Clearly the contributions to k_2' and k_2'' cannot be separated from a study of the hydrolysis of the total sulfamato complex. It was hoped that studies over a wide temperature range might yield a nonlinear temperature dependence of k_2' and k_2'' as would occur if the activation energies for the individual terms were much different. However, a nonlinear least-squares fit[8] of all the data in Table II to eq 8 with normal transition-state theory expressions for k_2' and k_2'' did not indicate any significant nonlinearity in the temperature dependence as can be seen by comparison of the calculated and observed values in Table II. Either the various terms have similar activation enthalpies or one of them is dominant but it cannot be determined which one it might be.

In the previous study[1] of the hydrolysis of the sulfamato complex in basic solution, a term in the rate

law independent of [OH$^-$] was observed. This term could be assigned either to the reaction of $(NH_3)_5$-CoNHSO$_3^+$ with water or to the reaction of $(NH_3)_5$Co-NH$_2$SO$_3^{2+}$ with hydroxide ion. The latter path was favored in the earlier work because a comparison of the ratio of the rate constants for reaction with hydroxide ion and water (results given here) was normal, *i.e.*, in the range of 10^4–$10^6 \ M^{-1}$. The detailed results given here show that the reaction of $(NH_3)_5$CoNH$_2$SO$_3^{2+}$ in aqueous acid is more complicated than supposed before. However, the observed rate constant for hydrolysis in acidic solution gives an upper limit for the aquation rate constant of the N-bonded isomer, so that the ratio of alkaline hydrolysis to aquation rates is $\geq 100/(2.6 \times 10^{-5})$ or $3.8 \times 10^6 \ M^{-1}$. Since this is a much more normal ratio than the value of 0.35 obtained if the alternative reaction path is assumed, then the arguments in ref 1 are still valid, and the alkaline hydrolysis of $(NH_3)_5$CoNH$_2$SO$_3^{2+}$ was observed in the previous work.

(8) L. L. Rines, J. A. Plambeck, and D. J. Francis, "ENNLLSQ Reprogrammed," Program Library, Department of Chemistry, University of Alberta, 1970.

A Laser Raman Study of Aqueous Copper Nitrate Solutions

By A. R. DAVIS* and C. CHONG

Raman spectra of aqueous copper nitrate solutions have been recorded using an argon ion laser. Absorption of Raman scattered light by the deeply colored copper solutions has necessitated corrections to measured Raman intensities. Corrected Raman intensities have been used to calculate concentration equilibrium constants of the species present in solution. Good agreement has been obtained between concentration quotients calculated from intensity variations of the 722- and 1052-cm^{-1} Raman bands, both originating from the solvated nitrate ion. The validity of the calculated concentration quotient for CuNO$_3^+$, $K_{assoc} = 0.07 \pm 0.02$ at 25°, is illustrated in the agreement between measured and calculated Raman intensities of copper nitrate solutions.

Introduction

The use of Raman spectroscopy to study interactions in metal nitrate systems is now well established.[1] The Raman spectrum of saturated aqueous copper nitrate has been reported and noted to be more complex than that of the alkali metal nitrates.[2] Mathieu and Lounsbury interpreted Raman spectral results by assuming that the saturated solution has a structure similar to that of the hydrated crystal.[3] Whereas, Hester and Plane interpreted their results in terms of complex ion formation,[2] an isopiestic study of aqueous copper nitrate solution led Robinson, *et al.*, to suggest that there is probably no appreciable complex formation in aqueous copper nitrate.[4]

A study of the system by Bjerrum has detected a very weak hydroxynitrato species (Cu(OH)$_{1.5}$(NO$_3$)$_{0.5}$).[5] Two authors have studied the uv and visible spectrum of copper(II) nitrate dissolved in an acetone–water mixture. Plane has suggested that there is evidence

for ion pairing.[6] Gazo has developed a photometric method of determining trace amounts of nitrate in acetone based on the formation of a complex species among the copper(II) ion, nitrate ion, and acetone.[7] The species is considered to be polymeric with the nitrate group acting as a bridge. An esr study of copper(II) ions in solutions has shown that the line width of the broad band observed was both concentration and anion dependent, above approximately $0.1 \ M$.[8] The reduction in half-width of the copper(II) resonance with concentration has been related to the equilibrium between the solvated copper(II) ions and an ion pair involving copper(II) and nitrate ions.

