MACROCYCLIC TETRAAZA COMPLEXES OF SILVER(II). THE KINETICS AND MECHANISM OF THE OXIDATION OF 2-MERCAPTOPYRIMIDINE

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The reaction kinetics of the oxidation of 2-mercaptopyrimidine by $Ag(cyclam)^{2+}$, $Ag(tmc)^{2+}$, and $Ag([15]aneN_4)^{2+}$, followed a second-order rate law at constant pH and ionic strength of 0.10 M. A rate – pH profile characterized by an acid – base equilibrium of the thiol was also observed. At 25°C, the second-order rate constants for the oxidation of the thiyl anions by $Ag(cyclam)^{2+}$, $Ag(tmc)^{2+}$, and $Ag([15]aneN_4)^{2+}$ are 177, 323, and 813 M^{-1} sec^{-1}, respectively. The rate constants for three additional temperatures have also been determined for the evaluation of the activation parameters. The $\Delta H^{\ddagger}$ values of the reactions range from 33.9 to 47.3 kJ/mole and the $\Delta S^{\ddagger}$ values from -42.7 to -83.3 J K^{-1} mol^{-1}. A mechanism has been postulated to account for the kinetic rate law and the pH-dependence of the reactions.

Keywords: silver(II), macrocycles, oxidation, kinetics, 2-mercaptopyrimidine

INTRODUCTION

Sulfur is very important for living organisms. In cells sulfur appears in three major chemical fractions which are interconvertible[1]: a sulfide fraction which is made up of $-SCH_3$ groups from methionine residues of cellular proteins, a sulfate fraction which is bound as ester or amide sulfate in polysaccharides and steroids, and a cellular $RSH-RSSR$ fraction (thiol-disulfide redox system) which is especially important in biological systems. This last fraction is commonly found in hormones, enzymes, proteins, and pharmacologically active polypeptides, and has been widely investigated.

Thiols are considered to be the most active groups found in cells, and they are easily oxidized to disulfides[2] by biochemical oxidants such as flavins, cytochrome c, dehydroxylascorbic acid, quinones, amino acids, and fumarates. The disulfides are much less reactive than thiols. However, these more stable RSSR molecules can be converted back to RSH by varous reductants such as sodium hydride and sodium borohydride.

Kinetics and mechanisms have been reported recently for the oxidaton of some thiols, such as thioamides,[3,4] 2-mercaptoethanol,[5] 2-mercaptosuccinic acid,[6] thiomalic cid,[7,8] 3-mercaptopropionic acid,[9] alkyl-, benzyl-, and aryl thiols,[10] 2-thiopyrimidine,[11] and 2-thiouracil,[11] by a large variety of metal ions and metal complexes. The oxidation of thioamides[3] by substitution-inert octahedral complexes such as hexachloroiridate(IV) and tris(bipyridine)iron(III) have been shown to undergo electron-transfer reactions *via* the outer-sphere mechanism. However, no study on the thiol oxidation with square-planar complexes has yet been made. In the present study, the kinetics and mechanism of the oxidation of 2-mercaptopyrimidine by square planar macrocyclic tetraaza silver(II) complexes: (1,4,8,11-tetraazacyclotetradecane)silver(II) perchlorate or silver(II) cyclam, (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)silver(II) perchlorate or silver(II) tmc, and (1,4,8,12-tetraazacyclopentadecane)

silver(II) perchlorate or silver(II)([15]aneN₄), will be reported. Structures of the macrocyclic tetraaza ligands are shown in Figure 1.

In general, due to the powerful oxidizing property of the hypervalent cations, the di- and trivalent silver ions are unstable in solution. However, the divalent silver in its $4d^9$ state is frequently stabilized when coordinated to nitrogen heterocyclic compounds.[12-18] In most cases, coordination occurs through the formation of square-planar complexes.[19-21] These square-planar complexes have been determined to be paramagnetic[15,16,22-28] due to the odd number of d electrons of silver in the plus 2 oxidation state.

The reactivity of the square-planar macrocyclic tetraaza silver(II) complexes is expected to vary according to the nature of the ligand such as the ring size and the substituents on the macrocycles. Thus, we have included in this study ring size and substituent effects on the rate of oxidation of 2-mercaptopyrimidine.

EXPERIMENTAL

Materials

The reducing agent, 2-mercaptopyrimidine (MP or RSH), was purchased from Aldrich Chemical Company and was recrystallized from aqueous ethanol before being used.

The ligands, 1,4,8,11-tetraazacyclotetradecane (cyclam), 1,4,8,11-tetramethyl-1,4,8, 11-tetraazacyclotetradecane (tmc), and 1,4,8,12-tetraazacyclopentadecane ([15]ane N₄), were purchased from Strem Chemical, Inc., and were used without further purification to prepare the silver(II)-cyclam complexes. Silver perchlorate, anhydrous grade, was from G. Frederick Smith Chemical Company, and tetrahydrofuran used to wash the complex was from J. T. Baker Chemical Co.

Mallinckrodt Chemical Company sodium acetate, glacial acetic acid, sodium monohydrogen phosphate and sodium dihydrogen phosphate were used to prepare buffer solutions of different pH for the kinetic experiments.

