REDUCTION OF SILVER AMINE COMPLEXES

BY CARBON MONOXIDE

by

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ABSTRACT

The kinetics of the reduction of silver amine complexes in aqueous solution by carbon monoxide were investigated. For a number of amines including ethyl-, methyl-, diethyl-ethanol-, diethanolamine and some primary diamines, the rate law was found to be of the form:

$$-\frac{d[\text{Ag(I)}]}{dt} = -2 \frac{d[\text{CO}]}{dt} = k_{\text{exp}} \frac{[\text{AgL}_2^+][\text{CO}]}{[\text{LH}^+]} = 2k [\text{L-Ag-OH}][\text{CO}] \quad (1)$$

where L denotes the amine. These kinetics were interpreted in terms of the following mechanism.

The rate constant of the rate-determining step (3) was found to be nearly independent of the nature of the amine molecule, L, coordinated to silver ion, using the basicity constants of the amines and dissociation constants of the corresponding silver amine complexes. The actual overall rate of the reaction varied with the nature of amine but this was attributable only to the different equilibrium concentrations of L-Ag-OH. The rate of this rate-determining bimolecular process was found to be surprisingly fast; $k_{250} = 5 \times 10^2 \text{ mole}^{-1} \text{ l. sec.}^{-1}$,

$\Delta H^* \sim 9 \text{ Kcal. mole}^{-1}$ and $\Delta S^* \sim -15 \text{ e.u.}$ The reduction of silver ion by CO in acidic or neutral media is known to be very slow and this can now be attributed to the base catalyzed nature of the reaction.

Silver complexes of primary diamines (ethylenediamine, 1,3-diaminopropane, etc.) were reduced more slowly; this was attributed to the stabilization of mono-complexed silver (I) species by chelate formation.

In the case of ammonia normal kinetics were observed at higher pH but at lower pH the rate became second order in $[\text{Ag(I)}]$ and inversely second order in $[\text{NH}_4^+]$. This was attributed to competition between decomposition of the intermediate complex and its further reaction with another Ag(I) species to give metallic silver and carbon dioxide. Evidence for similar competition was found with two tertiary amines, i.e., triethylamine and triethanolamine.

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I. INTRODUCTION

Recently, molecular hydrogen, although unreactive toward the majority of common inorganic oxidizing agents, was found to be oxidized under relatively mild conditions in aqueous solution by a few metal ions and complexes, notably Cu^{2+} , Ag^+ , Hg^{2+} , Hg_2^{2+} , and MnO_4^- . Halpern and his coworkers (1) have studied these systems extensively and have elucidated the mechanism through which the relatively strong H-H bond, having a dissociation energy of $103 \text{ Kcal. mole}^{-1}$, is activated, and the dependence of the reactivity on the electron configuration of the central metal ions. These studies have prompted similar studies on other inert reducing agents. The mechanism of these reactions and the nature of metal ions and complexes which activate those inert molecules are of great interest for the study of chemical reactivity, in general, and especially of the catalytic activity of transition metals and their compounds.

Amongst other relatively inert reducing agents whose reactions have been investigated in this laboratory are carbon monoxide and formic acid. The reactions of the latter with MnO_4^- , Hg^{2+} , Hg_2^{2+} and Tl^{3+} were studied by Taylor and Halpern (2) and their kinetics and mechanisms were elucidated. Harkness and Halpern (3) examined the reaction of CO with those metal ions which are active toward molecular hydrogen and found that

only Hg^{2+} and MnO_4^- showed measurable reactivity toward CO in homogeneous aqueous solution under moderate condition. They found Fe^{3+} , Tl^{3+} and $\text{Cr}_2\text{O}_7^{=}$ also to be inactive. At elevated temperature and pressure Bauch et al. (4) observed that silver sulfate and cupric sulfate in aqueous solution also were reduced by CO. They reported that the rate of the former reaction was second order in Ag(I) and was enhanced by buffering the solution with ammonium acetate. However, they did not study the dependence of the rate on pH. Following this work, and after commencement of the present study, Peters and McAndrew (5) studied the reaction of silver acetate in aqueous solution with CO in further detail under experimental conditions similar to those of Bauch et al. (4). These related studies are summarized below.

Hg^{2+} (3)...This is the only metal ion which was found to oxidize CO in aqueous solution under relatively mild conditions (atmospheric pressure and below $80^\circ\text{C}.$) in the absence of complexing agents. For the reduction of Hg^{2+} , i.e.,

kinetic measurements in dilute HClO_4 solution over the temperature range 26 to $54^\circ\text{C}.$ yielded the pH-independent rate law

$$-\frac{d[\text{CO}]}{dt} = k[\text{CO}][\text{Hg}^{2+}] \quad (1-2)$$

with $\Delta H^* = 14.6 \text{ Kcal. mole}^{-1}$ and $\Delta S^* = -13 \text{ e.u.}$ This was

interpreted in terms of the following mechanism.

Support for the proposed intermediate complex is provided by the isolation of a stable analogue, $\text{AcO}-\text{Hg}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OCH}_3$, formed by reaction of CO with mercuric acetate in methanol solution (6).

MnO₄⁻ (3)...The reduction of MnO_4^- by CO (to MnO_2 in acidic and neutral solutions and to MnO_4^{2-} in basic solutions) was found to proceed readily over the temperature range 28 to 50°C. The complete rate law was found to be

$$-\frac{d[\text{CO}]}{dt} = k[\text{CO}][\text{MnO}_4^-] \quad (1-6)$$

with $\Delta H^* = 13 \text{ Kcal. mole}^{-1}$ and $\Delta S^* = -17 \text{ e.u.}$, both substantially constant over the pH range 1 to 13, which confirmed and extended the earlier kinetic measurements on this system by Just and Kauko (7). Harkness and Halpern (3) also found that this system shows a remarkable catalytic effect on the addition of Ag^+ and Hg^{2+} (but not Cu^{2+} , Fe^{3+} , Cd^{2+} , or Tl^{3+}) which they attributed to favorable reaction paths involving intermediate such as

$\text{Ag}-\text{CO}-\text{OMnO}_3$ analogous to that postulated in the reaction of Hg^{2+} with CO.

