Kinetics of Silver(I)-catalysed Oxidation of Hydrazinium Ion by the [Ethylenebis(biguanide)]silver(III) Cation

Rupendranath Banerjee,* Amitava Das, and Subrata Dasgupta
Department of Chemistry, Jadavpur University, Calcutta 700032, India

Silver(I) strongly catalyses the quantitative oxidation of hydrazine to dinitrogen by the complex [ethylenebis(biguanide)]silver(III), $[Ag(H_2L)]^{3+}$. In the range pH 2—3 the reaction follows the rate law (i)

$$-d[\text{complex}]/dt = k^0 = 2K_1k_1[Ag^+]^2[N_2H_5^+]/[H^+] \qquad (i)$$

where k^0 is the observed zero-order rate constant for large excess of Ag^+, H^+, and $N_2H_5^+$ over the complex. Values of $10^4 K_1k_1$ were 2.22 ± 0.16, 4.1 ± 0.25, 7.17 ± 0.5, and 12.5 ± 0.8 $dm^3 mol^{-1} s^{-1}$ at 15, 20, 25, and 30 °C. Corresponding $\Delta H^‡$ and $\Delta S^‡$ values are 82 ± 8 kJ mol^{-1} and −8 ± 2 J $K^{-1} mol^{-1}$ respectively. Under experimental conditions where Ag^{II} is detectable in concentrations less than about 10^{-6} mol dm^{-3}, the whole reaction course is e.p.r. silent. No evidence for the formation of any radical intermediate is available. Apparently, a Ag^I–Ag^0 catalytic cycle is involved wherein Ag^+ slowly oxidises hydrazine of $[Ag(N_2H_4)]^+$, with use of the complex as an oxidant which rapidly regenerates Ag^+ from $Ag^0{}_2$ formed as an intermediate.

Hydrazine is a powerful reducing agent[1] whose thermodynamic reducing strength depends on the media acidity and oxidation products.[2] It is generally oxidised to dinitrogen by two-equivalent oxidants whereas one-equivalent oxidants generally produce a mixture of ammonia and dinitrogen.[2–7] Occasionally, hydrazoic acid is also formed[2,8] but the exact conditions necessary for this are not known.

Several kinetic investigations on redox reactions involving hydrazine has so far been attempted.[2–13] They include reactions with coinage metal ions, Cu^{II}, Ag^I, and Au^{III}. However, besides an observation that reactions of hydrazine with higher-valent silver are rapid,[13] no kinetic data have been reported on the reaction of hydrazine with this species. The involvement of such species has, however, been anticipated in the Ag^+-catalysed oxidation of hydrazine by peroxodiphosphate[9] and peroxodisulphate,[13] but the question of the detailed mechanism still seems open. A kinetic investigation of the oxidation of hydrazine by an authentic, isolable silver(III) species thus appeared interesting and the present study was therefore initiated.

The complex [ethylenebis(biguanide)]silver(III) perchlorate $[Ag(H_2L)][ClO_4]_3$ (Figure) is a rare example of an authentic[14–19] cationic complex of Ag^{III} extensively stabilised[20] (log ≈ 10^{52}) by an acyclic ligand environment and in acid solution it is reasonably resistant to autodecomposition.[19,21,22]

Experimental

Materials.—A dilute solution of hydrazine hydrate (G.R., E. Merck) was neutralised with dilute perchloric acid (G.R., E. Merck) and the resultant hydrazinium perchlorate, $[N_2H_5]ClO_4$, solution was standardised by cerium(IV) oxidimetry[23] as catalysed by Br^-.

Pure diamagnetic crystals of [ethylenebis(biguanide)]silver(III) nitrate, $[Ag(H_2L)][NO_3]_3$, were prepared by a known method.[19,22]

Whenever necessary, dispersions of Ag^0 were freshly prepared by heating a solution of $AgNO_3$ with hydrazinium perchlorate. The precipitate thus obtained was filtered off and repeatedly washed with water. All other materials were as used previously.[19,22,24]