Distilled water was passed through a series of two columns of ion exchange resins manufactures by the Illinois Water Treatment Company. The deionized water was

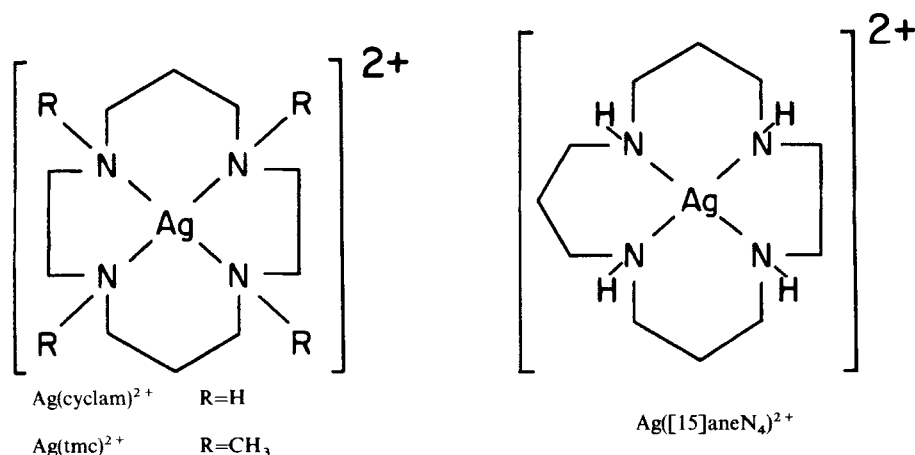Ag(cyclam)²⁺   R=H

Ag(tmc)²⁺   R=CH₃

Ag([15]aneN₄)²⁺

FIGURE 1   Structures of the Macrocyclic Tetraaza Silver(II) Complexes.

then redistilled in an all-glass apparatus and was used to prepare all the reaction solutions for the kinetic studies.

Preparation of Silver (II) Complexes

The silver(II) complexes were synthesized by modifying the procedure described by Barefield and Mocella.[29] To prepare a complex, 5 mmol of the ligand was added to 10 mmol of silver perchlorate in 30 cm^3 of water and stirred. The solution was filtered and the filtrate collected was cooled to 5°C. The orange crystals of silver(II)-cyclam perchlorate were collected by vacuum filtration, washed with cold distilled water, followed by tetrahydrofuran (5 cm^3), and dried in vacuo. Alternatively, small amounts of concentrated perchloric acid can be used to precipitate the complex salts. The colour of the needle-like crystals are: [Ag(cyclam)](ClO$_4$)$_2$ orange, [Ag(tmc)](ClO$_4$)$_2$ dark orange-brown, and [Ag[15]aneN$_4$](ClO$_4$)$_2$ deep reddish-orange.

Spectral Analysis and Kinetics

Spectral analysis of the Ag(cyclam)$^{2+}$, Ag(tmc)$^{2+}$, Ag([15]aneN$_4$)$^{2+}$, and MP was carried out using a Pye-Unicam SP-100 recording spectrophotometer. The absorption spectra of the silver(II) complexes in aqueous solution are characterized by an intense peak in the region from around 350 to 380 nm and a weaker peak at around 275 to 290 nm.[29,30]

The kinetics of the oxidation of MP by silver(II) complexes were followed at wavelengths where the silver(II) species absorbed most strongly using a Dionex 110 Durrum stopped-flow apparatus equipped with a constant temperature cell chamber. The kinetic experiments were conducted under pseudo-first-order conditions with the concentration of MP in at least a twelve-fold excess over the silver(II) complexes. From the disappearance of silver(II)-cyclam, the k$_{obs}$ values were determined from plots of log(A$_t$ − A$_\infty$) versus time. Excellent linear plots over three half-lives were obtained. For the Ag(tmc)$^{2+}$ and Ag([15]aneN$_4$)$^{2+}$ systems, Guggenheim plots were used to determine the pseudo-first-order rate constants since the infinity absorbances were difficult to determine in most cases. Replicate kinetic runs were always performed to verify the consistency of the k$_{obs}$ values.

The pH of the reaction solutions was maintained using phosphate buffers and the pH measured prior to the kinetic experiment usng a Beckman 4500 digital pH meter. In several instances, we have used acetate buffers at low pH with no observable change in rates compared with phosphate buffers. Temperature effects on pH were taken into account for those reactions at other than 25°C.

