Contribution from the Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881, and the Electrochemistry Division, Naval Ordnance Laboratory, White Oak, Maryland 20910

Kinetics of Silver(III) Complexation by Periodate and Tellurate Ions

L. J. KIRSCHENBAUM,* J. H. AMBRUS, and G. ATKINSON

The tetrahydroxoargentate(III) ion has been prepared in sodium hydroxide media by anodic oxidation of silver metal. The kinetics of Ag(III) complex formation with periodate and tellurate ions has been studied by the stopped-flow method at an ionic strength of 1.2 M. Both reactions result in a rate law attributable to stepwise formation of the bis complex. At 25° the second-order rate constants for formation of the mono- and bis(periodato)argentate(III) complex are 4.5×10^4 and $9.3 \times 10^3\ M^{-1}\ sec^{-1}$. The corresponding values for tellurate complexation are 2.72×10^3 and $1.0 \times 10^4\ M^{-1}\ sec^{-1}$ although the order of this assignment is less certain. Activation parameters have been determined and are consistent with the associative-type mechanisms common to other square-planar low-spin d^8 metal ions.

Introduction

The existence of silver in the 3+ oxidation state both in solid compounds and as soluble species has been well documented. In addition to the oxide $Ag^IAg^{III}O_2$ (formally AgO),[1] several oxy salts and tetrafluoroargentates are described in the literature.[2] Silver(I) nitrate can be oxidized to Ag(III) in the presence of complexing agents, such as periodate or tellurate, either by peroxydisulfate[3] or by electrolysis[4] in alkaline solutions. From these solutions, compounds of the general formula $M_7Ag(IO_6)_2 \cdot nH_2O$ and $M_9Ag(TeO_6)_2 \cdot nH_2O$, where M is Na, K, or H, can be crystallized out. The same compounds have also been obtained by direct reaction of the appropriate ligand with alkaline solutions saturated with AgO.[5] Organic ligands such as biguanidine[6a] and its derivatives[6b] also stabilize Ag(III) as has been confirmed by photoelectron spectroscopy.[6c] The stabilizing effect of the porphyrin ring has been indicated by esr measurements.[7]

All silver(III) compounds, for which magnetic susceptibility has been measured, are diamagnetic.[1-3,6-8] This is consistent with the tendency of Ag(III) to coordinate in the square-planar configuration found for the analogous spin-paired d^8 systems Au(III), Cu(III), Pt(II), Ni(II), and Pd(II).

The simplest species of Ag(III) to be prepared in solution has been reported by Cohen and Atkinson.[9] They found that when a smooth strip of silver is anodically oxidized in concentrated KOH solutions (1.2-12 M) a yellow solution results that contains silver in the 3+ oxidation state only. They identified the silver species present as the tetrahydroxoargentate(III) ion. The $Ag(OH)_4^-$ ion shows a single broad absorption band in the ultraviolet spectrum with the reported maximum at 271 nm. Addition of potassium periodate or potassium tellurate results in solutions whose electronic spectra are identical with those obtained by dissolving solid bis(periodato)argentate(III) or bis(tellurato)-argentate(III) salts in water.[9,10] Punkies, *et al.*,[11] have identified a silver(III) species produced in pulse radiolysis studies on Ag^+ in neutral solution. The absorption spectrum of this species closely matches that of the $Ag(OH)_4^-$ ion having a single broad peak with a maximum at 270 nm.

The tetrahydroxoargentate(III) ion is metastable; the silver(III) is reduced to AgO, presumably by the solvent, with a half-life ranging from about 100 min in 1.2 M KOH to approximately 240 min in 12 M KOH at 27.2°.[10] Cohen[10] was unable to prepare $Ag(OH)_4^-$ by electrolysis of silver in 12 M sodium hydroxide.

In this paper we report on the stoichiometry and kinetics of the ligand-exchange reaction between the OH^- ligands of the tetrahydroxoargentate(III) ion and periodate and tellurate, respectively. These reactions are rapid, necessitating the use of the stopped-flow technique. We also report on the preparation of $Ag(OH)_4^-$ in NaOH solution by an electrolytic technique somewhat different from that of Cohen and Atkinson.[9]

Experimental Section

Preparation of Tetrahydroxoargentate(III) Solutions. Approximately 200 ml of 1.2 M NaOH solution was placed in a 250-ml polyethylene beaker with cover. The cover was equipped with appropriate ports to accommodate the anode, the cathode compartment with cathode, and a glass capillary. The anode consisted of a 1 cm wide strip of silver foil (Handy and Harman) dipped into the solution to a depth of 5 cm giving a nominal surface area for electrolysis of 10 cm². The surface area of the silver foil, determined by a double-

* Address correspondence to this author at the University of Rhode Island.

(1) J. A. McMillan, *J. Inorg. Nucl. Chem.*, **13**, 28 (1960).

(2) J. A. McMillan, *Chem. Rev.*, **62**, 65 (1962).

(3) L. Malatesta, *Gazz. Chim. Ital.*, **71**, 467 (1941).