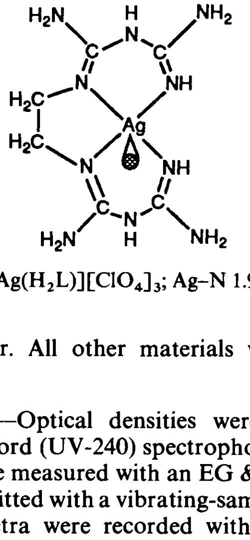

Figure. Structure of $[Ag(H_2L)][ClO_4]_3$; Ag–N 1.97 Å

Instrumentation.—Optical densities were measured on a Shimadzu Graphicord (UV-240) spectrophotometer. Magnetic susceptibilities were measured with an EG & G PAR magnetometer (model 155) fitted with a vibrating-sample magnetometer. *X*-Band e.p.r. spectra were recorded with a Varian EPR 4 spectrometer at varying stages of the reaction under conditions where less than about 10^{-6} mol dm^{-3} $[Ag(bipy)_2]^{2+}$ (bipy = 2,2′-bipyridine) was detectable.[19,22,25] Microanalytical data (C, H, N) were obtained with a Perkin-Elmer model 240C elemental analyser. A Systronics (model 335, India) digital pH meter having a combined glass–calomel electrode assembly was utilised for pH measurements.

Product Analysis and Stoicheiometry.—The analyses were carried out on product solutions obtained after all $[Ag(H_2L)]^{3+}$ had been consumed (optical density ⩽ 0.01 at 380 nm) under kinetic conditions. Immediately after completion of the reaction, all Ag^+ was precipitated as AgCl and removed by filtration. From the filtrate, the free ligand, ethylenebis(biguanide), was quantitatively isolated as the sparingly soluble [ethylenebis(biguanide)]copper(II) sulphate.[19,26] In separate experiments, hydrazine was determined spectrophotometrically with the use of *N,N*′-dimethylaminobenzaldehyde as the colour-forming reagent.[27]

Kinetic Measurements.—Disappearance of the silver(III) complex $[Ag(H_2L)]^{3+}$ was generally followed at 380 nm, its near-u.v. maximum (ε = 1 175 $dm^3\ mol^{-1}\ cm^{-1}$). Occasionally, the reaction was followed also at 480 nm. At both of these wavelengths the complex cation is the only absorbing species. The reaction temperature was controlled to within 0.1 °C and ionic strength was maintained at 1.0 mol dm^{-3} by addition of $NaClO_4$. A large excess of $AgClO_4$, hydrazine, and $HClO_4$ over the complex was used. Under such conditions the reaction was found to be zero order in [complex]. The zero-order rate constant $\{k^0 = -\text{slope of plots of [complex]}_t \text{ against time } (t)\}$ was evaluated from the slope (B) of the absorbance (A_t) *vs.* time (t) data and the known ε value [19] ($k^0 = -B/\varepsilon$) of the complex at the experimental pH. For this purpose the built-in linear least-squares program of a Casio (model fx-3600P) scientific calculator was utilised. Errors associated with kinetic parameters were estimated by using standard formulae and procedures. Average values of at least two independent determinations of k^0 were taken; values obtained under different reaction conditions are given in Table 1.

Results and Discussion

Preliminary Observations.—Within the range of acidity investigated, oxidation of hydrazine by the complex cation is insignificant and the rate is comparable to the autodecomposition rate of the complex. Silver(I) strongly catalyses the process. Thus at 30 °C, in the presence of 0.005 mol dm^{-3} hydrazine at pH 2.5, the initial absorbance of a 0.2 mmol dm^{-3} complex solution decreases by only 5% in the first hour. Under conditions otherwise the same but in the presence of 0.002 mol dm^{-3} $AgClO_4$, 70% of the complex is reduced within 1 h. The catalysis is strongly inhibited, however, by an increase in $[H^+]$ and practically ceased when $[H^+] \geqslant 0.05$ mol dm^{-3}. On the other hand, above pH 3.0 the catalysed reaction was too rapid to be followed by conventional spectrophotometry and precipitation of metallic silver interferes with kinetic measurements; the solubility of the complex also sharply decreases. These problems were absent at lower pH. We, therefore, had to select a rather narrow pH range (2—3) for the investigation. No external buffer was used 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 reaction did not change by more than 0.05 units.

Stoicheiometry.—In the experimental pH range, hydrazine should be mostly (99.9%) in the form $N_2H_5^+$. The average of three independent measurements of the consumption ratio, $|\Delta[Ag^{III}]|/|\Delta[\text{hydrazine}]|$ was 1.9 ± 0.1; 99 ± 2% of the free ligand, H_2L, was recovered from reaction media as the copper(II) complex. Ammonia was not detectable by Nessler's test. The stoicheiometric equation within the limits of experimental uncertainty thus appears to be (1). Addition of

$$2[Ag(H_2L)]^{3+} + N_2H_5^+ \longrightarrow 2Ag^+ + H_2L + N_2 + 5H^+ \quad (1)$$

$Fe(ClO_4)_3$ to the reaction media or holding $Fe(ClO_4)_3$-impregnated paper at the mouth of the reaction vessel during the reaction did not produce the characteristic red colour of iron(III) azide complex. This observation and the stoicheiometric results suggest that no significant amount of HN_3 is produced in the reaction of $[Ag(H_2L)]^{3+}$ with hydrazine.