RESULTS AND DISCUSSION

The pK$_a$ of 2-Mercaptopyrimidine

The pK$_a$ values of 2-mercaptopyrimidine in aqueous solution of ionic strength of 0.10 M have been determined spectrally from absorption changes as a function of the pH of solutions ranging from 5.00 to 12.00 and at 21.0°, 23.8°, and 29.6°C. Figure 2 shows the MP concentration determined from the calculated absorbance changes versus pH at 23.8°C for a pH$_a$ calculaton. The value of the pK$_a$ (7.24 at 25°C) determined in this study agrees closely with those reported in the literature, 7.14[31] and 7.2.[32] From the slope of the −log K$_a$ or pK$_a$ or pK$_a$ versus 1/T plot shown in
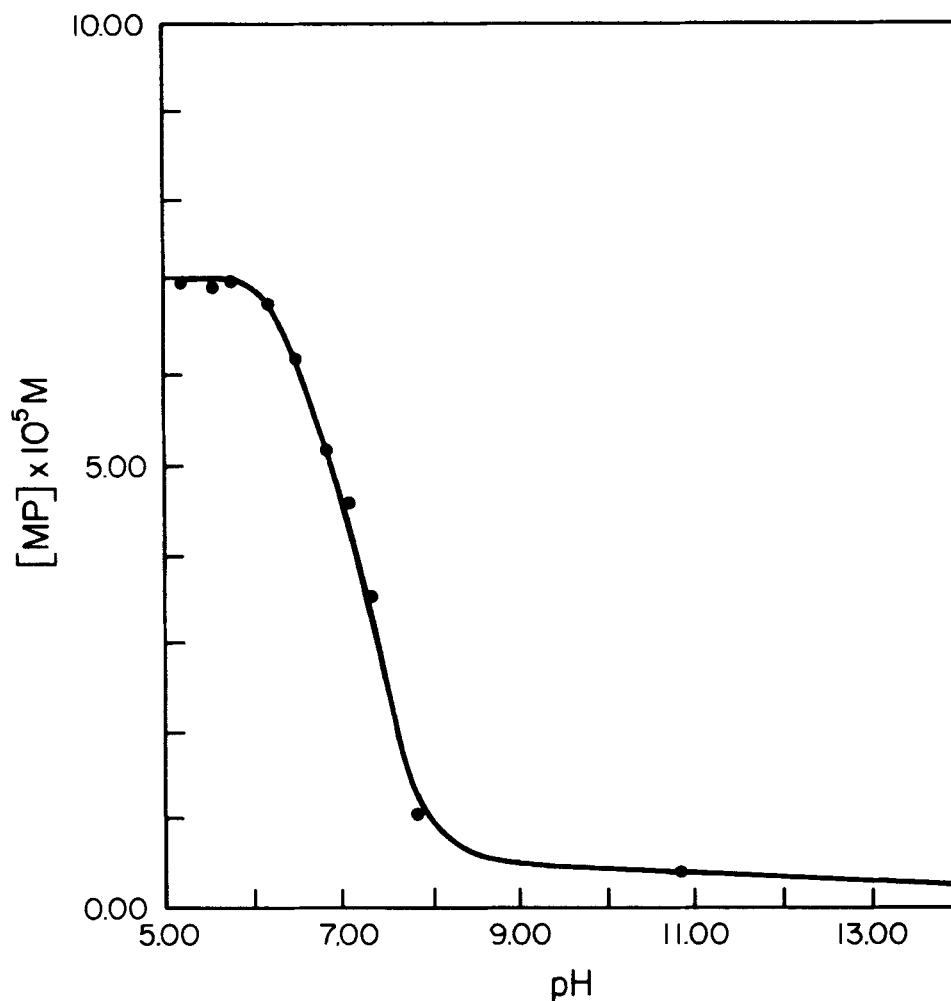
FIGURE 2   [MP] *versus* pH for 2-Mercaptopyrimidne pK$_a$ Determination. T = 23.8°C, I = 0.10 M, 346 nm.

Figure 3, the thermodynamic parameters for the acid-base equilibrium reaction of the 2-mercaptopyrimidine are calculated and is expressed as

$$\Delta G^\circ = 26.36 \text{ kJ/mole} - [T(-50 \text{ J K}^{-1} \text{ mol}^{-1})]$$ (1)

The K$_a$ value at the appropriate reaction temperature can then be calculated, using the above equation, so that the individual rate constants in the proposed reaction mechanism can be evaluated. Such a curve fitting procedure is described later in the Mechanism Section.