(4) L. Jensovsky and M. Skala, *Z. Anorg. Allg. Chem.*, **312**, 26 (1961).

(5) G. L. Cohen and G. Atkinson, *Inorg. Chem.*, **3**, 1711 (1964).

(6) (a) D. Sen, *J. Chem. Soc. A*, 1304 (1969); (b) D. Sen and K. Chakravarty, *J. Indian Chem. Soc.*, **21**, 47 (1944); (c) D. A. Zatko and M. L. Simms, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. INOR 41.

(7) K. Kadish, D. G. Davis, and J. H. Fuhrhop, *Angew. Chem., Int. Ed. Engl.*, **11**, 1014 (1972).

(8) L. Jensovsky and M. Ralek, *Z. Anorg. Allg. Chem.*, **314**, 76 (1962).

(9) G. L. Cohen and G. Atkinson, *J. Electrochem. Soc.*, **115**, 1236 (1968).

(10) G. L. Cohen, Ph.D. Thesis, University of Maryland, 1967.

(11) J. Punkies, W. Roebke, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **72**, 842 (1968).

layer capacitance method, was found to be 2.4 cm^2/nominal cm^2.[12] The cathode compartment consisted of a glass tube of 15-mm inside diameter fitted at one end with a medium-porosity glass frit. Into this was placed the cathode, a piece of platinum wire sealed through a glass rod to a copper lead. A diagram of the apparatus is shown in Figure 1. Nitrogen was bubbled through the solution from a capillary placed near the anode to provide stirring of the anolyte and minimize absorption of CO$_2$ from the air. The electrodes were connected to the terminals of a Lambda Electronics Model LP 412 FM constant-current power supply. Electrolysis was carried out at 0.7 A (70 mA/cm^2 nominal) for 35–60 min. At the end of this period the anolyte was of a deep yellow color with some finely divided dark gray solid floating in it and the anode had turned dark gray. The anolyte was then quickly filtered through a medium-porosity glass frit and the clear yellow solution stored in a capped polyethylene bottle. From this stock, solutions of appropriate concentration were prepared by dilution with 1.2 M NaOH and/or NaClO$_4$ solutions.

Chemical properties and electronic spectra of solutions prepared in the above manner are essentially the same as those previously reported for solutions of the tetrahydroxoargentate(III) ion in KOH,[9,10] and we conclude that our preparations do, indeed, yield this species. The spectrum of Ag(OH)$_4^-$ in NaOH, which is shown in Figure 2, exhibits one broad peak with an extinction coefficient of 1.17 × 10^4 1. mol^{-1} cm^{-1} at the 267-nm absorbance maximum.[13] Previously reported spectra[9,10] also result when these preparations react with periodate and tellurate ions. Ag(OH)$_4^-$ concentration was determined spectrophotometrically in the presence of excess periodate by measuring the absorbance at 362 nm where the extinction coefficient for the product bis(periodato)argentate(III) ion is 1.52 × 10^4 1. mol^{-1} cm^{-1}.[5]

The half-life for decomposition of freshly prepared tetrahydroxoargentate(III) ion in 1.2 M NaOH was found to be approximately 110 min at 25°, long enough to permit a series of rapid complexation experiments. Samples prepared in an open, stirred beaker or containing added Na$_2$CO$_3$ decompose somewhat more rapidly. In addition, decomposition seems to be catalyzed by the colloidal or precipitated reduction products.

All absorbance measurements were obtained with a spectrophotometer consisting of a Beckman DU monochromator with a Gilford Model 222 photometer and dual-regulated lamp power supply. A holmium oxide filter was used for wavelength calibration.

Preparation of Sodium Hydroxide, Sodium Perchlorate, Periodate, and Tellurate Solutions. Sodium hydroxide solutions were prepared from 50% NaOH (Baker "Analyzed," low CO$_2$) by dilution with distilled water. Concentrations were determined by potentiometric titration with standard acid using a Leeds and Northrup pH meter.

Sodium perchlorate solutions for ionic strength adjustment were prepared from standard stock solutions of HClO$_4$ and NaOH by neutralization and dilution to a final concentration of 1.2 M. The pH of the solutions so obtained was adjusted to 7 if necessary. The exact concentration of the solution was determined gravimetrically by evaporating the water from weighed aliquots and drying to constant weight at 130°.

The periodate and tellurate solutions were made from solid NaIO$_4$ (Fisher Scientific Certified ACS) and H$_2$TeO$_4$·2H$_2$O (Alfa Inorganics, reagent grade), respectively, and used without further purification. Weighed amounts of the solids were dissolved in distilled water; then sodium hydroxide and sodium perchlorate solutions were added to obtain the desired alkalinity and ionic strength. In the case of the tellurate solutions, enough additional NaOH was added to neutralize two protons, making the compound dissolved in water formally Na$_2$TeO$_4$·2H$_2$O.