Kinetic Results.—Dependence of rate on complex concentration. The rate constant k^0 was found to be independent of initial [complex]. Thus at 30 °C, in the presence of 0.007 mol dm^{-3} hydrazine and 0.002 mol dm^{-3} Ag^+ at pH 2.9, k^0 = (5.5 ± 0.3) × 10^{-8} mol $dm^{-3}\ s^{-1}$ for a range of [complex] varying from 0.1 to 0.4 mmol dm^{-3}.

Dependence on silver(I). Replacement of Na^+ (used as $NaClO_4$ for maintaining ionic strength) by Ag^+ appreciably increases k^0. Thus at 30 °C, with 0.005 mol dm^{-3} hydrazine at pH 2.5, $10^8\ k^0$ increases from 1.2 to 14.5 mol $dm^{-3}\ s^{-1}$ when $[Ag^+]$ is increased from 1.0 to 3.5 mmol dm^{-3}. Plots of k^0 against $[Ag^+]^2$ at all temperatures are good straight lines with finite slopes (m_1 say) and negligible intercepts.

Hydrazine and acid dependence. Plots of k^0 against [hydrazine] at fixed $[H^+]$ and $[Ag^+]$, against $1/[H^+]$ at fixed [hydrazine] and $[Ag^+]$, and against $[\text{hydrazine}]/[H^+]$ at fixed $[Ag^+]$ are good straight lines passing through the origin. Slopes of plots of k^0 against $[Ag^+]^2$ (m_1) and against $[\text{hydrazine}]/[H^+]$ (m_2) at different temperatures are collected in Table 2 wherefrom the experimental rate law (2) may be verified (see

$$-\frac{d[\text{complex}]}{dt} = k^0 = k[Ag^+]^2\,[\text{hydrazine}]/[H^+] \quad (2)$$

Appendix). Values of k^0 calculated from this relation agreed within 10% of the experimental k^0 (see Table 1) which itself is reproducible in duplicate runs within 5%.

Effect of other parameters. It has been found that k^0 is independent of purging of the reaction solution with purified dinitrogen, the presence or complete absence of ambient light, and change in monitoring wavelength from 380 to 480 nm (see Table 1).

E.p.r. experiments. Under the experimental conditions, where Ag^{II} is detectable in concentrations less than about 10^{-6} mol dm^{-3}, the whole reaction course is e.p.r. silent.

Polymerisation experiment. Some reactions were carried out in the presence of 5% (v/v) acrylonitrile. No polymerisation was visible within the time required for completion of the reaction, and k^0 was not appreciably affected by the addition of acrylonitrile (see Table 1).

Mechanism.—Reduction of the complex is extremely slow when either Ag^+ or hydrazine is absent. We observed that, in the experimental pH range, Ag^+ is slowly reduced by hydrazine and a faint blackish suspension of Ag^0 appears within a few hours. This was more prominent at higher pH, higher [hydrazine], and higher $[Ag^+]$. However, in the presence of the silver(III) complex no turbidity or blackening was noticeable at the experimental pH. Apparently, this complex oxidised any Ag^0 formed in the media and regenerated Ag^+ at a rate faster than the production of Ag^0; direct oxidation of hydrazine by the complex appears insignificant. We also observed that addition of freshly precipitated Ag^0 enhances perceptibly the rate of reduction of an acidified solution of the complex alone. There is no spectral (u.v.–visible) or kinetic evidence for hydrazine binding to the complex. From these observations the Scheme is proposed as a likely reaction sequence.

$$Ag^+ + N_2H_5^+ \xrightleftharpoons{K_1} [Ag(N_2H_4)]^+ + H^+ \quad (3)$$

$$[Ag(N_2H_4)]^+ + Ag^+ \xrightarrow{k_1} 2Ag^0 + N_2H_3^+ + H^+ \quad (4)$$

$$2Ag^0 \xrightleftharpoons{\text{fast}} Ag^0{}_2 \quad (5)$$

$$N_2H_3^+ \xrightarrow{\text{fast}} \tfrac{1}{2}N_2H_5^+ + \tfrac{1}{2}N_2 + \tfrac{1}{2}H^+ \quad (6)$$

$$N_2H_3^+ + 2Ag^+ \xrightarrow{\text{fast}} N_2 + Ag^0{}_2 + 3H^+ \quad (7)$$

$$Ag^0{}_2 + Ag^{III} \xrightarrow{\text{fast}} 3Ag^I \quad (8)$$

Scheme.