Stoichiometry

The reaction stoichiometry for the oxidation of 2-mercaptopyrimidine by silver(II)-cyclam had been reported earlier to be 1:1 and the products of oxidation are the
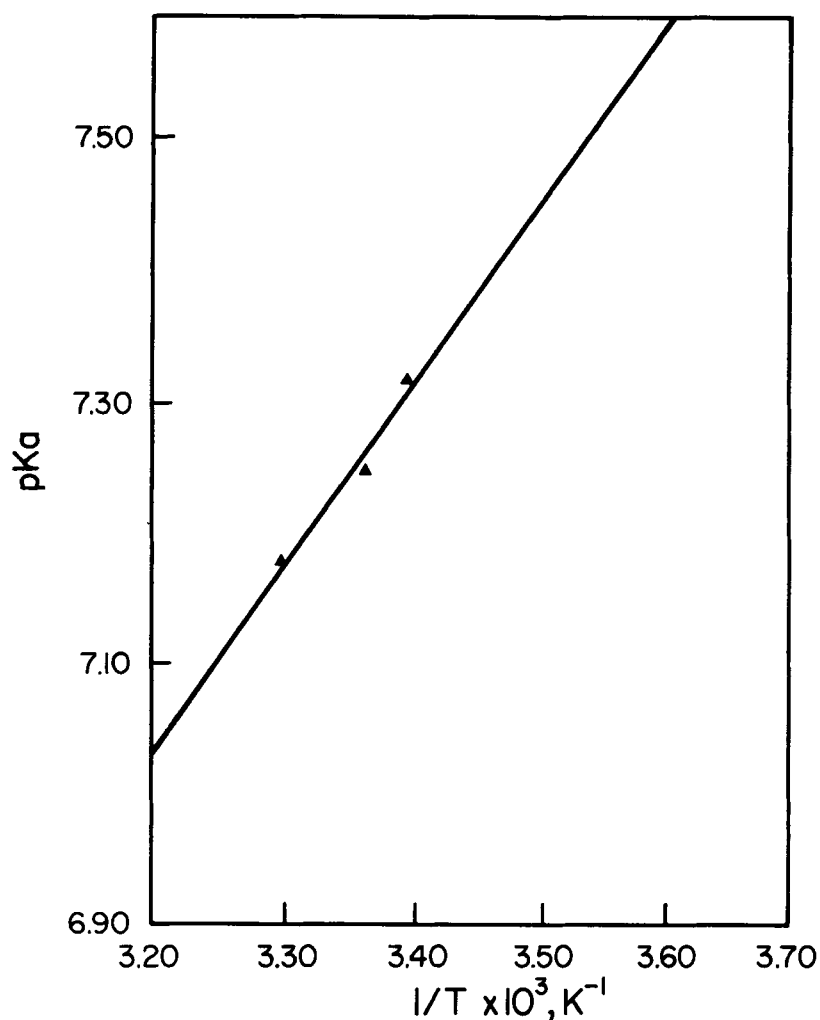
FIGURE 3 pK_a of MP versus $1/T$ for $\Delta H°$ Determination.

disulfide and silver(I)-cyclam which eventually demetallates.[30] The stoichiometry for the reaction can therefore be written as follows.

$$2\ RSH + 2\ Ag(cyclam)^{2+} \rightarrow RSSR + 2\ Ag(cyclam)^{+} + 2\ H^{+} \tag{2}$$
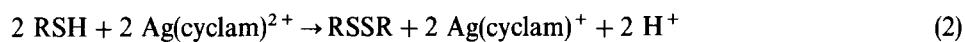
Kinetics of the Oxidation of 2-Mercaptopyrimidine

The pseudo-first-order kinetics of the oxidation of 2-mercaptopyrimidine by Ag $(cyclam)^{2+}$, $Ag(tmc)^{2+}$, and $Ag([15]aneN_4)^{2+}$ have been studied in buffered solutions at a constant ionic strength of 0.10 M. Several reaction conditions, such as the concentration of the reactants, the temperature, and the pH of the solutions were varied to obtain the kinetic rate expression. The concentration ranges of the silver(II) complexes used in the study were from 8.8×10^{-5} to 1.30×10^{-4} M while the MP

concentrations were from $(1.25 - 2.50) \times 10^{-3}$ M. The limited concentration range used in this study is due to the low solubility of the reactants in aqueous solution. However, this limitation did not hinder the kinetic measurements. The pH ranges of the reactions were varied from 4.5 to 6.5, and the temperature from 20° to 35°C. The observed rate constants, k_{obs}, were calculated from the linear semilog plots of $\log(A_t - A_\infty)$ versus time or from the Guggenheim plots when the infinity absorbancies were not constant. The Guggenheim plots were used extensively for the $Ag(tmc)^{2+}$ and $Ag([15]aneN_4)^{2+}$ systems because of the small drifts of absorption at the end of the reactions. Generally, these kinetic plots exhibit linearity over three half-lives. At constant pH, the rate order with respect to the concentration of the silver(II) complex is one. The rate order with respect to the thiol concentration is also one as show by the concentration and rate-pH profile analysis (vide infra). The values of k_{obs} for the three reactions under different reaction conditions and temperatures are listed in Tables I to IV.

Consistent with earlier reports, the rate of reaction is strongly pH dependent as in the oxidation of other thiol compounds such as thioureas,[4] thiouracil,[5] and thio-pyrimidine.[3,30] The rate dependence on the hydrogen ion concentration can be determined from the experimental plots of k_{obs} versus pH for the three silver(II) complexes. The slopes of the steep portions of these plots have been calculated and the average value is 0.98 ± 0.10. This value supports the inverse hydrogen ion concentration dependence of these reactions. Because of the instability of the silver(II)-cyclams in the high pH region, the normal sigmoidal pH-rate profiles were not obtained for these reactions as the pH can not be extended above 7. The pH-rate profiles which are presented in Figure 4 are typical of all the three reactions with 2-mercaptopyrimidine. For comparison, the experimental points are shown along with the calculated plots from the derived equation of the proposed mechanism, eq. (3).

