a Ag^{I}–Ag^{II} cycle (for H_2O_2). Which of these paths, catalysed or uncatalysed, predominates depends on a critical balance of thermodynamic and kinetic factors, but grossly speaking the catalysed path dominates when the thermodynamic reducing strength of the reductant is high and/or the reductant is a poor ligand for Ag^{III}.

As expected, deprotonation of the oxidant $[Ag(H_2L)]^{3+}$ decreases its reactivity towards an anionic reductant. The reductant, on the other hand, becomes less powerful on protonation. In the reactions with N^{III} only two reaction paths, *viz.* $[Ag(H_2L)]^{3+}$–HNO_2 (k_1) and –NO_2^- (k_2), are kinetically significant in the range pH 1.0–3.0; at higher pH 5.5–7.5, detectable reaction paths are $[Ag(HL)]^{2+}$–NO_2^- (k_3) and $[AgL]^+$–NO_2^- (k_4). All the reaction paths k_1–k_4 are plausibly outer-sphere processes. The species NO, NO_2 or NO^+ do not consume Ag^{III} and diazotisation of the bound ligand, H_2L, does not occur throughout the range of reaction conditions employed. It cannot be concluded at this stage whether the reaction involves one- or two-electron changes.

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References

1 M. T. Beck, L. Dozsa and I. Shilassy, *J. Indian Chem. Soc.*, 1974, **51**, 6.
2 J. H. Ridd, *Adv. Phys. Org. Chem.*, 1978, **6**, 1.
3 G. Stedman, *Adv. Inorg. Chem. Radiochem.*, 1979, **22**, 143.
4 J. C. Fanning, *Coord. Chem. Rev.*, 1991, **110**, 235.
5 M. R. Rhodes, M. H. Barley and T. J. Mayer, *Inorg. Chem.*, 1991, **30**, 629.
6 K. S. Suslik and R. A. Watson, *Inorg. Chem.*, 1991, **30**, 912.
7 M. M. deMaine and D. M. Stanbury, *Inorg. Chem.*, 1991, **30**, 2104.
8 K. Tanaka, N. Komeda and T. Matsui, *Inorg. Chem.*, 1991, **30**, 3282.
9 D. W. Johnson and D. W. Margerum, *Inorg. Chem.*, 1991, **30**, 4845.
10 K. Y. Lee, C. Amatora and J. K. Kochi, *J. Phys. Chem.*, 1991, **95**, 1285.
11 See, J. Colombeau, *Bull. Soc. Chim. Fr.*, 1955, 323.
12 D. Sen, N. N. Ghosh and P. Ray, *J. Indian Chem. Soc.*, 1950, **27**, 619.
13 P. Ray, *Nature (London)*, 1943, **151**, 643.
14 N. R. Kunchur, *Nature (London)*, 1968, **217**, 539.
15 M. L. Simms, J. L. Atwood and D. A. Zatko, *J. Chem. Soc., Chem. Commun.*, 1973, 46.
16 L. Coghi and G. Pellizzi, *Acta Crystallogr., Sect. B*, 1975, **31**, 131.
17 D. A. Zatko and J. W. Prather, *J. Electron Spectrosc. Relat. Phenom.*, 1973, **2**, 191.
18 R. Banerjee, R. Das and S. Mukhopadhyay, *J. Chem. Soc., Dalton Trans.*, 1992, 1317.
19 K. Das, R. Banerjee, A. Das and S. Dasgupta, *Bull. Electrochem.*, 1989, **5**, 477.
20 R. Banerjee, K. Das, A. Das and S. Dasgupta, *Inorg. Chem.*, 1989, **28**, 585.
21 R. Banerjee, A. Das and S. Dasgupta, *J. Chem. Soc., Dalton Trans.*, 1989, 1645.
22 R. Banerjee, A. Das and S. Dasgupta, *J. Chem. Soc., Dalton Trans.*, 1990, 1207.
23 R. Banerjee, A. Das and S. Dasgupta, *J. Chem. Soc., Dalton Trans.*, 1990, 2271.
24 P. Ray and N. C. Chakravarty, *J. Indian Chem. Soc.*, 1944, **21**, 47; P. Ray, *Inorg. Synth.*, 1960, **6**, 74.
25 A. I. Vogel, *Quantitative Inorganic Analysis*, English Language Book Society, London, 3rd edn., 1961, ch. 3, p. 297.
26 J. H. Wetters and K. L. Uglum, *Anal. Chem.*, 1970, **42**, 335.
27 S. Mukhopadhyay and R. Banerjee, *J. Chem. Soc., Dalton Trans.*, 1993, 933.
28 C. Gorgenson, *Mastering 123*, SYBEX(USA) (Indian edn.), BPB Publications, New Delhi, 1986.
29 Y. N. Lee and S. E. Schwartz, *J. Phys. Chem.*, 1981, **85**, 840.
30 R. G. Wilkins, *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes*, Allyn and Bacon, Boston, 1974, ch. 1, p. 46.
31 S. Mukhopadhyay and R. Banerjee, *Polyhedron*, in the press.
32 P. Lumme and J. Tummavuori, *Acta Chem. Scand.*, 1965, **19**, 617.
33 V. Zang and R. van Eldik, *Inorg. Chem.*, 1990, **29**, 4462.
34 J. B. Scarborough, *Numerical Mathematical Analysis*, 6th edn., John Hopkins Press, Baltimore, 1966, ch. 12.
35 S. K. Ghosh, R. N. Bose and E. S. Gould, *Inorg. Chem.*, 1987, **26**, 2688.
36 K. D. Asmus, M. Bonifacie, P. Toffel, P. O'Neill, D. S. Frohlinde and S. Steenken, *J. Chem. Soc., Faraday Trans. 1*, 1978, 1820.
37 W. M. Latimer, *The Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd edn., Prentice-Hall, Englewood Cliffs, NJ, 1952.

38 A. Viste, D. A. Holm, P. L. Wang and D. G. Veith, *Inorg. Chem.*, 1971, **10**, 631.
39 L. J. Kirschenbaum, I. Kouadio and E. Mentasti, *Polyhedron*, 1989, **8**, 1299.
40 E. T. Borish, L. J. Kirschenbaum and E. Mentasti, *J. Chem. Soc., Dalton Trans.*, 1985, 1789.
41 M. S. Ram and D. M. Stanbury, *J. Am. Chem. Soc.*, 1984, **106**, 8136.
42 V. Zang, M. Kotowski and R. van Eldik, *Inorg. Chem.*, 1988, **27**, 3279.
43 M. S. Ram and D. M. Stanbury, *Inorg. Chem.*, 1985, **24**, 2954.
44 P. Reveco and G. Stedman, *Z. Anal. Chem.*, 1979, **295**, 252.
45 J. C. Bates, P. Reveco and G. Stedman, *J. Chem. Soc., Dalton Trans.*, 1980, 1487.
46 S. P. Schmidt, F. Basolo and W. C. Trogler, *Inorg. Chim. Acta*, 1987, **131**, 181.
47 N. S. Bayliss, R. Dingle, D. W. Watts and R. J. Wilkie, *Aust. J. Chem.*, 1963, **16**, 927.
48 F. H. S. Curd, D. G. Davey and D. N. Richardson, *J. Chem. Soc.*, 1949, 1732.
49 P. Ray, *Chem. Rev.*, 1961, **61**, 313.
50 D. Sen and C. R. Saha, *J. Chem. Soc., Dalton Trans.*, 1976, 776.
51 D. Sen and C. R. Saha, *J. Indian Chem. Soc.*, 1977, **54**, 127.
52 R. Banerjee, unpublished work.

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