There has, in general, been reasonable agreement between equilibrium constants obtained from Raman spectroscopy and other physical measurements.[9] Although no formation constants have been measured for complex nitrate–copper species, it may be concluded from measurements made that if the species exist they will be weak.[4] An objective of this study is to extend the previous Raman measurements and measure the formation constants of complex nitrate–copper species.

(1) D. E. Irish, "Ionic Interactions," S. Petrucci, Ed., Academic Press, New York, N. Y., 1971, p 188.

(2) R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 769 (1964).

(3) J. P. Mathieu and M. Lounsbury, *Discuss. Faraday Soc.*, **9**, 196 (1950).

(4) R. A. Robinson, J. M. Wilson, and H. S. Ayling, *J. Amer. Chem. Soc.*, **64**, 1469 (1942).

(5) J. Bjerrum, *Kgl. Dan. Vidensk. Selsk., Mat.-Fys. Medd.*, **11**, 5 (1931).

(6) N. J. Friedman and R. A. Plane, *Inorg. Chem.*, **2**, 11 (1963).

(7) J. Gazo, *Sb. Pr., Chem. Fak. SVST*, 25 (1964).

(8) S. Fujiwara and H. Hayashi, *J. Chem. Phys.*, **43**, 23 (1965).

(9) A. R. Davis and R. A. Plane, *Inorg. Chem.*, **7**, 2565 (1968).

Experimental Section

Preparation of Solutions.—Solutions were prepared as follows: copper nitrate from $Cu(NO_3)_2 \cdot 3H_2O$ and checked volumetrically;[10] copper perchlorate, 2.64 M stock solution, by allowing copper carbonate to react with perchloric acid then analyzing for copper volumetrically[10] and for perchlorate ion by Raman spectroscopy; sodium nitrate, 7.0 M stock solution, from the dried salt; molar ratio solutions were prepared from copper perchlorate and sodium nitrate. Three sets of solutions were prepared with fixed copper ion concentrations of 1.0, 1.5, and 2.0 M. The nitrate to copper ratio was varied from 0.6 to 4.0.

Instrumentation.—Infrared spectra were recorded of thin-film samples pressed between silver chloride plates using a Perkin-Elmer spectrometer, Model 457. Raman spectra were recorded on a Jarrell-Ash 25-300 laser Raman spectrometer using a Coherent Radiation Model 54 argon ion laser. The laser was equipped with a Coherent Radiation Model 235 amplitude stabilization device. Laser power never varied by more than $\pm 1\%$ over a 12-hr period with the amplitude stabilization device in operation. The laser produced 250 mW at 488 nm, measured at the sample position with a Spectra Physics Model 401B power meter.

Laser stability over the period of an experiment was checked by recording the 459-cm^{-1} band of carbon tetrachloride before and after each run. If the intensity of this band differed, then the intervening spectrum was remeasured.

Depolarization measurements were carried out according to Allemand.[11] The technique was regularly checked using carbon tetrachloride, a value of 5×10^{-3} was obtained for the depolarization ratio of the 459-cm^{-1} band. Overlapping bands were resolved with the aid of a Du Pont Model 310 curve analyzer.

The optical density of the copper nitrate solutions was measured using a Beckman DBG spectrophotometer with water as the reference material.

With the availability of stable laser excitation sources it should be possible to measure Raman intensities with good precision. The use of lasers as excitation sources, with their narrow-beam dimensions, requires that the sample, laser beam, collecting optics, and monochromator entrance slit be kept in rigid alignment if reproducible intensity data are to be obtained. The thermostated Raman sample cell holder (Figure 1) allows a sample to be placed in a laser beam and the sample to be changed without disturbing the alignment of the sample, laser, or collection optics. The liquid sample is in a commercially available (Thermal Syndicate Limited) 1-cm path length fluorescence analysis cell. The cell has an optical window on the bottom as well as on all four sides, and it is held in a cuvette holder (Figure 1a) similar to the one used in uv–vis spectrometers. The holder was machined from a copper block. Channels were drilled into the sides to provide a path for thermostating liquid. The cell is held squarely in one corner of the holder by means of thin springs which extend the length of the holder. The cell holder is attached to the main support column with the aid of a sliding track (Figure 1b) so that the horizontal position of the cell holder may be varied.