Table 1. Values of k^0 under different reaction conditions. [complex] = 0.2 mmol dm^{-3}, I = 1.0 mol dm^{-3} ($NaClO_4$)

Temp. (°C)	$10^3[Ag^+]$/mol dm^{-3}	pH	$10^3[N_2H_5^+]$/mol dm^{-3}	$\frac{[N_2H_5^+]}{[H^+]}$	$10^8\,k^0$/mol dm^{-3} s^{-1}	
					Exptl.	Calc.
15	5.0	2.7	4.0	2.00	2.25	2.21
			6.0	3.00	3.17	3.32
			7.0	3.51	3.83	3.90
			7.5	3.76	4.18	4.14
			9.0	4.51	4.88	5.00
			10.0	5.01	5.50	5.51
		2.1	6.0	0.755	0.75	0.80
		2.3		1.20	1.33	1.32
		2.6		2.40	2.50	2.64
		2.9		4.77	5.17	5.25
		3.0		6.00	6.67	6.65
	2.0	2.7		3.00	0.50	0.53
	2.5				0.77	0.82
	3.0				1.20	1.19
	4.0				2.20	2.11
20	4.0	2.6	2.0	0.80	1.08	1.04
			3.0	1.19	1.58	1.56
			3.5	1.39	1.83	1.82
			4.0	1.59	2.25	2.08
			6.0	2.39	3.17	3.13
			7.0	2.79	3.67	3.66
			7.5	2.98	4.00	3.90
			9.0	3.58	4.50	4.70
		2.0	8.0	0.80	1.10	1.05
		2.2		1.27	1.67	1.66
		2.3		1.60	2.08	2.10
		2.5		2.53	3.33	3.32
		2.7		4.00	5.33	5.25
		2.9		6.35	8.20	8.33
	2.0	2.5		2.53	0.91	0.83
	2.5				1.25	1.29
	3.0				1.83	1.86
	5.0				5.33	5.18
25	4.0	2.7	2.0	1.00	2.31	2.29
			4.0	2.00	4.58	4.58
			5.5	2.76	6.25	6.33
			6.0	3.00	7.08	6.88
			8.0	4.01	9.08	9.20
			9.0	4.51	10.50	10.30
			10.0	5.01	11.33	11.50
		2.1	6.0	0.75	1.75	1.73
		2.3		1.20	2.50	2.75
		2.4		1.51	3.50	3.46
		2.6		2.40	5.67	5.50
		2.9		4.77	11.09	10.90
		3.0		6.00	13.83	13.70
	1.0	2.7	6.0	3.00	0.45	0.43
	2.0				1.73	1.72
	3.0				3.92	3.87
	4.0				7.10	6.80
	5.0				10.92	10.70
30	2.0	2.9	2.0	1.59	1.58	1.59
			3.0	2.38	2.34	2.38
			4.0	3.18	3.00	3.18
			4.5	3.57	3.62	3.57
			5.5	4.37	4.33	4.37
			6.5	5.16	5.17	5.16
			7.0	5.56	5.50	5.56
			8.0	6.35	6.00	6.35
			10.0	7.94	8.00	7.94
	2.0	2.2	6.0	0.95	1.00	0.95
		2.4		1.51	1.55	1.51
		2.6		2.39	2.33	2.39
		2.75		3.37	3.42	3.37
		2.9		4.76	4.75	4.76

Table 1 (*continued*)

Temp. (°C)	$10^3[Ag^+]$/mol dm^{-3}	pH	$10^3[N_2H_5^+]$/mol dm^{-3}	$\frac{[N_2H_5^+]}{[H^+]}$	$10^8 k^0$/mol dm^{-3} s^{-1} Exptl.	$10^8 k^0$/mol dm^{-3} s^{-1} Calc.
30	2.0	3.1	6.0	7.55	7.67	7.55
	1.0	2.9		4.76	1.18	1.19
	1.5				2.67	2.68
	2.5				7.42	7.44
	3.0				9.05	9.00
	3.5				14.55	14.60