Stoichiometry of the Tellurate Reaction. Job's method of continuous variations[14] was used to determine the number of tellurate ligands associated with one Ag(III) in solution. The absorbance of a series of solutions containing varying silver:ligand mole ratios was measured while keeping the total [silver] + [ligand] essentially constant. The total concentration of these solutions was (5.05 ± 0.20) × 10^{-4} F at [OH$^-$] = 1.2 M. The variation in the total concentration

(12) We gratefully acknowledge the assistance of Dr. Robert A. Myers of the Harry Diamond Laboratory in obtaining the surface area measurements.

(13) The difference of 4 nm between the absorbance maxima reported here and in ref 9 appear to be due, at least in part, to better instrumental resolution and calibration in the present measurements (*cf.* Figure 5 in ref 9).

(14) (a) P. Job, *Ann. Chim. (Paris)*, [10] **9**, 113 (1928); (b) W. C. Vosburgh and G. R. Cooper, *J. Amer. Chem. Soc.*, **63**, 437 (1941).
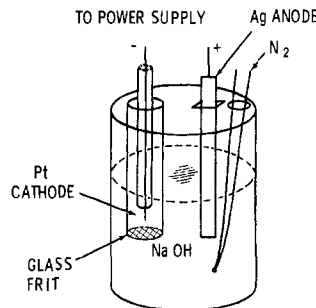

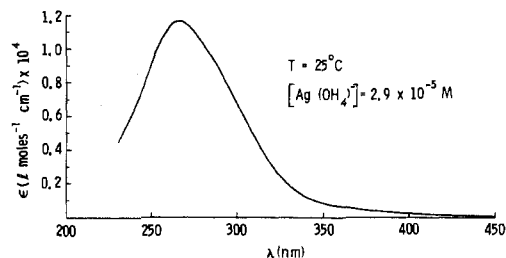**Figure 1.** Electrolysis cell for the preparation of tetrahydroxoargentate(III) solutions.

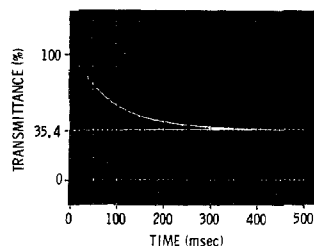**Figure 2.** Spectrum of tetrahydroxoargentate(III) in 1.2 M NaOH.

Figure 3. Oscillograph of a stopped-flow experiment at 25° and $\mu = 1.2$ M. The concentrations are [Ag(OH)$_4^-$] = 4.6 × 10^{-5} M, [periodate] = 2.5 × 10^{-4} M, and [OH$^-$] = 1.2 M.

arises from the change in Ag(OH)$_4^-$ concentration over the time span of the experiment.

Kinetics. An Aminco-Morrow stopped-flow apparatus was used for all kinetic measurements. All parts of this device coming into contact with the reagents are constructed of chemically resistant materials such as Kel-F, Teflon, glass, and quartz. The dead time of the apparatus is 4 msec and the efficiency of mixing greater than 98% at 1 msec. The reactions were monitored spectrophotometrically with the apparatus mounted on a Beckman DU monochromator. The tungsten lamp was powered by a Hewlett-Packard Model 6274 B regulated power supply. The light detection system consisted of an Aminco 4-8412 photomultiplier biased by a Kepco "ABC" high-voltage power supply and an Aminco high-performance kinetic photometer connected to an Analog Devices 901 low-voltage power supply. The resulting signal was displayed on the screen of a Tektronix Type 549 storage oscilloscope with a Type 1A6 plug-in differential amplifier and was photographed with a Tektronix Type C-12 oscilloscope camera.

All kinetic experiments were carried out at total ionic strength μ equal to 1.2 M in the OH$^-$ concentration range 0.12–1.2 M with ligand concentrations 20–200 times in excess over the Ag(OH)$_4^-$ concentrations. Because of the instability of the tetrahydroxoargentate(III) ion, its concentration was measured concurrently with each kinetic run. The reactions were followed by measuring the change in transmittance due to the appearance of the product as a function of time at 362 nm (periodate reaction) or 351 nm (tellurate reaction). A typical reaction trace is shown in Figure 3. All experiments were performed in duplicate or triplicate, the reproducibility being generally better than ±5%.

For obtaining proper temperature control, the stopped-flow apparatus was equipped with a thermostating assembly consisting of a metal block fitted around the mixing and observation cell. The bath liquid, maintained at constant temperature to ±0.1° in a Formatemp Junior constant-temperature bath, was circulated through the block around the mixing cell as well as around the reservoir syringes. The

temperature of the reaction was taken as that of the circulating liquid, measured in the line, returning to the bath. Since all reagents were thermally equilibrated in the bath before the syringes were filled, we feel that our stated temperatures are good to within ±0.5° even at the extremes of the temperature dependence study.

Results and Treatment of Data

Ag(OH)$_4^-$ in Sodium Hydroxide Solutions. Although Cohen and Atkinson[9] were able to prepare solutions of the tetrahydroxoargentate(III) ion in potassium hydroxide solutions of KOH from 1.2 to 12.0 M, Cohen[10] was unable to prepare this species in very concentrated (12.0–19.3 M) NaOH. We have found, however, that the electrolytic production of Ag(OH)$_4^-$ proceeds quite easily in 1.2 M NaOH. This is a convenient medium in that Ag(III) is reasonably stable (half life $\approx$ 2 hr) with respect to reduction during the time required to prepare for and carry out the kinetic experiments. Maintaining constant ionic strength with perchlorate solution would not be possible in KOH media due to the low solubility of KClO$_4$.