Ag_2SO_4 and CuSO_4 (4)...Bauch et al. studied the aqueous Ag_2SO_4 system over the temperature range 70 to 110°C. under CO pressure up to 50 atmosphere and found the reaction

proceeded according to the rate law given by (1-8).

$$-\frac{d(\text{Ag}^+)}{dt} = 1.28 \times 10^6 [\text{Ag}^+]^2 P_{\text{CO}} e^{-14,000/RT} \quad (1-8)$$

They also observed that the rate was increased by buffering the solution with ammonium acetate, the kinetics for the buffered silver sulfate system being given by (1-9).

$$-\frac{d(\text{Ag}^+)}{dt} = 6.02 \times 10^4 [\text{Ag}^+]^2 P_{\text{CO}} e^{-9,300/RT} \quad (1-9)$$

They attributed this difference in rate to the favorable dependence of the equilibrium on increasing pH, and proposed the same mechanism for both buffered and unbuffered system, i.e.,

In support of this mechanism, they cited the existence of carbonyl complex of the "first subgroup" such as $[\text{Cu}(\text{Cl}, \text{Br})\text{CO}]_4$, $\text{Ag}_2(\text{CO})\text{SO}_4$ and $(\text{AuCl} \cdot \text{CO})_4$. It is obvious from their results that there must be some pH-dependent process contributing to the overall rate but this was not elucidated. For the reduction of CuSO_4 by CO they also observed second order dependence of the rate on $[\text{Cu}^{++}]$, the rate over the temperature range 160 to 190°C. being given by

$$-\frac{d[\text{Cu}^{++}]}{dt} = 2.56 \times 10^{13} [\text{Cu}^{++}]^2 P_{\text{CO}} e^{-33,500/RT} \quad (1-12)$$

In this system the effect of buffering was not reported because of experimental difficulties.

Recently, Peters and McAndrew (5) have extended this work on the reduction of silver salts in acidic solution. Both in acetate-buffered and perchlorate media the rate was found to be very slow, requiring the use of elevated temperature (>90°C.) and CO pressure (10 to 30 atm.). The results of this work will be considered later.

The present study is concerned with the reduction of silver amine complexes by CO in basic media. In contrast to the behaviour in acid solutions the reaction under these conditions is rapid and readily measureable at room temperature and atmospheric pressure.

II. EXPERIMENTAL

MATERIALS

Silver perchlorate was G. F. Smith Reagent grade and was unaffected by recrystallization. Perchloric acid was Baker and Adamson 60% Reagent grade. Ethylenediamine, Fisher certified reagent, was used without further purification. Distillation of this product had no effect on the reaction rate. Matheson triethylamine, which contained a reducing impurity, was purified by passing through a molecular sieve column and then distilled under 120 mm. Hg nitrogen atmosphere. Matheson 33% aqueous solution of ethylamine, and diethylamine (b.p. 55-56°C.); B.D.H. 25/30% methylamine aqueous solution, pure-ethanolamine, diethanolamine and triethanolamine, and K & K Laboratories' 1,3-diaminopropane were used without further purification. K & K Laboratories' 1,4-diaminobutane was redistilled at 20 mm. Hg before use. Ordinary distilled water was used in the preparation of all solutions and gave rates identical with those obtained with water distilled from alkaline permanganate. Nitrogen gas was supplied by the Canadian Liquid Air Co. Carbon monoxide (C.P. grade) and CO-N₂ gas mixtures were obtained from Matheson of Canada Ltd. The chromatographic analysis of all these gases revealed substantially no contamination by oxygen. In all experiments the amine perchlorate was prepared

by neutralizing the amine with perchloric acid. The experimental solutions were prepared by diluting aliquots of standardized stock solutions.

ANALYSIS

The normality of amines and aqueous amine solutions was determined by titration with standard hydrochloric acid. Silver ion concentration was determined by thiocyanate titration in acidic solution with ferric indicator. Carbon monoxide and nitrogen gas mixtures were analyzed with a Beckman GC-2 gas chromatograph using a molecular sieve column.

PROCEDURES

Kinetic measurements Except for the ammonia system, rates of all the reactions were determined at atmospheric pressure, by bubbling the CO gas (or a CO-N₂ mixture) through the solution in the glass apparatus depicted in Figure I. The gas was passed through a presaturator filled with aqueous solution of NaNO₃ and the amine to establish the same partial pressure of water and the amine as the reaction solution, and was then dispersed through a sintered glass plate into the reaction solution. The effluent gas was led to a gas flame and was burned. The whole apparatus was immersed in a constant temperature bath thermostated to $\pm 0.03^{\circ}\text{C}$. It was established that the flow rate of the gas did not affect the observed reaction rate; hence it may be assumed that the solutions were saturated with the gas.

Fig. 1.
Gas Bubbling
Glass Apparatus

- A. Gas Inlet
- B. Presaturator Solution
- C. Sintered Glass Plate
- D. Reaction Mixture
- E. Gas Outlet
- F. Gas Outlet Stopper
- G. Sampling Tube
- H. Sample Outlet

After placing 250-500 ml. of the reaction mixture of the desired composition in the apparatus, the system was allowed to attain thermal equilibrium under nitrogen flow. The stability of the reaction mixture was checked by sampling and analyzing the solution several times under the nitrogen flow and then the gas flow was switched to CO or to a CO-N₂ mixture. The solution was sampled periodically and the samples were analyzed as described previously. The time required for saturation of the solution with the gas was usually negligible; less than 30-60 sec. For reaction solutions in which the total solute concentrations were lower than 0.5-0.6 molar, the partial pressure of the gas was assumed to be atmospheric pressure minus the vapor pressure of pure water at the reaction temperature. In the case of triethylamine, which required a very high amine concentration to obtain stable solutions, Lattey's (8) data for the total vapor pressure of triethylamine-water mixtures were used. Variation of the CO partial pressure was achieved, when desired, by using analyzed CO-N₂ mixtures.

With ammonia, whose partial pressure is very high and whose reaction rate was very low at atmospheric pressure, an autoclave was used. The apparatus used was a Parr Series 4500 autoclave with a glass-lined stainless steel reaction vessel, provided with a stirrer, gas inlet tube, sampling tube fitted with a stainless steel filter, pressure gauge and thermowell, surrounded by an electric heating mantle controlled by a rheostat.

Fine temperature control was achieved by use of an auxiliary electric heater, immersed in the reaction mixture through the glass-lined thermowell, and controlled by a Thermistemp Temperature Controller (Model 71) actuated by a thermistor immersed in the solution. This arrangement gave temperature control of $\pm 0.3^{\circ}\text{C}$.