The path of the laser beam through the sample is defined by two pinholes (Figure 1c and d), accurately drilled to be in the same vertical plane as the support column. In this arrangement the polarization of the incident laser beam may be varied by using a quarter-wave plate between the two pinholes. The support column for the cell holder and pinhole arrangement is suspended by means of an adjustable track from a rider base holder (Figure 1e).

Before using the cell holder it is necessary to ensure that the laser beam is parallel to the entrance slit. The cell holder is aligned so that the laser beam passes through both pinholes and the center of the cell compartment. A sample is placed in the cell and fine adjustments are made to ensure maximum Raman signal. Finally, all adjustable controls are tightened down.

The sample cell, collection lens system, and spectrometer entrance slit are arranged so that the image overfills the slit by a factor of 2. This allows some variation in alignment of the incident laser beam with the entrance slit and compensates for slight misalignment of laser beam or beam movement resulting from changes of solution refractive index. The reproducibility of intensity measurements over a 3-month period was $\pm 2\%$.
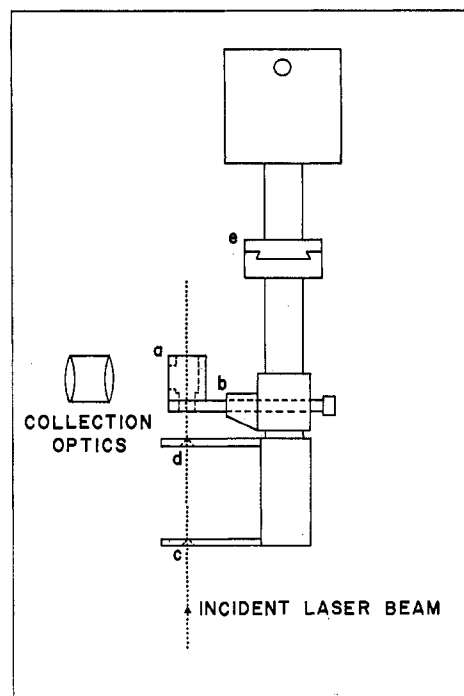

Figure 1.—Thermostated Raman sample cell holder.

Results and Discussion

A 4.68 M solution of copper nitrate has a strong visible absorption band around 740 nm and of approximately 125-nm half-width. The band tails off on the short-wavelength side to around 500 nm (at 488 nm the molar extinction coefficient of aqueous copper nitrate is 0.03). Excitation of Raman spectra by means of an argon laser operating at 488 nm will result in some of the incident laser light being absorbed by the copper nitrate solution. Since the more intense Raman scattered light from the copper nitrate solution occurs to the long-wavelength side of 488 nm, it also can be absorbed by electronic processes. This is probably a more important effect than the absorption of incident laser light. These two errors in Raman intensity measurements have been corrected by the use of an internal standard. The internal standard chosen consists of known concentrations of sodium perchlorate. The perchlorate ion has two desirable features: first, it has negligible ability to form complexes in aqueous systems;[2] second, it has Raman bands at 632 and 938 cm^{-1}, conveniently close to the Raman bands of the nitrate ion, 722 and 1052 cm^{-1}. This means that any attenuation of scattered Raman light by electronic absorption will be the same for the nitrate and standard perchlorate bands. Compensation for Raman intensity attenuation by electronic absorption can be expressed more concisely. The Raman scattering intensity, I_0, is proportional to the concentration of scattering species, C. The proportionality constant, J, is called the molar scattering coefficient. Raman intensities of nitrate bands are expressed relative to those of perchlorate bands

$$\frac{I_0(NO_3^-)}{I_0(ClO_4^-)} = \frac{J(NO_3^-)C(NO_3^-)}{J(ClO_4^-)C(ClO_4^-)} \quad (1)$$

The concentration of perchlorate ion, $C(ClO_4^-)$, and its

(10) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," Wiley, New York, N. Y., 1966, p 358.