Stoichiometry. The stoichiometry of the complex formed between Ag(III) and periodate ion has been shown to be two ligands per metal ion.[9] Spectrophotometric data for the Job method of study of the tellurate complexation are given in Figure 4. The maximum absorbance occurs where the ligand:metal mole ratio equals 2. Thus, there are two tellurate ligands associated with each Ag(III) species in solution. Since the spectrum of the complex at very high [tellurate]/ [Ag(III)] ratios is identical with the spectrum at a 2:1 mole ratio, we conclude that no higher order complexes are formed in the concentration range of our kinetic studies.

In the OH$^-$ concentration range of our experiments the predominant ligand species are H$_2$IO$_6^{3-}$ for periodate[15] and H$_4$TeO$_6^{2-}$ for tellurate.[16] Dimerization, while important in less basic media, does not occur for periodate[15,17] and is probably insignificant for tellurate[16,18] under these conditions. The extent of protonation of the reaction products has not been experimentally determined.

In the periodate and tellurate complexes, each coordinated ligand is bidentate with the I or Te atom octahedrally surrounded by six oxygens.[5,19]

Kinetics. It is apparent from Figure 3 that the kinetics of Ag(III) complexation with periodate do not follow a simple one-term rate law. Similar stopped-flow traces were obtained for the tellurate study and we shall consider both systems together. Reaction traces for both systems were successfully treated as resulting from two consecutive pseudo-first-order processes[20,21] corresponding to the stepwise formation of the bis complex. Accordingly, the transmittance data were converted to absorbance and log (A_∞ – A_t) was plotted against time. The slopes of the linear portion of these plots yield the pseudo-first-order rate constant, $k_s{}'$, for one process (the slower one). The pseudo-first-order rate constant for the faster process, $k_f{}'$, was obtained by extrapolating the linear portion back to zero time and replotting the difference between the extrapolated and observed absorbances as a function of time.[21] An example of this

(15) G. J. Buist, W. C. P. Hipperson, and J. D. Lewis, *J. Chem. Soc. A*, 307 (1968).
(16) (a) J. E. Early, D. Fortnum, A. Wojcicki, and J. D. Edwards, *J. Amer. Chem. Soc.*, 81, 1295 (1959); (b) J. E. Early, Ph.D. Thesis, Brown University, 1957.
(17) G. J. Buist, private communication.
(18) J. E. Early, private communication.
(19) L. Jensovsky, *Omagiu Raluca Ripan*, 293 (1966).
(20) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, Chapter 8.
(21) J. H. Baxendale, P. L. T. Bevan, and D. A. Stott, *Trans. Faraday Soc.*, 64, 2389 (1968).
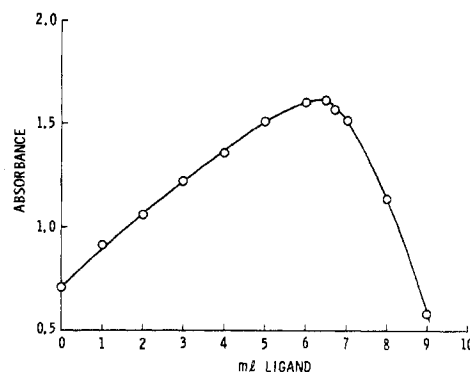

Figure 4. Variation of absorbance at 351 nm with changing [ligand]:[metal] ratio represented by the number of milliliters of ligand solution in a total volume of 10 ml. The starting concentrations are [Ag(OH)$_4^-$] = (5.65 ± 0.20) × 10^{-4} M, [tellurate] = 5.85 × 10^{-4} M, and [OH$^-$] = 1.2 M.
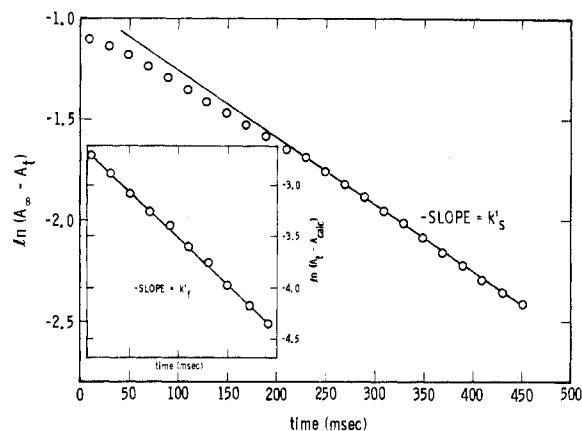

Figure 5. Graphical method for obtaining the pseudo-first-order rate constants $k_s{}'$ and (insert) $k_f{}'$.

treatment is shown in Figure 5. Routinely, the value of $k_s{}'$ was obtained using a linear least-squares computer program which also calculated the data used in the difference plots. For all conditions, values of $k_f{}'$ and $k_s{}'$ were sufficiently different to justify this treatment; however, for a number of cases, not enough data points were available for an accurate determination of k_f.