Table 2. Values of m_1 and m_2 at different temperatures

Temp. (°C)	$10^3 m_1{}^a$/ dm^3 mol^{-1} s^{-1}	$10^8 m_2{}^b$/ mol dm^{-3} s^{-1}
15	1.24	1.106
20	2.14	1.305
25	4.37	2.3
30	11.83	1.00

[a] For evaluation of m_1, [hydrazine]/[H$^+$] and temperature respectively are: 3.00, 15; 2.53, 20; 3.00, 25; and 4.76, 30 °C. [b] For evaluation of m_2, [Ag$^+$] and temperature respectively are: 0.005, 15; 0.004, 20; 0.004, 25; and 0.002 mol dm^{-3}, 30 °C.

Table 3. Values of K_1k_1 at four different temperatures

Temp. (°C)	15	20	25	30
$10^4K_1k_1$/ dm^3 mol^{-1} s^{-1}	2.22 ± 0.16	4.1 ± 0.25	7.17 ± 0.5	12.5 ± 0.8

Protonated diazene $N_2H_3^+$ is a well established[2,6,8,10,28] intermediate in the oxidation of $N_2H_5^+$ to N_2. It may be further oxidised by additional Ag$^+$. Reaction (7) most probably occurs in steps. In this scheme the rate of decay of the silver(III) complex should be equal to the rate of decay of $[Ag(N_2H_4)]^+$ and one obtains the observed rate law (2) with $k = 2K_1k_1$, provided $[H^+] \gg K_1[N_2H_5^+]$. The equilibrium constant[12] for the formation of $[Ag(N_2H_4)]^+$ from Ag$^+$ and N_2H_4 is 1 700 dm^3 mol^{-1}. This when coupled with the acid dissociation constant ($K_a = 10^{-8}$ mol dm^{-3}) of $N_2H_5^+$ gives $K_1 = 1.7 \times 10^{-5}$ and the inequality seems justified.

In the Scheme, formation of the Ag^0_2 dimer has been conceived to avoid the improbable termolecular step (9).

$$2Ag^0 + Ag^{III} \longrightarrow 3Ag^I \qquad (9)$$

Dimeric Ag^0_2 has been observed in a radiolytic study[29] and is a likely precursor of the silver sols formed when reducing agents are added to silver(I) salts.[30] In presence of the silver(III) complex such dimers cannot probably coagulate further. Rather, they are quickly oxidised to Ag^I. At higher pH the formation of Ag^0 and its subsequent coagulated form may be more rapid than their reoxidation by Ag^{III}. Precipitation of metallic silver therefore interferes with kinetic measurements at higher pH. Solubility data for Ag^0_2 are not available. However, in aqueous media metallic silver is slightly soluble and exerts a lethal effect upon lower life forms.[19,31] This suggests that silver metal in the form of small clusters of Ag atoms (Ag^0_2 for example) should have some solubility in water.

The comproportionation reaction (8) may be replaced by a combination of the two consecutive reactions (10) and (11)

$$Ag^{III} + Ag^0 \longrightarrow Ag^{II} + Ag^I \qquad (10)$$

$$Ag^{II} + Ag^0 \longrightarrow 2Ag^I \qquad (11)$$

involving intermediate silver(II) species. This results in a reaction sequence which is kinetically indistinguishable from that of the Scheme. But there is no direct evidence for the involvement of Ag^{II} in the reaction; neither the e.p.r. experiment nor the reaction stoicheiometry suggests the formation of Ag^{II}. Again Ag^{II}, a one-electron oxidant,[32] is likely to oxidise hydrazine rapidly to a mixture of N_2 and NH_3 through the free radical $N_2H_3^\bullet$. It may be anticipated, therefore, that if any Ag^{II} were generated then it should react with $N_2H_5^+$ to produce an equivalent amount of ammonia. Since no ammonia could be detected in the product and since there is no formation of any free radical, it might safely be concluded that Ag^{II} doesn't accumulate to any extent that might be detected through e.p.r. spectroscopy or that could affect the products or stoicheiometry of the reaction.