A 1,500 ml. ^{*} reaction mixture was made up from stock solutions and placed in the reaction vessel. Nitrogen gas was run into the mixture through the sampling tube and the porous stainless steel filter, under agitation by the stirrer, for some five minutes; then the vessel was sealed and brought to the desired temperature. The stability of the solution was established by taking samples and analyzing them for silver ion over a one hour period. The internal pressure was then reduced to one atmosphere by opening the gas outlet once, and the CO gas was introduced from a CO cylinder and maintained at a desired pressure. The partial pressure of CO was calculated as the difference between the total pressure and the combined vapor pressure of the solution and residual nitrogen pressure. Samples were taken at appropriate intervals and analyzed for silver ion. After each sampling more CO gas was supplied to

* The nichrome wire coil of the auxiliary heater was made to occupy the lower half of the thermowell and a volume of solution sufficient to fill the glass liner was used so as to avoid undesirable superheating of the thermowell.

the system to establish a constant pressure. The stirrer was rotated, usually at 600 r.p.m., after establishing that the rate of reaction was independent of the stirring rate.

Stoichiometry measurements The amount of CO gas consumed was measured by means of a gas burette apparatus. A 125 ml. conical flask reaction vessel was placed in a small polyethylene water bath (diameter ca. 5 in.) which was connected to a thermostated water circulator. The reaction vessel flask was connected to a 50 c.c. burette provided with a mercury balancing bottle. The reaction solution was stirred with a teflon-coated magnetic stirrer. 100 ml. of reaction solution was placed in the reaction vessel; nitrogen gas was first passed through the solution to remove oxygen from the reaction system, and finally after displacing the nitrogen by CO and filling the reaction vessel with CO, the whole system was closed, the gas burette mercury level was balanced and the magnetic stirrer was turned on. A dibutylphthalate auxiliary manometer was used for fine adjustment of the mercury level. When the rate of gas uptake became sufficiently slow the burette was read, the reaction vessel was disconnected from the burette and the solution was analyzed. The volume of gas uptake was corrected for the solubility of CO, temperature and pressure.

In several cases the reaction mixture was titrated for

amine and carbonate before and after the reaction. In those cases, an original reaction solution was flushed with carbon dioxide-free nitrogen gas before it was placed into the reaction vessel. A 25 ml. aliquot was taken for analysis and 100 ml. was pipetted under N_2 into the reaction vessel. The original and the final solutions were analyzed for amine and carbonate by potentiometric titration with standard hydrochloric acid using a Beckman pH meter.

Silver metal deposited in the reaction vessel was collected on a glass crucible and weighed. Its purity was determined by dissolving in nitric acid and titrating with thiocyanate.

The amount of carbonate in the final reaction mixture was determined more directly by a gravimetric method, as barium carbonate. Barium nitrate or barium hydroxide was used to precipitate the carbonate. For weakly basic amines barium hydroxide was used. In some cases ethylenediamine or propylenediamine was added to stabilize the remaining silver ion before barium hydroxide was added.

III. RESULTS AND DISCUSSIONS

STOICHIOMETRY

For all the amines which were used in the present study, when aqueous silver (I) amine solution was reacted with CO, a brown or black solid separated from the solution, which proved on analysis to be pure silver metal. In many cases the glass wall of the reaction vessel also was covered by a silver mirror. The amount of silver metal formed was found to be equal to the amount of silver ion reduced (Table 1).

TABLE 1

RESULTS OF STOICHIOMETRY MEASUREMENTS (I)

Amine	Initial [Ag(I)] mole/l	Amine Per- chlorate mole/l	Amine mole/l	Silver Reduced mole/l	Carbon- Monoxide Uptake mole/l	Silver Metal Recovered mole/l
ethylamine	0.0299	0.000	0.300	0.0299	0.015	0.0295
1,3-diamino- propane	0.0297	0.000	0.300	0.0297	0.015	0.0295
diethanol- amine	0.0296	0.000	0.300	0.0296	0.0129	0.0294

TABLE 2

RESULTS OF STOICHIOMETRY MEASUREMENTS (II)

Amine	Initial [Ag(I)] mole/l	Amine Per- chlorate mole/l	Amine mole/l	Silver Reduced mole/l	1 Carbon- Monoxide Uptake mole/l	2 Hydrogen Ion Produced mole/l	Carbon- ate ² Produced mole/l
ethylamine	0.0300	0.000	0.0963	0.0300	0.015	0.0606	0.0151
methylanine	0.0299	0.000	0.0937	0.0299	0.015	0.0605	0.0150
diethyl- amine	0.0296	0.100	0.0933	0.0292	0.0146	0.0620	0.0145
ethanol- amine	0.0300	0.000	0.100	0.0178	0.00809	*** ³	*** ³
diethanol- amine	0.0296	0.000	0.0988	0.0250	0.0114	(0.0532) ³	(0.0133) ³
	0.0297	0.000	0.300	0.0296	0.0129	*** ³	*** ³
triethanol- amine	0.0298	0.000	0.300	0.0199	0.0091	*** ³	*** ³
ethylene- diamine	0.0300	0.000	0.0648	0.0298	0.0150	0.0618	0.0148
1,3-diamine- propane	0.0297	0.000	0.300	0.0297	0.015	***	***

1 In those experiments where the reaction was continued to completion a slow further uptake of CO was observed even when all the silver had been reduced. This zero order uptake of CO is presumably attributable to reaction of CO and H₂O on the silver metal surface to form formate (9).

2 These are the results from pH-titration of the final solution.

3 In the case of ethanolamines, which are the least basic of all these amines, pH titration was not readily applicable. For diethanolamine, this method yielded only the combined concentration of amine and carbonate. These results in the parentheses were calculated from this assuming hydrogen ion produced: carbonate = 4:1, hence subject to error.

Results of CO uptake measurements in Table 2 show that two gram-ions of silver ion were reduced for each mole of CO*. The pH titration of the final solution (results are summarized in Table 2 and typical titration curves are given in Figure II) showed that two gram-ions of hydrogen ion and one-half gram ion of carbonate (identity of this product is to be discussed later) were produced for each gram-ion of silver ion reduced by one-half mole of CO. The overall reaction can therefore be represented by

under conditions where the amine (represented by L) is present in excess.

The results of direct carbonate determinations (gravimetrically as barium carbonate) on the same final reaction solutions are shown in Table 3. Only triethylamine, diethylamine and ammonia systems gave those yields of carbonate expected from the titration results. In the other cases a portion of the

* In the case of the three ethanolamines the CO uptake was about 10% lower than the theoretical value (Table 2). In these cases, some silver apparently also was reduced by the amines or by an impurity. These side reactions were most pronounced at the high pH of these CO uptake experiments in which, in order to increase the rate of reaction, no amine perchlorate was added. Such solutions deposited some metallic silver on standing even in the absence of CO, while solutions containing amine perchlorate (i.e. those used for the kinetic experiments) were stable. The amount of silver reduced by these side reactions seemed to be directly dependent on the amine concentration as indicated by the two experiments with diethanolamine in Table 2.