(11) C. D. Allemand, *Appl. Spectrosc.*, **24**, 348 (1970).

molar scattering coefficient, $J(ClO_4^-)$, are constant and may be incorporated into $J'(NO_3^-)$

$$I_0(NO_3^-)/I_0(ClO_4^-) = J'(NO_3^-)C(NO_3^-) \quad (2)$$

A measurement of I_0 and J' can therefore be used to determine the concentration of solvated nitrate ion. If the solution is absorbing in the region of Raman scattering then the measured intensity will be lower than the correct intensity. The intensity will be diminished according to the Beer–Lambert law. At a fixed wavelength the correct intensity of the Raman scattered light, I_0, is related to the measured intensity, I_x, by the transmittance T of the solution

$$T = I_x/I_0 \quad (3)$$

When 488-nm light is used to excite the Raman spectrum of a solution containing nitrate and perchlorate ions, the absolute position of the nitrate 722-cm^{-1} band is 505 nm; similarly that of the perchlorate 632-cm^{-1} band is 502 nm. From eq 3

$$I_0(ClO_4^-) = \frac{I_x(ClO_4^-)}{T_{502}} \qquad I_0(NO_3^-) = \frac{I_x(NO_3^-)}{T_{505}}$$

T_{502} and T_{505} correspond to the transmittance of the solution at 502 and 505 nm, respectively. Therefore

$$\frac{I_0(NO_3^-)}{I_0(ClO_4^-)} = \frac{I_x(NO_3^-)T_{502}}{I_x(ClO_4^-)T_{505}}$$

The intensity of the electronic absorption band of the copper nitrate solution does not markedly change over the region 502–505 nm. Also the path length for the Raman light originating from perchlorate and nitrate is the same, as of course is the extinction coefficient of the solution. Therefore $T_{502} \simeq T_{505}$ and

$$\frac{I_0(NO_3^-)}{I_0(ClO_4^-)} = \frac{I_x(NO_3^-)}{I_x(ClO_4^-)}$$

A similar derivation may be obtained for the 1052-cm^{-1} nitrate and 938-cm^{-1} perchlorate Raman bands, whose absolute wavelength positions are 513 and 510 nm, respectively. Therefore, relative intensities of nitrate to perchlorate Raman bands are obtained which are independent of solution optical density. These relative intensities may be used to derive the concentration of solvated nitrate ion in solutions of copper nitrate.

Previous Raman studies of aqueous nitrate systems have characterized the spectra of solvated nitrate ions and complex metallonitrate species.[1] The vibrational spectrum of copper nitrate solution (Table I) may be interpreted in terms of the following species: the solvated copper ion $Cu(H_2O)_6^{2+}$ generating a polarized Raman band at 436 cm^{-1};[12] the solvated nitrate ion with Raman bands at 722, 1052, 1352, and 1420 cm^{-1};[13] complex nitratocopper species generating Raman bands at 757, 1040, 1315, and 1490 cm^{-1}; and a copper–oxygen stretch vibration at 272 cm^{-1}. The broad weak Raman band at 688 cm^{-1} has been ascribed to a librational mode of the nitrate ion.[13]

It is worth noting that the frequencies here ascribed to the solvated nitrate ion do not correspond exactly to those reported.[13] This may be indicative of a cou-

TABLE I
RAMAN AND INFRARED FREQUENCIES (CM^{-1}) AND
RAMAN DEPOLARIZATION RATIOS (ρ) (IN PARENTHESES)
ORIGINATING FROM A 4.68 M SOLUTION OF COPPER NITRATE

Ir	Raman[a]	Ir	Raman[a]
	272 (0.40)	1030 m	1040 (0.08)
	436 (0.07)		1052 (0.05)
	688 (~0.5)	1300 s	1215 (0.18)
	722 (0.70)		1352 (~0.10)
		b	
	757 (0.23)		1420 (~0.6)
805 w[c]		1400 s	1490 (~0.5)
820 w			

[a] Depolarization results in the 1300–1500-cm^{-1} region should be only regarded as approximate in view of the curve-resolving difficulties in this region. [b] Infrared absorption is broad and intense in the region 1300–1400 cm^{-1}. [c] Key: w, weak; m, medium; s, strong.

lombic interaction between copper and solvated nitrate ions through intervening water molecules.