Values of $k_f{}'$ and $k_s{}'$ at 25° and μ = 1.2 M are given in Table I for periodate complexation and in Table II for tellurate complexation.

In Figure 6, the values of $k_s{}'$ for the periodate reaction are plotted vs. [periodate]. The following points are to be noted: (i) the plot is linear with a slope equal to 1.0 and an intercept equal to zero within experimental uncertainty and (ii) the rate constant is independent of [OH$^-$] in the range 0.12–1.2 M. Similar treatment of all the data reveal that all four rate constants are first order in [ligand] and independent of hydroxide ion concentration. Since the intercepts of Figure 6 and analogous plots are essentially zero, individual values of second-order rate constants, k_f and k_s (unprimed), were computed by dividing the appropriate pseudo-first-order constant by ligand concentration. These are also listed in Tables I and II.

The integrated rate law for the appearance of a bis complex, ML$_2$, from metal, M (initial concentration [M]$_0$), and ligand, L, reacting in consecutive pseudo-first-order rate steps is given in eq 1,[20] where the observed rate constants

$$[ML_2] = [M]_0 \left\{ 1 + \frac{1}{k_1{}' - k_2}(k_2{}'e^{-k_1{}'t} - k_1{}'e^{-k_2{}'t}) \right\} \quad (1)$$

Table I. Kinetic Data for Silver(III)–Periodate Reaction at $T = 25°$ and $\mu = 1.2\,M$

$10^5[\text{Ag(OH)}_4^-]$, M	$10^4[\text{periodate}]$, M	$[\text{OH}^-]$, M	k_f', sec^{-1}	$10^{-4}k_f$, M^{-1} sec^{-1}	k_s', sec^{-1}	$10^{-3}k_s$, M^{-1} sec^{-1}
3.5	50	1.20			46.2	9.24
2.1	50	1.20			49.6	9.92
3.1	25	1.20			23.6	9.44
4.6	25	1.20	90.4	3.62	19.6	7.84
4.3	25	1.20	97.5	3.89	22.5	9.00
3.2	10	1.20	62.2	6.22	10.2	10.2
3.0	5	1.20			5.03	10.1
1.4	25	0.90	119	4.77	24.5	9.80
3.9	50	0.60			49.0	9.80
2.5	25	0.60			23.9	9.56
2.9	25	0.60	104	4.26	24.0	9.60
2.9	10	0.60	46.2	4.16	9.68	9.68
3.3	5	0.60			4.55	9.12
2.1	25	0.30			22.9	9.16
5.6	25	0.30	144	5.76	23.1	9.24
5.1	10	0.30	54.5	5.45	9.36	9.36
4.8	5	0.30	32.4	6.40	4.34	8.68
2.5	50	0.12	158	3.16	41.6	9.54
2.3	25	0.12	86.9	3.58	22.9	9.16
2.2	10	0.12	35.6	3.56	8.36	8.37
2.1	5	0.12	17.3	3.66	4.29	8.58
			Av	4.50 ± 1.11[a]	Av	9.30 ± 0.58[a]

[a] Standard deviation.

Table II. Kinetic Data for Silver(III)–Tellurate Reaction at $T = 25°$ and $\mu = 1.2\,M$

$10^5[\text{Ag(OH)}_4^-]$, M	$10^4[\text{tellurate}]$, M	$[\text{OH}^-]$, M	k_f', sec^{-1}	$10^{-4}k_f$, M^{-1} sec^{-1}	k_s', sec^{-1}	$10^3 k_s$, M^{-1} sec^{-1}
2.0	125	1.20	106	0.847	31.8	2.54
2.0	100	1.20	102	1.02	20.0	2.00
2.2	75	1.20	84.7	1.12	14.9	1.99
2.8	25	1.20	21.2	0.846	7.90	3.16
2.8	25	1.20	27.1	1.07	7.27	2.80
4.0	25	1.20			5.99	2.40
2.6	10	1.20	10.7	1.07	3.62	3.62
3.0	10	1.20			3.13	3.13
2.8	50	0.90	50.5	1.01	11.5	2.30
2.3	50	0.90	48.5	0.970	10.5	2.10
2.8	50	0.90	55.5	1.11	11.8	2.46
1.9	25	0.90	26.0	1.04	6.26	2.50
1.7	10	0.90	10.7	1.07	3.46	3.46
4.3	25	0.60	29.8	1.19	8.89	3.54
4.5	25	0.60	26.5	1.06	5.43	2.17
3.3	10	0.60			2.77	2.77
3.8	5	0.60			1.17	3.44
2.5	25	0.30	24.4	0.968	6.75	2.70
2.1	10	0.30			2.46	2.46
2.3	5	0.30			1.67	3.34
3.1	25	0.12	23.8	0.954	8.45	3.38
2.9	10	0.12	10.3	1.03	2.26	2.26
2.7	5	0.12	4.35	0.889	1.39	2.78
			Av	1.01 ± 0.10[a]	Av	2.72 ± 0.53[a]