Fig. II. Typical Titration Curves of Final Reaction Mixtures

— See Table 2 for experimental conditions.

"carbonate", resulting from the oxidation of the CO apparently combines with the amine to form a substance which decomposes on acidification. Decomposition with release of carbonate also occurred on treatment with base. Thus, when the final reaction solution was left standing with an excess of barium hydroxide, the amount of barium carbonate precipitated increased slowly with time. In the case of methylamine, boiling with barium hydroxide resulted in a 100% yield of barium carbonate.

These results suggest that the product in question is a carbamate or similar compound, which is known to form by reaction of carbon dioxide and amines or ammonia under moderately basic condition, and which is decomposed by acid or by strong base. However, attempts to isolate and characterize this product were unsuccessful and some question as to its identity remains. The representation of the reaction products by equation (3-1) is thus subject to qualification, in certain cases, although the reactant stoichiometry appears to apply in every case.

TABLE 3
RESULTS OF STOICHIOMETRY MEASUREMENTS (III)

Amine	Initial [Ag(I)] mole/l	Amine Per- chlorate mole/l	Amine mole/l	Silver Reduced mole/l	Carbonate Produced mole/l	Carbonate Yield $\text{CO}_3^{=}/\frac{1}{2}\text{Ag}$
Triethyl- amine	0.0374	0.1	0.9	0.0356	0.0179	99%
Diethylamine	0.0314	0.100	0.386	0.0281	0.0136	97%
Ammonia	0.0300	0.00	0.300	0.0172	0.0083	97%
Methylamine	0.0500	0.00	0.300	0.0455	0.0069	31%
Ethylamine	0.0400	0.00	0.300	0.0317	0.0053	33%
Ethanolamine	0.0500	0.00	0.300	0.0301	0.0086	57%
Diethanol- amine	0.0500	0.00	0.300	0.0339	0.0094	55%
Triethanol- amine	0.0304	0.010	0.100	0.0243	0.0087 ¹	72%
Ethylene- diamine	0.0114	0.00	0.200	0.0111	0.001	20%
1,3-Diamino- propane	0.0400	0.00	0.300	0.0345	0.0084	49%

1 CO uptake was 0.0105 mole l^{-1} (86%).

KINETICS AND MECHANISM

Among the silver amine complexes which were examined in this study, a number, including the complexes of ethylamine, methylamine, diethylamine, ethanolamine and diethanolamine exhibited very similar behaviour (designated as "standard") and will be discussed first. The triethylamine-, triethanolamine-

and certain diamine- complexes, exhibited some departures from this "standard" behaviour and will be considered later.

ETHYLAMINE COMPLEX

This system, typical of those exhibiting "standard" behaviour, will be considered in some detail.

The disappearance of Ag(I) at constant CO pressure obeyed first order kinetics in all experiments as shown by the typical first order plots of $\log [Ag(I)]$ vs. time in Figure III. This was verified by the fact that the same rate constant was obtained for two different initial silver ion concentrations keeping the other conditions unchanged (Experiments 1c and 1g). The rate-law obeyed during the course of each experiment is thus

$$-\frac{d \log [Ag(I)]}{dt} = k''t \quad (3-2)$$

where $[Ag(I)]$ is the total concentration of all the Ag(I) species, t is time in seconds and $\log$ is common logarithm.

When all the other conditions were kept constant at 25°C., k'' exhibited first order dependence on the CO partial pressure as shown by the plot of k'' vs. $[CO]$ in Figure IV. The CO concentration in the reaction solution was calculated using the solubility data of Seidell (10), assuming that the solution is saturated with CO and the solubility can be approximated by that in pure water. Equation (3-2) can then be rewritten, as a second order rate-law.

Fig. III. Typical Rate Plots for Ethylamine Complex

— See Table 4 for experimental conditions.

Fig.IV. Dependence of Rate on Carbon Monoxide Concentration

at 25° for Ethylamine Complex; $[LH^+] = 0.1$ & $[L] = 0.2 \text{ mole l}^{-1}$

$$-\frac{d[Ag(I)]}{dt} = k^{\circ} [Ag(I)] [CO] \quad (3-3)$$

where

$$k^{\circ} = \frac{2.303}{[CO]} k'' \quad (3-4)$$

Values of the second order rate constants, k° , measured under various conditions are summarized in Table 4.

TABLE 4

RATES OF REACTION OF ETHYLAMINE AND RELATED AMINE COMPLEXES OF SILVER AND OF SOME OTHER SIMILAR SYSTEMS

Amine	Initial [Ag(I)] Mx10 ⁻³	CO Pressure mm. Hg.	Amine M	Amine Per- chlorate M	T°C.	k' M ⁻¹ sec. ⁻¹	k _{exp} sec. ⁻¹ x10 ⁻²	No.
Ethylamine	10.0	730	0.200	0.0500	25	0.310	1.55	1a
	10.0	730	0.200	0.0750	25	0.206	1.55	1b
	10.0	730	0.200	0.100	25	0.152	1.52	1c
	10.0	730	0.200	0.200	25	0.077	1.54	1d
	10.0	730	0.300	0.100	25	0.153	1.53	1e
	10.0	730	0.100	0.100	25	0.156	1.56	1f
	20.0	730	0.200	0.100	25	0.149	1.49	1g
	10.0	562	0.200	0.100	25	0.156	1.56	1h
	10.0	490	0.200	0.100	25	0.154	1.54	1i
	10.0	395	0.200	0.100	25	0.152	1.52	1j
	10.0	234	0.200	0.100	25	0.143	1.43	1k
	10.0	742	0.200	0.100	20	0.103	1.03	1l
	10.0	723	0.200	0.100	30	0.223	2.23	1m
	10.0	712	0.200	0.100	35	0.337	3.37	1n
Methylamine	10.0	730	0.200	0.100	25	0.283	2.83	2a
	10.0	730	0.200	0.200	25	0.152	3.04	2b
	10.0	730	0.200	0.300	25	0.094	2.88	2c
	10.0	730	0.100	0.200	25	0.152	3.04	2d
	20.0	730	0.200	0.200	25	0.152	3.04	2e
	10.0	562	0.200	0.100	25	0.283	2.83	2f
	10.0	395	0.200	0.100	25	0.287	2.87	2g
	10.0	234	0.200	0.100	25	0.286	2.86	2h
	10.0	747	0.200	0.100	15	0.110	1.10	2i
	10.0	742	0.200	0.100	20	0.174	1.74	2j
	10.0	723	0.200	0.100	30	0.424	4.24	2k