It was originally intended to use both intensity variations of bands due to complex species: 272 and 757 cm^{-1} and those due to free nitrate; 722 and 1052 cm^{-1} in the calculation of stability constants. However, the band at 272 cm^{-1} is only observable in the 4.68 M solution of copper nitrate and the 757-cm^{-1} band disappears rapidly on dilution of the stoichiometric solutions and only occurred very weakly in the molar ratio solutions. Therefore the stoichiometry and stability of the complex nitrate–copper species was obtained simply from measured free nitrate Raman intensity, *i.e.*, 722 and 1052 cm^{-1}. Intensities were measured relative to perchlorate ion intensities to compensate for solution transmittance changes. A comparison of intensities from copper nitrate solutions and a standard sodium nitrate solution, which is completely dissociated below 5 M, leads to the concentration of uncomplexed nitrate ion. Since the total concentration of nitrate present is known, it is possible to calculate the concentration of complexed nitrate. Subsequent calculations of $\bar{n}$, the average number of nitrate ions bound per copper ion,[14] indicated that this did not rise above 0.4, Table II. An association constant has been calculated on the assumption that only $CuNO_3^+$ is present in solution. These calculations were carried out for the three series of molar ratio solutions using both the 722- and 1052-cm^{-1} bands. Table II illustrates the reasonable agreement between four series of measurements of K and indicates that both the 722- and 1052-cm^{-1} bands may be used as indicators of solvated nitrate ion concentration. Also, the calculated values of K do not show any significant dependency on metal ion concentration indicating an absence of polynuclear formation. The possibility of the existence of the species $Cu(NO_3)_2$ was explored using the relationship[14]

$$\frac{(1 - \bar{n})(NO_3^-)}{\bar{n}} = \frac{1}{\beta_1} - \frac{\beta_2}{\beta_1} \frac{(2 - \bar{n})(NO_3^-)^2}{\bar{n}}$$

Good agreement was obtained between K, calculated on the basis of only $CuNO_3^+$ being present, and β_1, calculated for $CuNO_3^+$ assuming $Cu(NO_3)_2$ was also present. Nevertheless the values for β_2 were small (approximately 0.001) and widely scattered. It can be

(12) R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 768 (1964).
(13) D. E. Irish and A. R. Davis, *Can. J. Chem.*, **46**, 943 (1968).

(14) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill, New York, N. Y., 1961.

Table II
SUMMARY OF DATA FROM MOLAR RATIO SOLUTIONS

722-Cm⁻¹ Band

| | [Cu²⁺]total = 1.5 M | | | | [Cu²⁺]total = 2.0 M | | |
R^a	$[NO_3^-]^b$	$\bar{n}^c$	K^d	R	$[NO_3^-]$	$\bar{n}$	K
0.6	0.82	0.06	0.07	0.6	1.09	0.06	0.05
1.0	1.37	0.09	0.07	1.0	1.81	0.10	0.06
1.3	1.78	0.12	0.07	1.3	2.37	0.12	0.06
1.6	2.19	0.14	0.08	1.6	2.93	0.14	0.05
2.0	2.74	0.17	0.08	2.0	3.67	0.17	0.05
2.3	3.15	0.20	0.08	2.3	4.20	0.20	0.06
2.7	3.69	0.24	0.09	2.7	4.94	0.23	0.06
3.2	4.37	0.29	0.09	3.2	5.85	0.28	0.07
				3.6	6.59	0.31	0.07

1052-Cm⁻¹ Band

| | [Cu²⁺]total = 1.5 M | | | | [Cu²⁺]total = 1.0 M | | |
R	$[NO_3^-]$	$\bar{n}$	K	R	$[NO_3^-]$	$\bar{n}$	K
0.2	0.27	0.02	0.09	0.6	0.56	0.04	0.07
0.8	1.09	0.07	0.09	1.0	0.93	0.07	0.08
1.2	1.66	0.10	0.06	1.5	1.39	0.11	0.09
1.8	2.48	0.15	0.07	2.0	1.87	0.13	0.08
2.2	3.05	0.17	0.07	2.3	2.15	0.15	0.08
2.7	3.74	0.21	0.07	2.72	2.54	0.18	0.09
3.0	4.21	0.24	0.07	3.12	2.91	0.21	0.09
3.3	4.57	0.25	0.07	3.60	3.36	0.24	0.09
3.8	5.27	0.29	0.08	4.0	3.74	0.26	0.09