[a] Standard deviation.

k_1' and k_2' for the first and second steps, respectively, are products of second-order constants (k_1 and k_2, respectively) times ligand concentration. From the symmetry of eq 1 it can be seen that the analysis of the rate data from the present study does not lead to a particular association between the experimental rate constants k_s and k_f and the rate constants k_1 and k_2 corresponding to the formation of the mono and bis complexes. Since the products of both reactions absorb strongly in the same region as Ag(OH)_4^-,[9,10] it was impossible to determine k_1 directly for either system by monitoring Ag(OH)_4^- disappearance; nor could a suitable wavelength be found for following absorbance due to the mono complex. Absorption of both the mono and the bis complexes in the same region would not affect the results or data treatment. We shall defer further discussion of rate constant assignments until the next section.

Activation studies were carried out at $\mu = 1.2\,M$ in the temperature range 6–35° with $[\text{OH}^-] = 1.2\,M$, [ligand] $= 2.5 \times 10^{-3}\,M$, and [Ag(III)] between 2×10^{-5} and 4×10^{-5} M. The results are listed in Table III. Enthalpies of activation were determined from plots of ln (kNh/RT) vs. $1/T$. Activation entropies were calculated for each experiment from the transition-state expression[22]

$$k = \frac{RT}{Nh}e^{-\Delta H^{\ddagger}/RT}e^{\Delta S^{\ddagger}/R}$$

using the appropriate enthalpy value. We estimate the maximum uncertainty in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ at 1 kcal mol^{-1} and 3 eu, respectively.

(22) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 129.

Table III. Variation of Second-Order Rate Constants with Temperature[a]

Temp, °C	Periodate		Tellurate	
	k_f	k_s	k_f	k_s
6	(1.15×10^4)[b]	4.94×10^3	4.48×10^3	1.13×10^3
15	2.05×10^4	7.32×10^3	8.13×10^3	1.83×10^3
25	4.50×10^4	9.30×10^3	9.85×10^3	3.02×10^3
35	7.36×10^4	1.42×10^4	1.67×10^4	4.80×10^3
	Activation Parameters			
$\Delta H^{\ddagger}$, kcal mol^{-1}	10	6	7	9
$\Delta S^{\ddagger}$, eu	-4	-20	-16	-13

^{a} $\mu = 1.2\ M$, $[OH^-] = 1.2\ M$, and [ligand] $= 2.5 \times 10^3\ M$; all rate constants in M^{-1} sec^{-1}. ^{b} This value could not be experimentally determined. It is based on an extrapolation of the other numbers in this column.
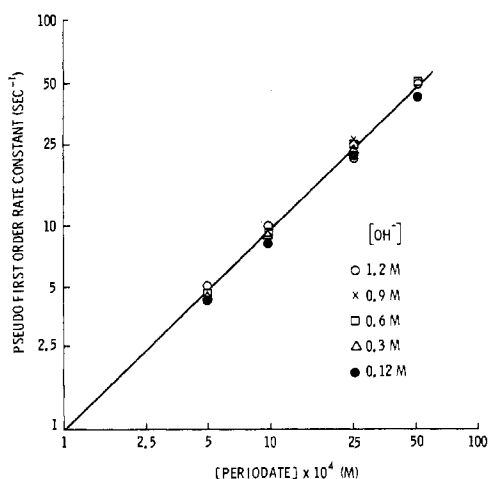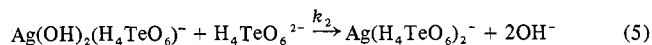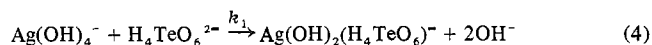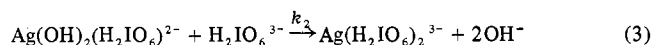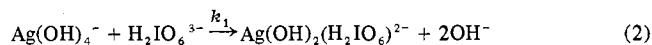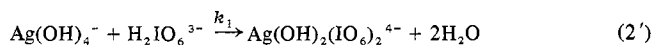

Figure 6. Pseudo-first-order rate constants k_s' vs. periodate concentration at 25° and $\mu = 1.2\ M$ for all experimental NaOH concentrations.
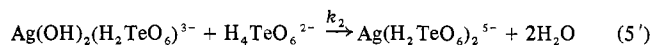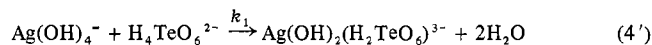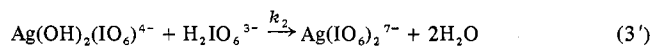
Discussion

A mechanism consistent with the kinetic results is given in eq 2 and 3 for the periodate reaction and eq 4 and 5 for the tellurate reaction.