TABLE 4 (Continued)

Amine	Initial [Ag(I)] Mx10 ⁻³	CO Pressure mm. Hg.	Amine M	Amine Per- chlorate M	T°C.	k' M ⁻¹ sec. ⁻¹	k _{exp} sec. ⁻¹ x10 ⁻²	No.
Diethylamine	10.0	234	0.200	0.100	25	0.83	8.3	3a
	10.0	234	0.200	0.200	25	0.435	8.7	3b
	10.0	234	0.200	0.300	25	0.271	8.1	3c
	10.0	234	0.400	0.100	25	0.69	6.9	3d
	10.0	234	0.100	0.100	25	0.87	8.7	3e
	20.0	234	0.200	0.100	25	0.76	7.6	3f
	10.0	730	0.200	0.200	25	0.425	8.5	3g
	10.0	562	0.200	0.200	25	0.445	8.9	3h
	10.0	395	0.200	0.200	25	0.435	8.7	3i
	10.0	742	0.200	0.200	20	0.295	5.9	3j
	10.0	728	0.200	0.200	30	0.66	13.2	3k
	10.0	712	0.200	0.200	35	0.91	18.3	3l
Ethanolamine	10.0	736	0.200	0.0500	25	0.057	0.29	4a
	10.0	736	0.200	0.0250	25	0.109	0.27	4b
	10.0	736	0.100	0.0250	25	0.109	0.27	4c
	10.0	728	0.200	0.0500	30	0.091	0.46	4d
	10.0	718	0.200	0.0500	35	0.147	0.74	4e
Diethanola- mine	10.0	736	0.200	0.0250	25	0.122	0.31	5a
	10.0	736	0.200	0.0500	25	0.060	0.30	5b
	10.0	736	0.100	0.0250	25	0.127	0.32	5c
	10.0	728	0.200	0.0500	30	0.107	0.53	5d
	10.0	718	0.200	0.0500	35	0.170	0.85	5e

The rate is seen to be independent of the free amine concentration, but inversely dependent on the concentration of the conjugate acid of the amine (amine perchlorate, designated as LH^+) as shown in Figure V. Thus the complete rate-law is

$$-\frac{d[\text{Ag(I)}]}{dt} = k_{\text{exp}} \frac{[\text{Ag(I)}][\text{CO}]}{[\text{LH}^+]} \quad (3-5)$$

where

$$k_{\text{exp}} = k' [\text{LH}^+] \quad (3-6)$$

Fig. V. Dependence of Rate on Ammonium Ion Concentration at 25° for Ethylamine Complex ; $[L] = 0.2 \text{ M}$, $P_{CO} = 730 \text{ mmHg}$

Referring to (3-1) and (3-5), some retardation of the rate as the reaction proceeds due to increase of (LH^+) is expected. Usually the initial concentration of amine perchlorate was made sufficiently high so that this effect was negligible and good first order plots were obtained. However, in some cases at low (LH^+) , $[\text{Ag(I)}]$ vs. t plots showed the expected retardation in later stages of the reaction (Expt. 1-a in Figure III). In these cases the initial linear portion of the rate plots was employed for the determination of the rate constant.

OTHER "STANDARD" SYSTEMS

Among those amines which were investigated, methylamine, diethylamine, ethanolamine and diethanolamine showed the same type of kinetics as ethylamine, i.e., first order dependence on Ag(I) and CO , independence of free amine concentration and inverse first order dependence on ammonium ion concentration. The experimental results expressed in terms of the second order rate constant, k' (3-3) and k_{exp} (3-5) are summarized in Table 4. Most of the kinetic measurements were done at 25°C . Typical rate plots for these systems are shown in Figure VI. In some cases the first order rate plots exhibited some downward concavity in the later part of the reaction. This may be attributable to some zero order reaction of silver (I) with a little impurity in the amines or amine itself, or it may be due to some heterogeneous reaction on silver metal.

Fig. VI. Typical Rate Plots for Ethylamine-type Complexes

—See Table 4 for experimental conditions

In those cases slope of the initial linear portions of the rate plots were employed to determine the rate constants.

Mechanism The inverse dependence of the rate on (LH^+) may be understood by taking account of the following equilibria which prevail in the solution.

Referring to the stability constants of silver amine complexes which are summarized in Appendix I, it is seen that the silver ions in these solutions are present predominantly as the bis-complex, AgL_2^+ , so that

$$[\text{Ag(I)}] \cong [\text{AgL}_2^+] \quad (3-9)$$

The resulting rate expression obtained from equations (3-5, 7, 8 and 9) is

$$-\frac{d[\text{Ag(I)}]}{dt} = k_{\text{exp}} K_b^{-1} K_{d1}^{-1} [\text{AgL}^+][\text{OH}^-][\text{CO}] \quad (3-10)$$

This may be identified with the following reaction mechanism

The apparent rate constant of disappearance of Ag(I) , k_{exp} , defined by equation (3-5) and the bimolecular rate constant, k ,

of the process (ii) are thus related through

$$k_{\text{exp}} = 2kK = 2kK_b K_{d1} K_h \quad (3-11)$$

where K_h is the association constant of AgL^+ with OH^- , i.e.,

The factor of 2 reflects the fact that each rate-determining reaction results in the reduction of two silver ions. Hence, it is more appropriate to express the rate of the reaction in terms of the rate of consumption of CO, i.e., the rate of the rate-determining step. Thus,

$$-\frac{d[\text{CO}]}{dt} = -\frac{1}{2} \frac{d[\text{Ag(I)}]}{dt} = k[\text{L-Ag-OH}][\text{CO}] \quad (3-13,a)$$

$$= kK_h [\text{AgL}^+][\text{OH}^-][\text{CO}] \quad (3-13,b)$$

$$= kK_h K_b K_{d1} \frac{[\text{Ag(I)}][\text{CO}]}{[\text{LH}^+]} \quad (3-13,c)$$

$$= \frac{1}{2} k_{\text{exp}} \frac{[\text{Ag(I)}][\text{CO}]}{[\text{LH}^+]} \quad (3-13,d)$$

Processes (3-7), (3-8) and (3-12), which are involved in equilibrium (i) or the process (i) itself is presumably sufficiently rapid that (i) can be regarded as a pre-equilibrium.