[a] $R = [NO_3^-]_{total}/[Cu^{2+}]$. [b] $[NO_3^-]$ is free nitrate concentration calculated from Raman intensity of 722-cm⁻¹ band using eq 2. [c] $\bar{n} = [NO_3^-]_{bound}/[Cu^{2+}]_{total}$; $[NO_3^-]_{bound} = [NO_3^-]_{total} - [NO_3^-]$. [d] $K = [CuNO_3^+]/[Cu^{2+}][NO_3^-]$; $[CuNO_3^+] = [NO_3^-]_{bound}$; $[Cu^{2+}] = [Cu^{2+}]_{total} - [CuNO_3^+]$.
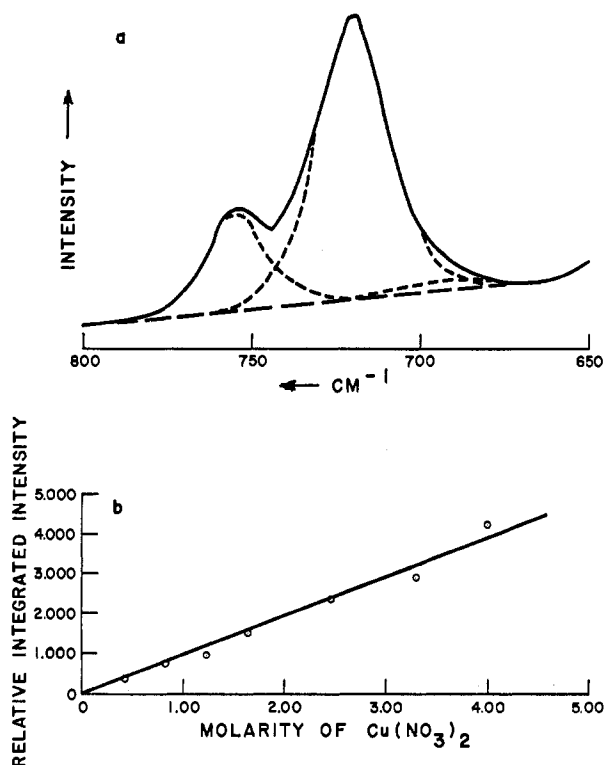

Figure 2.—(a) Analysis of the Raman spectrum of 4.68 M copper nitrate solution, 600–800 cm⁻¹. (b) Intensity variation of 722-cm⁻¹ nitrate band relative to 632-cm⁻¹ perchlorate band for stoichiometric copper nitrate solutions; O, experimental results; —, calculated using $K_1 = 0.07$.

concluded that $CuNO_3^+$ is the important species. The accuracy of K may be judged by the subsequent calculations on stoichiometric solutions of copper nitrate. Using the calculated association constant for $CuNO_3^+$,

free nitrate ion concentrations and resultant intensities of the 722- and 1052-cm⁻¹ bands have been calculated. The results for the stoichiometric solutions are tabulated in Table III. The solid lines in Figures 2b and

Table III
CALCULATED FREE NITRATE ION CONCENTRATIONS AND RAMAN INTENSITIES FOR STOICHIOMETRIC COPPER NITRATE SOLUTIONS

$[Cu(NO_3)_2]$, M	$[NO_3^-]$, M Calcd^a	$I_{722}{}^b$ Measd	$I_{722}{}^b$ Calcd	$I_{1052}{}^c$ Measd	$I_{1052}{}^c$ Calcd
4.11	6.91	4.21	3.73	4.82	5.22
3.29	5.66	2.88	3.06	4.24	4.27
2.46	4.40	2.36	2.38	3.21	3.32
1.64	2.99	1.49	1.62	2.21	2.26
1.23	2.29	0.92	1.24	1.71	1.73

[a] Calculated using $K = 0.07$ for $CuNO_3^+$. [b] I_{722} calculated using $J_{722} = 0.54$. [c] I_{1052} calculated using $J_{1052} = 0.76$.
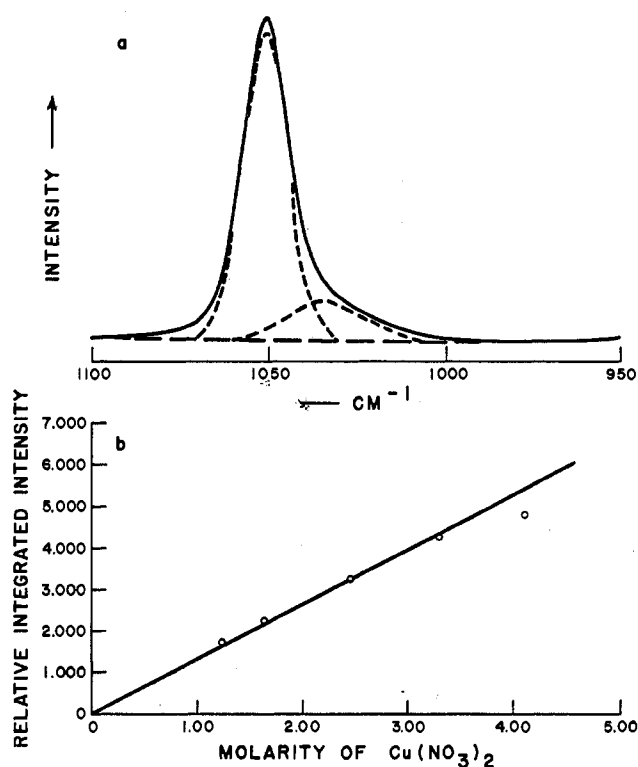