$$Ag(OH)_4^- + H_2IO_6^{3-} \xrightarrow{k_1} Ag(OH)_2(H_2IO_6)^{2-} + 2OH^- \quad (2)$$

$$Ag(OH)_2(H_2IO_6)^{2-} + H_2IO_6^{3-} \xrightarrow{k_2} Ag(H_2IO_6)_2^{3-} + 2OH^- \quad (3)$$

$$Ag(OH)_4^- + H_4TeO_6^{2-} \xrightarrow{k_1} Ag(OH)_2(H_4TeO_6)^- + 2OH^- \quad (4)$$

$$Ag(OH)_2(H_4TeO_6)^- + H_4TeO_6^{2-} \xrightarrow{k_2} Ag(H_4TeO_6)_2^- + 2OH^- \quad (5)$$

The assignments of reacting species are based on the predominant form of the ligands (*vide supra*). If other forms were present in significant amounts (unlikely for periodate but possible for tellurate[23]), a variation in observed rate constant with $[OH^-]$ or [ligand] would be expected to accompany a shift in protolytic or polymerization equilibrium. It must be mentioned that there is no definite evidence for the number of hydroxyl ions released to the solution as OH^- or the degree of protonation on the complexed ligand. An alternate formulation of eq 2–5 is given by eq 2'–5'.

$$Ag(OH)_4^- + H_2IO_6^{3-} \xrightarrow{k_1} Ag(OH)_2(IO_6)_2^{4-} + 2H_2O \quad (2')$$

$$Ag(OH)_2(IO_6)^{4-} + H_2IO_6^{3-} \xrightarrow{k_2} Ag(IO_6)_2^{7-} + 2H_2O \quad (3')$$

$$Ag(OH)_4^- + H_4TeO_6^{2-} \xrightarrow{k_1} Ag(OH)_2(H_2TeO_6)^{3-} + 2H_2O \quad (4')$$

$$Ag(OH)_2(H_2TeO_6)^{3-} + H_4TeO_6^{2-} \xrightarrow{k_2} Ag(H_2TeO_6)_2^{5-} + 2H_2O \quad (5')$$

Objections to these reactions can be found in the high negative charges on the products and the fact that a greatly increased charge on the mono complex might result in a larger difference between the rate constants than is observed.

Of course, an intermediate number of protons might be lost during, or subsequent to, any one of these reactions. Indeed, from the $[OH^-]$ dependence of the apparent equilibrium constant for $Cu(OH)_4^-$ reacting with two tellurate ions, Lister[24] concluded that two of the four hydroxyls are neutralized. In the copper(III)–periodate reaction ($[OH^-] \geqslant 0.4\ M$) it was postulated[24] that all four protons are lost resulting in a 7– charge on the product, although a more recent study[25] indicates that the complex is protonated in basic media ($pK_a \approx 13$ for the loss of the first of an unspecified number of protons).

The fully deprotonated periodate complex does not seem likely for the Ag(III) system since solid salts of the complex precipitated from basic solutions generally have formulas involving at least two and, more often, four protons.[3,4,26] Solid tellurates, on the other hand, can contain even fewer protons than indicated in eq 5'.[3]

Information concerning the actual mode of ligand exchange in these Ag(III) systems as well as some elucidation of rate constant assignments can be obtained from an examination of the activation parameters (Table III). It can be inferred from magnetic measurements,[8] stoichiometries of Ag(III) complexes,[1–9] and comparison with other d^8 systems[5,27] that trivalent silver has a square-planar geometry. Thus, we may presume that, by analogy with other low-spin d^8 metals, ligand substitution on $Ag(OH)_4^-$ with the periodate and tellurate ions proceeds by reaction paths which are essentially associative in nature.[28–30]

The data in Table III do tend to support an associative mechanism for these reactions.[28,30] Thus, we note that the activation enthalpies are moderate (6–10 kcal mol^{-1}) while entropies of activation are negative for all four reactions. This is as expected for processes in which the rate-determining

(24) M. W. Lister, *Can. J. Chem.*, 31, 638 (1953).
(25) W. G. Movius, *Inorg. Chem.*, 12, 31 (1973).
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(28) Reference 22, Chapter 5.
(29) C. H. Langford and T. R. Stengle, *Annu. Rev. Phys. Chem.*, 19, 193 (1968).
(30) (a) L. Cattalini, *Progr. Inorg. Chem.*, 13, 263 (1970); (b) *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Inorg. Chem., Ser. One*, 9, 269 (1972).

(23) From the data of Early[16b] we estimate that the maximum percentage of tellurate existing as $H_3TeO_6^{3-}$ is ~25% at $[OH^-]$ = 1.2 M and ~7% at $[OH^-]$ = 0.12 M. Absence of a demonstrated dependence of complexation rate on $[OH^-]$ supports the probability that (unless alternate paths have similar rate constants) the percentages $H_3TeO_6^{3-}$ in this $[OH^-]$ range are even less than these amounts.

step is attack of the ligand onto the four-coordinated Ag(III) with expansion of the inner coordination sphere of the metal. Although we are dealing with a very few reactions involving metal and ligand species for which no analogous kinetic data are available, the foregoing characterizations seem most reasonable at the present time.