The overall stoichiometry requires that the reaction intermediate containing a CO molecule, and one silver ion, L-Ag-COOH , reacts with another silver (I) species (the identity of which is to be discussed later). However, this step (iii) appears to be fast, compared with (ii), so that the kinetics are first order in Ag(I) .

This intermediate complex, L-Ag-C(=O)-OH , is analogous to the one

which was previously proposed by Harkness and Halpern (3) as an intermediate complex in the reaction of Hg^{2+} , i.e., $-\text{Hg}-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$. Support for the structure of the latter was provided by the observation by Halpern and Kettle (6) that when methanolic solution of mercuric acetate takes up CO under similar conditions, a stable methylformate derivative, $\text{AcO}-\text{Hg}-\overset{\text{O}}{\parallel}\text{C}-\text{OCH}_3$, analogous to the proposed complex was formed, isolated and spectroscopically identified. They also reported that attempts to prepare analogous CO adduct of silver acetate were unsuccessful, but this can presumably be attributed to the poor solubility of silver acetate in methanol and instability of the CO adduct toward decomposition into metallic silver.

In terms of this mechanism it might be expected that the rate constants k (and also kK_h) should be relatively insensitive to the nature of L and thus that the large dependence of k_{exp} on the nature of the amine should reflect largely the variation of K_{d1} and K_b . This is shown to be the case in Table 5 where it is seen that notwithstanding a 30-fold variation in k_{exp} (which ranges from 2.8×10^{-3} to $8.6 \times 10^{-2} \text{ sec.}^{-1}$, for the five amines under consideration) the value of kK_h is substantially constant, ($1 \times 10^5 \text{ mole}^{-2} \text{ l.}^2 \text{ sec.}^{-1}$) for all the systems.

TABLE 5
SUMMARY OF KINETIC AND RELATED THERMODYNAMIC DATA
FOR "STANDARD" SYSTEM AT 25°C.

Amine	k_{exp} sec. ⁻¹	1)	2)	3)	
		K_{d1} $\times 10^4$ mole l. ⁻¹	K_b $\times 10^4$ mole l. ⁻¹	$K_{d1}K_b$ $\times 10^8$ mole ² l. ²	kK_h $\times 10^{-5}$ mole ⁻² l. ² sec. ⁻¹
$\text{C}_2\text{H}_5\text{NH}_2$	1.55×10^{-2}	1.2	6.5	7.6	1.0
CH_3NH_2	2.85×10^{-2}	2.9	5.2	15	0.9
$(\text{C}_2\text{H}_5)_2\text{NH}$	8.6×10^{-2}	5.0	9.1	46	1.0
$\text{HOC}_2\text{H}_4\text{NH}_2$	2.8×10^{-3}	2.8	0.55	1.5	1.0
$(\text{HOC}_3\text{H}_4)_2\text{NH}$	3.1×10^{-3}	16	0.10	1.6	1.0

1) and 2) Refer to Appendix I.

3) Calculated by use of equation (3-11).

The temperature dependence of the rate constants was determined for all these systems over the temperature range 15 to 35°C. In all cases good linear Arrhenius plots were obtained, which are given in Figure VII. The activation parameters are summarized in Table 6.

Fig. VII. Arrhenius Plots for Ethylamine-type Complexes

TABLE 6
APPARENT ENTHALPY AND ENTROPY OF ACTIVATION
FOR "STANDARD" SYSTEMS

Amine	1) $\frac{1}{2}k_{\text{exp}}$	ΔH^*_{exp}	ΔS^*_{exp}
	sec. ⁻¹	Kcal. mole ⁻¹	e.u.mole ⁻¹
$\text{C}_2\text{H}_5\text{NH}_2$	7.8×10^{-3}	14.3	-20.0
CH_3NH_2	1.43×10^{-2}	15.5	-14.9
$(\text{C}_2\text{H}_5)_2\text{NH}$	4.3×10^{-2}	14.1	-17.5
$\text{HOC}_2\text{H}_4\text{NH}_2$	1.4×10^{-3}	17.4	-13.1
$(\text{HOC}_2\text{H}_4)_2\text{NH}$	1.6×10^{-3}	18.3	- 9.9

1) $\frac{1}{2}k_{\text{exp}} = kK_h K_{d1} K_b$ is used for the calculation of the activation parameters.

The present result shows that the only silver (I) species that is active toward CO under the conditions investigated for these five amines is the hydrolyzed mono-amine complex, L-Ag-OH while other silver (I) species involving the bis-complex, AgL_2^+ , and free silver ion or aquo complex, Ag^+ , make a negligible contribution.

Although metallic silver was precipitated during the course of reaction, its heterogeneous catalytic effect, at least during the early stages, was small.

TRIETHYLAMINE COMPLEX

The triethylamine complex exhibited somewhat different kinetic behaviour, from the "standard" systems described above, notably in that the rate of reaction was no longer independent of the free amine concentration but exhibited an inverse dependence on the latter. The rate was inversely proportional to ammonium concentration but the effect of silver concentration was somewhat more complicated. The experimental results are summarized in Table 7 and typical rate plots are shown in Figure VIII.

This complex exhibited the fastest overall rate of all the amine complexes investigated in this study, so that a 32.3% CO - 67.7% N₂ mixture was used in most of the experiments to obtain a reaction rate convenient for measurement. A fairly high concentration of triethylamine (up to 0.8 mole·l⁻¹) was employed to prevent the hydrolysis of silver and precipitation of silver oxide because the triethylamine-silver complex is much less stable than the complexes of primary and secondary amines, while the basicity of the amine is almost the same. Because of the high vapor pressures of the resulting solutions Lattey's (8) data on the vapor pressure of aqueous triethylamine solution were used to calculate the partial pressure of CO.

TABLE 7

RATE OF REACTION OF TRIETHYLAMINE COMPLEX AT 25°C.