According to the Scheme, the measured rates are those for the oxidation of hydrazine by Ag$^+$ and not by the silver(III) complex. The complex acts as an oxidant regenerating Ag$^+$ from Ag^0_2 which is known to be a strong reductant, much stronger than silver metal.[29] The superiority of Ag^I over Ag^{III} as an oxidant for hydrazine or for $N_2H_3^+$ (as the Scheme demands) may therefore reflect here the circumstances that Ag^{III}, but not Ag^I, is strongly ligated. This ligation also probably makes $[Ag(H_2L)]^{3+}$ somewhat selective in its oxidation reactions. The weakly oxidising nature of the complex has recently been established[33] by us from cyclic voltammetric measurements which reveal a complex electrochemical process but confirm that in perchlorate media the complex is a weaker oxidant than Ag$^+$. An earlier polarographic study[34] on the same complex corroborates this conclusion. The present investigation thus involves an extremely rare situation where a Ag^I–Ag^0 catalytic cycle operates in the presence and with the help of a silver(III) species. The kinetics of oxidation of hydrazine by Ag^I had been measured earlier.[12] However, in that study the formation of a silver mirror on the walls of the reaction vessel strongly affected the kinetics and reaction course. We could not extrapolate and compare those rate data with ours. However, the $\Delta H^\ddagger$ value (97 kJ mol^{-1}) reported in the earlier work[12] for the oxidation of hydrazine by Ag$^+$ at pH 5 compares favourably with the present value ($\Delta H^\ddagger = 82 \pm 8$ kJ mol^{-1} and $\Delta S^\ddagger = -8 \pm 2$ J K^{-1} mol^{-1}). This may be additional evidence for the operation of the presumed Ag^I–Ag^0 cycle in the present case. It thus appears that the silver(III) complex is capable of oxidizing Ag^0 but not $N_2H_5^+$ at an appreciable rate. This may be because (*i*) the (two-electron) potential of Ag^{III} is rather high, (*ii*) 'nascent' Ag^0 is a very strong reducing agent, and (*iii*) the cationic silver(III) complex disfavours the cationic reductant $N_2H_5^+$. The direct uncatalysed reaction between Ag^{III} and hydrazine may be observable at a region of higher pH where deprotonated hydrazine is more strongly reducing. The zero-order rate law observed in this system was previously found by us for the oxidation of formic acid by this complex;[19] formic acid is a weaker reducing agent, which is reflected in a lower reaction rate. Thus k [equation (2)] for HCO_2H is 1.6×10^{-6} dm^3 mol^{-1} s^{-1} at 30 °C, I 1.0 mol dm^{-3}. Under similar conditions k for $N_2H_5^+$ is 6.25×10^{-4} dm^3 mol^{-1} s^{-1}.

A 1:1 silver–hydrazine complex has been postulated in the Scheme. If it is formed, then the binding site is likely[28,35] to be the free NH_2 end of $H_2N\text{-}\overset{+}{N}H_3$. However, according to an earlier report,[36] a dinuclear silver(I)–hydrazine complex $[Ag_2(N_2H_4)]^{2+}$ is formed at pH 5. Formation of this complex and its subsequent unimolecular decomposition (with other parts of the Scheme kept identical) explains equally well the observed kinetics provided that the formation constant for $[Ag_2(N_2H_4)]^{2+}$ is small.

Appendix

Derivation of rate law (2).—For the Scheme we can write equations (A1) and (A2) where $c_{Ag^+} \approx [Ag^+] + [Ag(N_2H_4)^+]$ and $[N_2H_5^+] \approx c_{\text{hydrazine}}$. Hence, expression (A3) is obtained; K_1 is very small, 1.7×10^{-5}, hence, $[H^+] + K_1[N_2H_5^+] \approx [H^+]$ and $[Ag^+] \approx c_{Ag^+}$. Thus we obtain equation (A4). Considering the stoicheiometric factor, and comparing with equation (3), $k = 2K_1k_1$.

$$-\mathrm{d}[\text{complex}]/\mathrm{d}t = -\mathrm{d}[Ag(N_2H_4)^+]/\mathrm{d}t = k_1[Ag(N_2H_4)^+][Ag^+] \qquad \text{(A1)}$$

$$K_1 = \frac{[Ag(N_2H_4)^+][H^+]}{[Ag^+][N_2H_5^+]} = \frac{[Ag(N_2H_4)^+][H^+]}{\{c_{Ag^+} - [Ag(N_2H_4)^+]\}[N_2H_5^+]} \qquad \text{(A2)}$$

$$[Ag(N_2H_4)^+] = \frac{K_1 c_{Ag}[N_2H_5^+]}{[H^+] + K_1[N_2H_5^+]} \qquad \text{(A3)}$$

$$-\frac{\mathrm{d}[\text{complex}]}{\mathrm{d}t} = k^0 = \frac{K_1k_1[Ag^+]^2}{[H^+]} \qquad \text{(A4)}$$

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