We may now say that each of the second-order rate constants listed in Tables I and II represents the forward rate constant for direct ligand replacement on square-planar Ag(III) with no observable contribution from a "solvent path"[28] or reverse reaction. It remains for us to attempt an association between these values of k_f and k_s and the constants k_1 and k_2. The ratio of the observed rate constants k_f/k_s at 25° is similar and quite moderate for both periodate (~4.8) and tellurate (~3.3) with the periodate system reacting somewhat faster. However, the temperature dependence and resultant activation parameters (Table III) exhibit different trends for the two systems.

The difference in $\Delta S^{\ddagger}$ is sufficiently large for the two periodate complexations that we make the assignments $k_1 \equiv k_f$ and $k_2 \equiv k_s$ for periodate in accordance with statistical and steric considerations. That is (assuming similar solvation effects), a more negative activation entropy is expected for the second step because of a reduced number of possible coordinating sites and increased hindrance to ligand attack on the monoperiodate complex compared to the Ag(OH)$_4^-$ anion. In addition, even if no periodate protons are lost upon complexation, the mono(periodato)argentate-(III) anion will be more negatively charged than Ag(OH)$_4^-$ (eq 2, 2'). Although this does not necessarily lead to a decrease in $\Delta S^{\ddagger}$,[30,31] increased electron density on the mono

(31) R. M. Milburn and L. M. Venanzi, *Inorg. Chim. Acta*, **2**, 97 (1968).

complex might play some part in reducing the activation enthalpy for the second step.

In the case of tellurate complexation, there is no large difference in either $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$ for the two steps. As noted above, $\Delta S^{\ddagger}$ for the second complexation would be expected to be more negative than for the first step. We thus tend to favor the association $k_1 \equiv k_s$ and $k_2 \equiv k_f$ for tellurate, although this must be considered a very tenuous assignment. A more negative $\Delta S^{\ddagger}$ for substitution on Ag(III) by tellurate as compared to periodate might be due in part to the higher degree of protonation on H$_4$TeO$_6^{2-}$ resulting in a decrease in the number of possible attacking sites.

Because of the limited stability of the tetrahydroxoargentate(III) anion and the dearth of well-characterized silver(III) complexes, we have chosen ligands for this initial study of Ag(III) substitution rates which have not previously been used in complexation kinetics studies. Thus, until data on analogous reactions are available, no meaningful comparison of the rates of Ag(III) substitution reactions with those of other square-planar d^8 systems can be made. It is interesting to note, however, that, in spite of possibly unfavorable electrostatic interactions between Ag(OH)$_4^-$ and the incoming ligand, the reactions of this study are more rapid than typical substitution rates on gold(III) or palladium(II)—both of which, in turn, react faster than platinum(II).[28]

Synthesis and Reactions of Aminotellurium Pentafluoride

KONRAD SEPPELT

R$_3$SiNHTeF$_5$ (R = CH$_3$) is produced by reaction of (R$_3$Si)$_2$NH with tellurium hexafluoride. *N*-Trimethylsilylaminotellurium pentafluoride reacts with hydrogen fluoride to yield the title compound. The preparation of the derivatives H$_2$NTeF$_5$· AsF$_5$, Cs$^+$NHTeF$_5^-$, and [-HgN(TeF$_5$)-]$_x$ is described.

Aminosulfur pentafluoride (H$_2$NSF$_5$) is not stable toward hydrogen fluoride elimination.[1] The existence of H$_2$NSeF$_5$ seems to be unlikely, considering the oxidation potential of selenium in the VI valence state. Known derivatives, R$_2$NTeF$_5$,[2] decompose rapidly above 35°, suggesting that only limited stability can be expected for H$_2$NTeF$_5$.

In the present work, aminotellurium pentafluoride is produced by a double silicon–nitrogen cleavage reaction. Contrary to the suggestions described above, H$_2$NTeF$_5$ was found to be stable up to 150°. Further, its behavior as acid or base was studied. The base character of H$_2$NTeF$_5$ is lower than that of H$_2$NSF$_5$, and some acid character is proved by the

existence of the salts Cs$^+$NHTeF$_5^-$ and [-HgN(TeF$_5$)-]$_x$, both of which were made by cleavage of R$_3$SiNHTeF$_5$[1] with cesium fluoride and mercuric fluoride.

Experimental Section

General Information. Fluorine and proton nmr spectra were taken on a JEOL 60 HL instrument, using CFCl$_3$ as an internal reference. Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer with KBr windows. Raman spectra were taken on a Coderc PH 1 instrument, using a He–Ne laser for excitation, 190 mW. Mass spectra were recorded on a Varian CH 7 instrument with 70-eV excitation energy.

Materials. Bis(trimethylsilyl)amine was prepared by ammonolysis of chlorotrimethylsilane.[3] Fluorination of elemental tellurium, ar-

(1) A. F. Clifford and L. C. Duncan, *Inorg. Chem.*, **5**, 692 (1966).
(2) C. W. Fraser, R. D. Peacock, and P. M. Watkins, *J. Chem. Soc. A*, 1125 (1971).

(3) R. O. Sauer and R. H. Hasek, *J. Amer. Chem. Soc.*, **68**, 241 (1946).