TABLE I

Valves of k_{obs} as a Function of MP concentration, pH, and Temperature for the $Ag(Cyclam)^{2+}$ Reaction

T = 20°C $10^3[MP]$, M	$10^2 k_{obs}$, sec^{-1}			
	pH = 4.59[a]	4.77[a]	4.93[a]	5.10[a]
1.25	.95	1.05	1.30	1.43
1.50	1.22	1.32	1.59	1.66
1.75	1.45	1.62	1.79	1.88
2.00	1.71	1.90	2.18	2.22
2.25	1.96	2.14	2.50	2.40
2.50	2.18	2.50	2.89	2.55
	pH = 5.28[a]	5.43	5.70	5.86
1.25	1.44	1.46	1.62	1.89
1.50	1.71	2.15	2.14	2.17
1.75	2.11	2.70	2.17	2.86
2.00	2.34	3.13	2.68	3.44
2.25	2.58	3.75	3.42	3.68
2.50	2.74	3.89		4.16

TABLE I (continued)

T = 20°C

$10^3[MP]$, M

$10^2 k_{obs}$, sec^{-1}

	pH = 6.11	6.23	6.40	6.55
1.25	2.31	2.87	3.92	4.98
1.50	2.97	3.89	5.46	6.10
1.75	3.53	5.31	6.62	8.78
2.00	5.26	6.28	9.05	11.0
2.25	5.92	7.21	11.2	14.3
2.50	6.43	8.60	12.7	16.3

T = 25°C (Data are Published in Ref. 30)

T = 30°C

	pH = 5.13[a]	5.31	5.87	6.12
1.25	2.34	2.48	3.05	4.30
1.50	2.93	3.18	3.99	5.34
1.75	3.46	3.87	4.76	6.19
2.00	4.35	4.24	5.60	
2.25	4.63	4.99	6.41	9.62
2.50	5.65	5.70	7.80	11.3

	pH = 6.24	6.41	6.56
1.25		8.90	12.1
1.50	7.04	14.2	19.2
1.75	9.38	19.7	24.2
2.00	12.8	23.1	28.7
2.25	16.9	26.5	35.4
2.50	19.0	30.0	39.4

T = 35°

	pH = 5.52	5.73	5.91
1.25	3.51	3.80	6.16
1.50	4.64	4.94	6.36
1.75	6.02	6.04	8.50
2.00	6.75	6.97	10.1
2.25	8.61	8.68	12.7
2.50	8.97	9.60	14.1

	pH = 6.09	6.26	6.46
1.25	8.69	9.94	13.4
1.50	10.5	12.9	
1.75		20.9	26.4
2.00	16.8	26.5	32.9
2.25	23.4	34.4	41.4
2.50	27.2	38.4	48.4

Reaction Conditions: $[Ag(cyclam)^{2+}] = 8.90 \times 10^{-5}M$, $I = 0.10M$, and in phosphate buffers. [a] Acetate buffers

TABLE II
Values of k_{obs} at Various pH and [MP] for Ag(tmc)$^{2+}$ Reaction at 25°C

10^3[MP]	$10^2 k_{obs}$, sec^{-1}			
	pH = 4.77	5.16	5.36	5.53
1.25	0.72	1.79	3.27	4.96
1.50	0.94	1.99	3.50	5.41
1.75	1.14	2.25	4.27	6.44
2.00	1.24	2.98	4.81	6.69
2.25	1.27	3.59	5.81	7.62
2.50	1.60	3.71	6.06	8.08
	pH = 5.74	5.94	6.13	6.34
1.25	5.94	8.00	8.20	13.5
1.50	6.57	8.99	9.28	14.1
1.75	6.88		10.9	15.9
2.00	8.09	10.9	13.9	17.8
2.25	9.32	13.6	15.5	18.9
2.50	11.0	15.2	18.7	20.1

Reaction Conditions: [Ag(tmc)$^{2+}$] = 9.94 × 10^{-5}M, I = 0.10M, and in phosphate buffers.

TABLE III
Values of k_{obs} at Various pH and Temperature for Ag(tmc)$^{2+}$

	pH	$10^2 k_{obs}$, sec^{-1}
T = 20°C	5.18	2.32
	5.37	3.63
	5.57	4.66
	5.77	6.35
	5.95	8.58
	6.15	10.05
	6.34	12.45
T = 30°C	4.94	2.96
	5.20	4.91
	5.40	7.90
	5.60	9.18
	5.76	12.0
	5.96	16.3
	6.15	20.7
	6.34	23.7
T = 35°C	4.92	4.14
	5.28	7.65
	5.45	10.7
	5.57	15.8
	5.78	19.9
	5.93	23.3
	6.16	27.7
	6.34	35.5

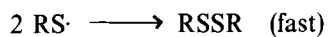Reaction conditions: [Ag(tmc)$^{2+}$] = 9.94 × 10^{-5}M, [MP] = 2.00 × 10^{-3} M, I = 0.10M, and in phosphate buffers.