Initial [Ag(I)] mole·l ⁻¹	Amine [L] mole·l ⁻¹	1) Amine Vapor		CO Pres- sure mmHg	k' mole ⁻¹ ·l sec ⁻¹	k _{exp} sec ⁻¹	Expt. No.
		Per- chlorate mole·l ⁻¹	Pres- sure mmHg				
0.010	0.809	0.600	79	220	1.02	0.61	6a
0.010	0.802	0.480	79	220	1.31	0.63	6b
0.010	0.794	0.400	78	220	1.71	0.68	6c
0.010	0.784	0.300	78	220	2.27	0.68	6d
0.010	0.205	0.600	47	230	2.32	1.39	6e
0.010	0.250	0.600	51	229	2.16	1.30	6f
0.010	0.263	0.600	53	228	2.12	1.27	6g
0.010	0.309	0.600	57	227	1.91	1.15	6h
0.010	0.342	0.600	60	226	1.74	1.04	6i
0.010	0.412	0.600	65	224	1.62	0.97	6j
0.010	0.508	0.600	70	223	1.45	0.87	6k
0.010	0.619	0.600	74	222	1.20	0.72	6l
0.005	0.080	0.300	34	234	5.1	1.53	6m
0.005	0.180	0.300	45	231	3.4	1.02	6n
0.005	0.180	0.200	45	231	4.9	0.98	6o

1) Reference (8).

Although triethylamine was very carefully purified as described in the experimental section, there was an appreciable amount of initial reduction of silver (up to 25% of total silver (I) concentration) which may be attributed to some impurity* in the amine, and which introduced some complications,

* The reaction mixture was usually stable toward the initial reduction under nitrogen flow especially at high ammonium concentration. This initial reduction occurred usually after CO gas was introduced into the reaction vessel, as can be seen in the rate plots (Figure VIII). The amount of the initial reduction of silver was directly dependent on the total amine concentration (free amine and ammonium) in the reaction solution. However, it seemed to have no significant effect on the rate of the subsequent reduction by CO.

Fig. VIII. Typical Rate Plots for Triethylamine Complex

— See Table 7 for experimental conditions.

particularly in the determination of the effect of initial silver concentration on the reaction rate, since at low initial $[Ag(I)]$ a large portion of $Ag(I)$ was lost by the initial reduction while high $[Ag(I)]$ could not be employed because of the instability of the complex toward hydrolysis of silver ion and precipitation of silver oxide.

Two alternative interpretations of the inverse dependence of the rate on the free amine concentration were considered. The first of these involved the possibility that not only the mono-complexed silver ion but also uncomplexed ion (or aquo ion) contributes to the overall reaction to an appreciable extent. This failed to yield a rate-law which fitted the observed dependence of the rate on the silver (I) and amine concentrations in detail, and, furthermore, required that the reactivity of free silver ion, which is present in very low concentration compared to the mono-complex, be much higher (some 300-fold) than that of the latter. This could not be readily reconciled with the observed insensitivity of the rate of various other mono-complexes to the nature of the amines, and with the measurements of Peters and McAndrew (5) on the reduction of uncomplexed Ag^+ ions by CO in perchlorate media. Consequently this interpretation was rejected.

A more satisfactory account of the kinetic behaviour of this system was obtained in terms of the following mechanism in which the competitive reaction of the intermediate, $L-Ag-COOH$,

are considered.

Here, processes k_{-1} and k_2 are competing for the intermediate complex, L-Ag-COOH, the back reaction of the first step (ii) no longer being negligible. Assuming steady state approximation for L-Ag-COOH, the kinetics are found to be

$$\begin{aligned} -\frac{d[\text{CO}]}{dt} &= -\frac{1}{2} \frac{d[\text{Ag(I)}]}{dt} = \frac{1}{2} k_{\text{exp}} \frac{[\text{Ag(I)}][\text{CO}]}{[\text{LH}^+]} \\ &= k_1 K_h K_b K_{d1} \frac{[\text{Ag(I)}][\text{CO}]}{[\text{LH}^+]} \frac{k_2 K_{d1} [\text{Ag(I)}]/[\text{L}]}{k_{-1} + k_2 K_{d1} [\text{Ag(I)}]/[\text{L}]} \end{aligned} \quad (3-14)$$

$$= k_1 K_h \cdot k_2 K_b K_{d1}^2 \frac{[\text{Ag(I)}]^2 [\text{CO}]}{[\text{LH}^+]} \frac{1}{k_{-1} [\text{L}] + k_2 K_{d1} [\text{Ag(I)}]} \quad (3-15)$$

$$k_{\text{exp}} = 2k_1 K_h \cdot k_2 K_b K_{d1}^2 [\text{Ag(I)}] \frac{1}{k_{-1} [\text{L}] + k_2 K_{d1} [\text{Ag(I)}]} \quad (3-16)$$

Thus, k_{exp} is no longer a constant. Taking reciprocals

$$\frac{1}{k_{\text{exp}}} = \frac{1}{2k_1 K_h \cdot k_2 K_b K_{d1}^2 [\text{Ag(I)}]} (k_{-1} [\text{L}] + k_2 K_{d1} [\text{Ag(I)}]) \quad (3-17)$$

From the equation (3-25), we expect a linear relation between $1/k_{\text{exp}}$ and $[\text{L}]$ at a fixed total silver ion concentration, $[\text{Ag(I)}]$. The plots of $1/k_{\text{exp}}$ vs. $[\text{L}]$ in Figure IX based on the experimental results in Table 7 are in complete accord with this. From equation (3-17) the intercept and the slope of the linear plots are given by

Fig. IX. Dependence of Rate on Free Amine Concentration
at 25° for Triethylamine Complex

$$\text{Intercept} = \frac{1}{2k_1 K_h K_b K_{d_1}} \quad (3-18)$$

$$\text{Slope} = \frac{1}{2k_1 K_h K_b K_{d_1}} \cdot \frac{k_{-1}}{k_2} \cdot \frac{1}{K_{d_1} [\text{Ag(I)}]} \quad (3-19)$$

Thus, the intercept should be independent of $[\text{Ag(I)}]$ and the slope should be inversely proportional to $[\text{Ag(I)}]$, in accord with Figure IX, which also shows k_{exp} to be independent of $[\text{LH}^+]$. From the intercept and slopes of the plots in Figure IX, and using equation (3-18) and (3-19), the following values were obtained for the rate constants.

$$k_1 K_h = 2.5 \times 10^5 \text{ mole}^{-2} \cdot \text{l}^2 \cdot \text{sec}^{-1} \quad (3-20)$$

$$k_2/k_{-1} = 3.4 \times 10^3 \text{ mole}^{-1} \cdot \text{l} \quad (3-21)$$

The value of $k_1 K_h$ in this case is about 2.5 times as large as that found for ethylamine and related complexes.