Figure 3.—(a) Analysis of the Raman spectrum of 4.68 M copper nitrate solution, 900–1100 cm⁻¹. (b) Intensity variation of 1052-cm⁻¹ nitrate band relative to 938-cm⁻¹ perchlorate band for stoichiometric copper nitrate solutions: O, experimental results; —, calculated using $K_1 = 0.07$.

3b correspond to free nitrate ion concentrations calculated using $K = 0.07$ for the $CuNO_3^+$ species. The agreement between experiment and calculations is satisfying and justifies the conclusion that $CuNO_3^+$ is the important complex species. The geometry of the $CuNO_3^+$ is possibly similar to that of $CdNO_3^+$,[9] neglecting the disposition of solvating water molecules. The depolarization ratios of the 1040-, 757-, and 1315-cm⁻¹ Raman bands would support a C_{2v} model for the $CuNO_3^+$ species with the nitrate bonded in a monodentate fashion. Nevertheless the occurrence of a polarized band at 1490 cm⁻¹ could be used as evidence for bidentate bonding of the nitrate ion.[15] The 1215-

cm^{-1} band is quite well resolved from the ~1400-cm^{-1} envelope and it is possible to measure its depolarization ratio more accurately than for the 1490-cm^{-1} band.

(15) H. Brintzinger and R. E. Hester, *Inorg. Chem.*, **5**, 980 (1966).

However, since it is not possible accurately to measure the depolarization ratio of the 1490-cm^{-1} band, it is not possible completely to rule out the possibility of bidentate nitrate group bonding.

Kinetics of Oxidation of Some Hydroxylamines by Silver(II)[1]

By DAN S. HONIG, KENNETH KUSTIN,* and JOSEPH F. MARTIN

The kinetics and stoichiometry of the oxidation of hydroxylamine and O-methylhydroxylamine by silver(II) have been determined in acid perchlorate media (1.03 $M <$ [HClO$_4$] < 5.83 M) at 22°. The kinetics of the reaction with N-methylhydroxylamine, but not the stoichiometry, has also been determined. In the presence of excess silver(II), stoichiometric measurements indicated that the product of reaction with NH$_3$OH$^+$ is NO$_3^-$; with NH$_3$OCH$_3^+$ the products are NO$_3^-$ and CO$_2$, the latter directly detected in stoichiometric amounts by gas chromatographic analysis. No dependence of rate on [Ag(I)] or ionic strength was observed, within experimental error, for hydroxylamine; for O-methylhydroxylamine, the rate was inversely dependent on acidity and ionic strength. The acidity variation for both hydroxylamines has been ascribed to the difference in reactivity of Ag^{2+} and AgOH$^+$, which coexist in rapid equilibrium at these hydrogen ion concentrations. For K_H = [AgOH$^+$][H$^+$]/[Ag^{2+}], graphical analysis of the rate data at ionic strength 5.95 M yields K_H = (0.32 ± 0.14) M. With the primed rate constant designating reaction with AgOH$^+$, the rate constants are: for NH$_3$OH$^+$, $k < 10^4$ M^{-1} sec^{-1} and k' = (1.4 ± 0.5) × 10^6 M^{-1} sec^{-1}; for NH$_3$OCH$_3^+$, $k < 10^3$ M^{-1} sec^{-1} and k' ≃ (2 ± 1) × 10^4 M^{-1} sec^{-1}. For CH$_3$NH$_2$OH$^+$, the apparent second-order rate constant, k_{app}, determined by the stopped-flow technique is k_{app} = (1.6 ± 0.6) × 10^5 M^{-1} sec^{-1}. The mechanisms of these reactions are discussed in terms of free-radical intermediates. Comparison is made with analogous results for oxidation of hydroxylamines by Mn(III), for which the comparable rate constants are approximately one order of magnitude less (NH$_3$OH$^+$), and as much as three orders of magnitude less (NH$_3$OCH$_3^+$). In this and other studies the stoichiometric consumption ratio may vary with the ratio of initial moles of reactants present. An explanation is provided for this behavior in terms of competitive intermediate steps.