TABLE IV
Values of k_{obs} at Various pH and Temperature for $Ag([15]aneN_4)^{2+}$
Reaction

	pH	$10^2 k_{obs}$, sec^{-1}
T = 20°C	5.16	3.50
	5.43	4.98
	5.59	8.24
	5.77	10.8
	5.87	11.7
	6.06	20.9
	6.24	27.7
	6.41	39.4
T = 25°C	5.09	4.06
	5.37	5.94
	5.52	10.6
	5.74	13.7
	5.83	20.9
	6.02	23.1
	6.20	29.9
T = 30°C	5.07	5.66
	5.30	10.5
	5.52	14.7
	5.68	21.4
	5.77	26.2
	5.97	33.6
	6.14	51.0
	6.34	57.1
T = 35°C	5.01	7.42
	5.27	13.4
	5.43	18.3
	5.65	22.1
	5.74	32.9
	5.92	44.7
	6.12	56.8
	6.32	76.8

Reaction conditions: $[Ag([15]aneN_4)^{2+}] = 9.98 \times 10^{-5}$ M, $[MP] = 2.00 \times 10^{-3}$ M, $I = 0.01$ M, and in phosphate buffers.

Mechanism of the Oxidation of 2-Mercaptopyrimidine

A mechanism that satisfies al the experimental conditions and the kinetic results for the three systems, $Ag(cyclam)^{2+} + MP$, $Ag(tmc)^{2+} + MP$, and $Ag([15]aneN_4)^{2+} + MP$, is shown below.

$RSH \xrightleftharpoons{K_a} RS^- + H^+$

$RS^- + Ag(cyclam)^{2+} \xrightarrow{k_2} RS\cdot + Ag(cyclam)^+$

$RSH + Ag(cyclam)^{2+} \xrightarrow{k_2'} RS\cdot + Ag(cyclam)^+ + H^+$

$2 RS\cdot \longrightarrow RSSR$ (fast)
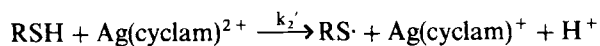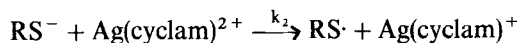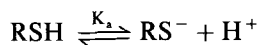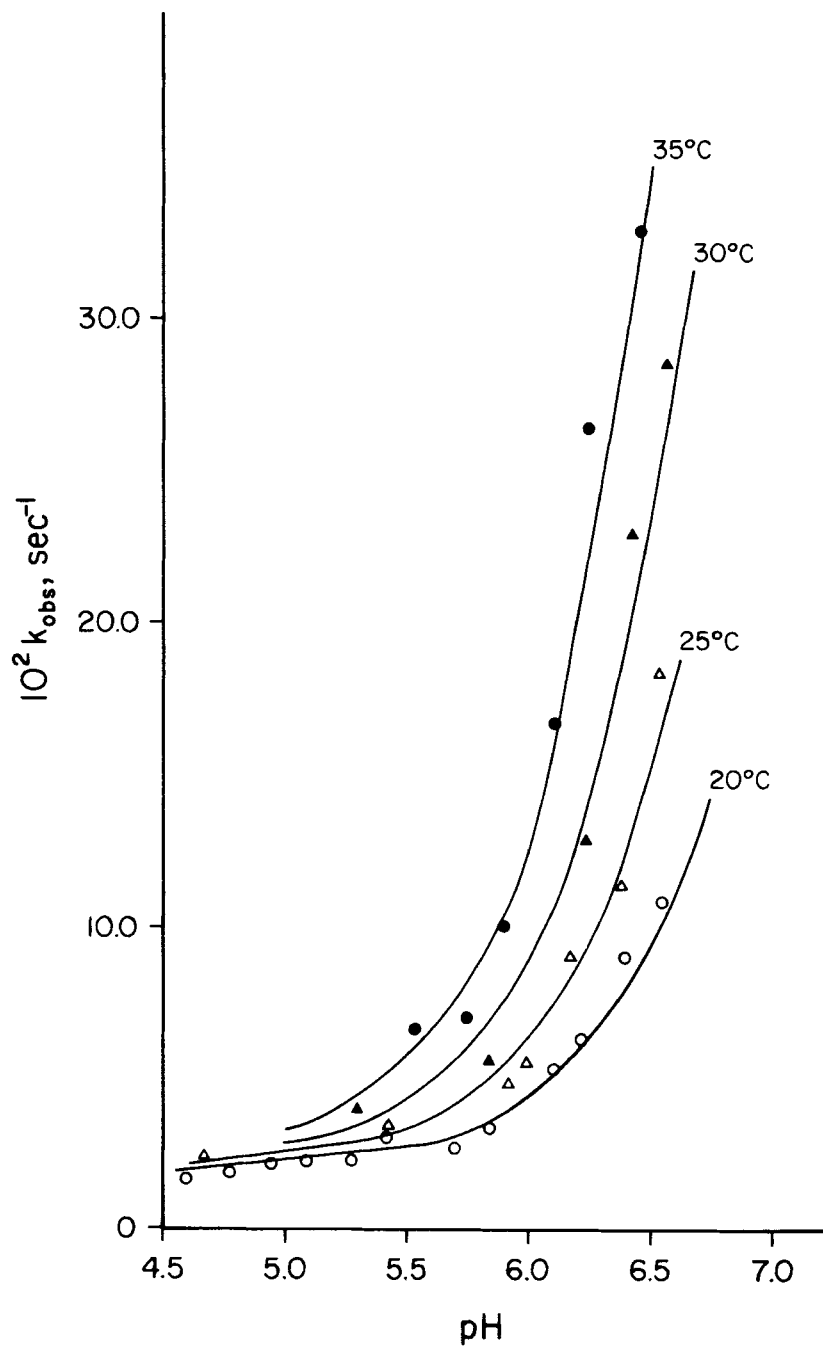
FIGURE 4   pH-Rate Profile: Plots of Ag(cyclam)$^{2+}$ + MP at Four Different Temperatures. Solid lines are generated from equation (3) using the rate constant and K_a data listed in Table V and [MP] = 2.00 × 10^{-3} M. T = 20 (circles); 25 (triangles); 30 (filled triangles); 35° (filled circles).

In the above, mechanism, the macrocyclic tetraaza complexes of silver(II) are represented by $Ag(cyclam)^{2+}$ and the 2-mercaptopyrimidine by RSH. The thiyl radicals of 2-thiopyrimidine and 2-thiouracil have been reported in studies involving biological systems.[33] The k_2 and k_2' paths are therefore a reasonable account of the oxidation of the 2-mercaptopyrimidine by the silver(II) complexes. The pH dependence of the oxidation reaction can be accounted for by involving the acid-base equilibrium reaction of the thiol whose pK_a has been measured in this study in aqueous solution of ionic strength 0.10 M. Knowing the pK_a facilitates the evaluation of the rate constants of the oxidation of thiol and its anion by the silver(II) complexes (k_2 and k_2') at the four reaction temperatures. Finally, The fast step of the reaction mechanism involving the thiyl radical dimerization to form the disulfide is consistent with the product study. From the mechanistic scheme above, a rate expression, equation (3), can be derived with reasonable and appropriate assumptions.[34] Because of the shape of the pH-rate profile, the reactivity of the thiyl anions can be assumed to be higher than the neutral thiol molecules and with the assumptions of $[RS^-] < [RSH]$ and $[H^+] > K_a$, equation (3) is obtained.

$$- d\ln[Ag(cyclam)^{2+}]/dt = 2(k_2' + K_a k_2/[H^+]) \, [RSH] \tag{3}$$

Under pseudo-first-order conditions, the experimental k_{obs} is equal to the right hand side of equation (3). This permits the calculation of the individual second-order rate constants, k_2 and k_2', graphically from plots of $k_{obs}/[RSH]$ versus $K_a/[H^+]$. The

TABLE V

Calculated values of k_2 and k_2' for $Ag(cyclam)^{2+}$, $Ag(tmc)^{2+}$, and $Ag([15]aneN_4)^{2+}$ at Various Temperatures

	k_2, $M^{-1} s^{-1}$	k_2', $M^{-1} s^{-1}$
$T = 20.0°C$, $K_a = 4.79 \times 10^{-8}$		
$Ag(cyclam)^{2+}$	120 (± 5)	4.05 (± 0.55)
$Ag(tmc)^{2+}$	250 (± 42)	5.98 (± 2.75)
$Ag([15]aneN_4)^{2+}$	630 (± 40)	5.35 (± 1.48)
$T = 25.0°C$, $K_a = 5.73 \times 10^{-8}$		
$Ag(cyclam)^{2+}$	177 (± 5)	5.38 (± 0.57)
$Ag(tmc)^{2+}$	323 (± 17)	9.63 (± 5.31)
$Ag([15]aneN_4)^{2+}$	8.13 (± 94)	7.44 (± 4.00)
$T = 30.0°C$, $K_a = 6.84 \times 10^{-8}$		
$Ag(cyclam)^{2+}$	241 (± 33)	6.45 (± 1.88)
$Ag(tmc)^{2+}$	412 (± 9)	13.1 (± 0.8)
$Ag([15]aneN_4)^{2+}$	1180 (± 33)	11.3 (± 1.3)
$T = 35.0°C$, $K_a = 8.10 \times 10^{-8}$		
$Ag(cyclam)^{2+}$	330(± 25)	7.70 (± 2.21)
$Ag(tmc)^{2+}$	540 (± 44)	18.8 (± 4.0)
$Ag([15]aneN_4)^{2+}$	1310 (± 128)	13.8 (± 1.6)

values of the individual rate constants and the K_a calculated for the three systems at the four different temperatures are listed in Table V. A curve fitting procedure was used to fit the data for each temperature, each pH, and thiol concentration using equation (3) and the best results of k_2 and k_2' are listed. The average standard deviation for k_2 is 7.6% while that for the k_2' is 26%. The large uncertainty on the intercept determination from the described graphical method is responsible for the relatively low accuracy of k_2'. However, since the thiyl anions are much more reactive than the neutral molecules, the low accuracy of k_2' did not present any problem in the curve fitting of the data. This is shown in Figure 4 in which k_{obs} for Ag(cyclam)$^{2+}$ + MP at four reaction temperatures have been calculated at [MP] = 2.00×10^{-3} M and plotted using equation (3). The rate constants, k_2 and k_2', and the equilibrium constants of MP used in the calculation are from Table V.