Silver(II) is generally an extremely strong, rapidly reacting oxidizing agent in perchlorate media. In fact, for a given substrate, a comparison of its reactivity with that of manganese(III) shows silver(II) to be at least one order of magnitude more rapidly oxidizing than even this highly reactive species.[2,3] The high oxidation potential (~ −2 V)[4] of silver(II) also causes most of its reactions to be irreversible. Consequently, the only fast reaction method available for kinetic measurement is rapid mixing, which has been used in this study.

Reactions of silver(II) with some substrates were too fast to be studied definitively by this method. Its reaction with hydrogen peroxide, hydroquinone, and nitrous acid were found to be essentially complete within the resolution time (2–5 msec, depending on experimental conditions) of our stopped-flow apparatus. O-Methylhydroxylamine, present as NH$_3$OCH$_3^+$ at high acid concentration,[5] was found to have one of the

slowest rates of reaction with Mn(III) of the substrates studied.[3a,6] Its rate of reaction with Ag(II) is found to be well within detectable range, suggesting other, more reactive, substrates could also be studied. Hydroxylamine and N-methylhydroxylamine, present as NH$_3$OH$^+$ and CH$_3$NH$_2$OH$^+$, respectively, at high acid concentration[5] are of obvious interest due to their similarity to O-methylhydroxylamine; they were also found to have rates of reaction within a detectable range. Since few studies on the rates of rapid, multistep reactions of silver(II) have been decribed, we are reporting on the reactions with NH$_3$OH$^+$ and NH$_3$OCH$_3^+$. (A more limited study of the reaction with CH$_3$NH$_2$OH$^+$ is included as it helps in elucidating the mechanisms.) The results afford a comparison with those obtained for manganese(III).[6]

Experimental Section

Reagents.—Preparation and standardization procedures for silver(I) perchlorate, sodium perchlorate (for maintaining ionic strength, μ), and perchloric acid were as described previously.[7] Solutions of hydroxylamine were made up immediately before use. Reagent grade hydroxylamine hydrochloride (NH$_2$OH·HCl) from Fisher was used without further purification. Excess silver(I) perchlorate was added to precipitate chloride, which was then removed by filtration. Solutions of N-methylhydroxylamine were prepared in a similar manner with N-methylhydroxylamine hydrochloride (CH$_3$NHOH·HCl) from Aldrich.

(1) The authors gratefully acknowledge partial support from Public Health Service Research Grant GM 08893-09 from the National Institute of General Medical Sciences, U. S. Public Health Service, and in part by National Science Foundation Grant GP 11529.

(2) G. Davies, K. Kustin, and L. J. Kirschenbaum, *Inorg. Chem.*, **7**, 146 (1968), reported the rate of reaction between Mn(III) and H$_2$O$_2$ but could not resolve the time course of the Ag(II) + H$_2$O$_2$ reaction; *cf.* H. N. Po, Ph.D. Thesis, University of California, Davis, Calif., 1967.

(3) Compare results in (a) G. Davies and K. Kustin, *Trans. Faraday Soc.*, **65**, 1630 (1969), with (b) D. H. Huchital, N. Sutin, and B. Warnqvist, *Inorg. Chem.*, **6**, 838 (1967).

(4) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1952, p 189.

(5) T. C. Bissot, R. W. Parry, and D. H. Campbell, *J. Amer. Chem. Soc.*, **79**, 796 (1957).

(6) G. Davies and K. Kustin, *Inorg. Chem.*, **8**, 484 (1969).

(7) (a) D. Honig and K. Kustin, *J. Inorg. Nucl. Chem.*, **32**, 1599 (1970). (b) No reduction of silver(I) by the hydroxylamines was observed to occur for several hours in these media, a period of time considerably longer than the actual experiment; *cf.* C. P. Lloyd and W. F. Pickering, *ibid.*, **29**, 1907 (1967).