Attempts to use the complete derived rate expression resulted in a poorer fit between the experimental points and the calculated rate constants. The fit was particularly poor at higher pH where the reaction is most senstitive to the higher reactivity of the thiyl anions.

Activaton Energies of the Reactions

Listed in Table VI are the $\Delta H^{\ddagger}$ values of the reactions calculated from the slopes of the $\ln(k_2/T)$ versus $1/T$ plots as shown in Figure 5. The $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$ values are calculated from the corresponding values of k_2 at 25.0°C using the transition state equation[35]

$$k = (RT/Nh) \, e^{-\Delta G^{\ddagger}/RT}$$

and the $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ equation. The calculated activation parameters are listed in Table VI. Because of the lesser accuracy of the k_2' values, no attempt was made to calculate $\Delta H^{\ddagger}$ for this path. The order for the overall rate of oxidation of the 2-mercaptopyrimidine by the silver(II) complexes based on $\Delta G^{\ddagger}$ is Ag([15]aneN$_4$)$^{2+}$ > Ag(tmc)$^{2+}$ > Ag(cyclam)$^{2+}$ which is expected based on the comparison of k_2. However, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for Ag(tmc)$^{2+}$ are the lowest among the three systems. The larger negative entropy of activation increases the overall $\Delta G^{\ddagger}$ and thus reduces the rate of reaction even though $\Delta H^{\ddagger}$ for Ag(tmc)$^{2+}$ is more favourable than for the other two systems.

Because of the square-planar geometry of the silver(II) macrocyclic tetraaza complexes, it is possible that the reaction mechanism could involve a five-coordinate intermediate as the result of axial complexation of thiol. Such a postulate has been used to explain reactions of tetrahydroxoargentate(III) ion with arsentite ion,[36] hydrogen peroxide,[37] azide ion,[38] and thiosulfate ion[39] where large negative entropies of activation have been observed. However, no conclusive inner-sphere mechanism

TABLE VI

Activaton Parameters Calculated from k_2

Oxidant	$\Delta G^{\ddagger}$/kJ mol^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
Ag(cyclam)$^{2+}$	60.2	47.2 ± 6.3	-42.6 ± 8.4
Ag(tmc)$^{2+}$	58.6	33.9 ± 2.6	-83.3 ± 8.4
Ag([15]aneN$_4$)$^{2+}$	56.5	39.6 ± 3.7	-55 ± 12.6
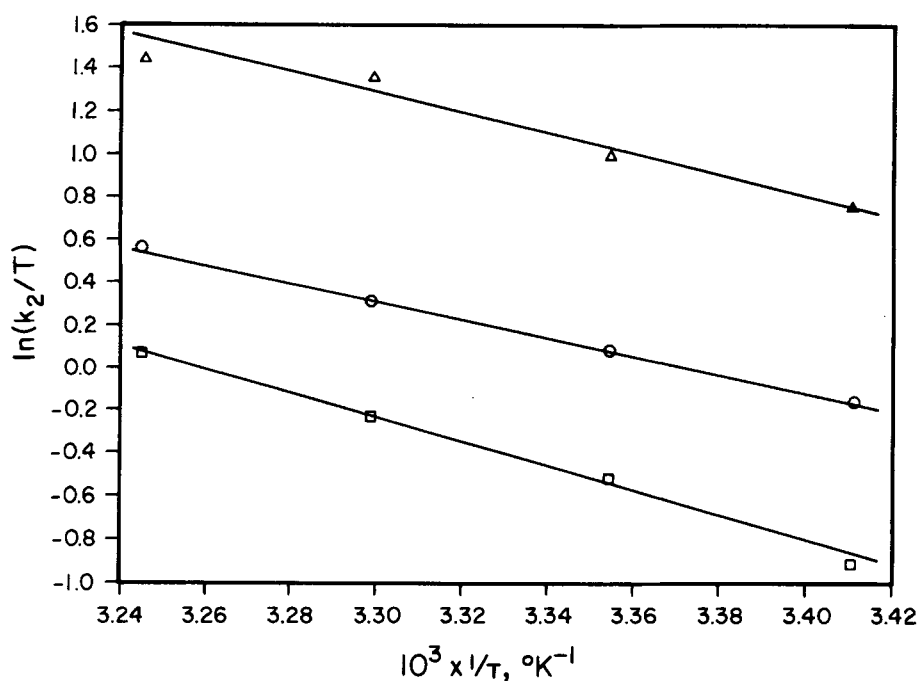
FIGURE 5 Ln (k_2/T) *versus* $1/T$ Plots. $Ag(cyclam)^2 + MP$ (squares); $Ag(tmc)^{2+} + MP$ (circles); $Ag([15]aneN_4)^{2+} + MP$ (triangles).

can be advanced for the present system since there is no direct evidence of such an intermediate. Furthermore, the entropies of activation obtained in this study are not large and negative enough to support a five-coordinate intermediate.

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ACKNOWLEDGEMENTS