It is obvious that when the second term in the denominator of the equation (3-16) is much larger than the first term, (i.e., $k_2 K_{d_1} [\text{Ag(I)}] \gg k_{-1} L$), the overall kinetics approach those for the ethylamine complex. For some reason, in the case of triethylamine, these two terms are comparable in their magnitudes. Since K_d for triethylamine is actually larger (70 times) than for ethylamine, the observed kinetics must reflect either an abnormally large value of k_{-1} or an abnormally small value of k_2 .

TRIETHANOLAMINE COMPLEX

The only other tertiary amine that was investigated in this study was triethanolamine. The silver complex of this amine exhibited almost the same kinetics as ethylamine, the rate in this case being almost independent of the free amine concentration, with only a slight dependence in the opposite direction to that for triethylamine (i.e., the rate increasing with amine concentration) and inversely proportional to the ammonium concentration. The experimental results are summarized in Table 8 and typical rate plots are given in Figure X. The dissociation constant of the triethanolamine complexes is so large ($K_{d_1} = 0.046$) that it is no longer valid to approximate $[AgL_2^+]$ by $[Ag(I)]^*$. This would give rise to a dependence of the rate on the free amine concentration even if the reaction followed the same kinetics as for the ethylamine complex. The observed dependence of the rate on the amine concentration is in the direction expected from this (i.e., the rate increases with the amine concentration), but is much smaller than predicted. This suggests that there is also superimposed upon this an inverse dependence of the rate on the free amine concentration, similar to that found for triethylamine complex. This is not unexpected in

* Actually, using the value for K_{d_1} given above, the calculation shows that more than 30% of the silver is present in the form of AgL^+ at $[L] = 0.1 \text{ mole} \cdot \text{l}^{-1}$.

TABLE 8
RATE OF REACTION OF TRIETHANOLAMINE COMPLEX

Initial [Ag(I)] mole·l ⁻¹	Amine L mole·l ⁻¹	Amine Per- chlorate mole·l ⁻¹	CO Pres- sure mmHg	T°C.	k' mole ⁻¹ ·l sec ⁻¹	k _{exp} sec ⁻¹	Expt. No.
0.010	0.100	0.0500	705	40	0.23	1.2x10 ⁻²	7a
0.010	0.100	0.100	705	40	0.13	1.3x10 ⁻²	7b
0.007	0.100	0.200	705	40	0.069	1.4x10 ⁻²	7c
0.07	0.100	0.100	705	40	0.13	1.3x10 ⁻²	7d
0.007	0.200	0.100	705	40	0.13	1.3x10 ⁻²	7e
0.007	0.040*	0.0500	730	25	0.049	2.4x10 ⁻³	7f
0.007	0.100*	0.0500	730	25	0.060	3.1x10 ⁻³	7g
0.007	0.190*	0.0500	730	25	0.062	3.1x10 ⁻³	7h
0.014	0.040*	0.0500	730	25	0.051	2.6x10 ⁻³	7i
0.007	0.040*	0.0250	730	25	0.091	2.3x10 ⁻³	7j
0.007	0.100	0.0500	728	30	0.106	5.3x10 ⁻³	7k
0.007	0.100	0.0500	718	35	0.17	8.5x10 ⁻³	7l

* Free amine concentrations corrected for the dissociation of silver complex.

view of the similar stability constants of the two complexes. The dissociation constants of both complexes are much larger than that of the ethylamine complex and in both cases the order of the first and second dissociation constants ($K_{d_1} > K_{d_2}$) is the reverse of that for ethylamine and other primary and

Fig. X. Typical Rate Plots for Triethanolamine Complex

— See Table 8 for experimental conditions.

secondary amines (Appendix I). Applying the same mechanism to triethanolamine, as previously to triethylamine, and assuming

$$[Ag(I)] = [AgL_2^+] + [AgL^+] \quad (3-22)$$

i.e.,

$$[AgL^+] = \frac{K_{d1} [Ag(I)]}{K_{d1} + [L]} \quad (3-23)$$

and neglecting other silver species, then the rate law is expected to be of the form

$$\begin{aligned} -\frac{d[CO]}{dt} &= -\frac{1}{2} \frac{d[Ag(I)]}{dt} = \frac{1}{2} k_{exp} \frac{[Ag(I)] [CO]}{[LH^+]} \\ &= k_1 K_h [AgL^+] [OH^-] [CO] \frac{k_2 [AgL^+]}{k_{-1} + k_2 [AgL^+]} \quad (3-24) \end{aligned}$$

$$\begin{aligned} &= k_1 k_2 K_h K_{d1}^2 K_b \frac{[Ag(I)]^2 [CO]}{[LH^+]} \times \\ &\quad \frac{[L]}{k_{-1} (K_{d1} + [L])^2 + k_2 K_{d1} [Ag(I)] (K_{d1} + [L])} \quad (3-25) \end{aligned}$$

It was not possible to make sufficiently accurate kinetic measurements to test this equation in detail and determine all the rate constants involved. However, an attempt was made to estimate the rate constant k_1 from the experimental rate constants.

It is seen from equation (3-25) that when $[L]$ is very small, the first term in the denominator becomes negligible compared to the second term and the kinetics approach the following form.

$$-\frac{d[CO]}{dt} = k_1 K_h K_b K_{d1} \frac{[Ag(I)] [CO]}{[LH^+]} \frac{[L]}{K_{d1} + [L]} \quad (3-26)$$

Among the experimental data Expt. 7-f is the one done at lowest $[L]$ ($=0.040 \text{ mole} \cdot \text{l}^{-1}$). For the experimental condition of this experiment the ratio of the two terms in the denominator of (3-25) was calculated to be

$$\frac{k_{-1}}{k_2} \frac{(K_{d1} + [L])^2}{K_{d1}(\text{Ag(I)})(K_{d1} + [L])} \approx 0.08 \quad (3-27)$$

using the value of K_{d1} given in Appendix I ($K_{d1} = 0.046$) and assuming the same value of k_{-1}/k_2 as for triethylamine given by (3-21). This ratio seems to be sufficiently small to approximate the kinetics at these experimental conditions of Expt. 7-f by (3-26). (Simple comparisons of the numerical values of $[L]/(K_{d1} + [L])$ with these experimental results in Table 8 show that below $[L] = 0.1$, the results agree fairly well with the kinetics given by (3-26) but deviate from it very rapidly as $[L]$ increases. This is expected since the first term in the denominator of (3-25), which was neglected in (3-26), is second order in $[L]$.) From (3-26) $k_1 K_h$ is given by (3-28).

$$k_1 K_h = \frac{k_{\text{exp}}}{2K_b K_{d1}} \frac{K_{d1} + [L]}{[L]} \quad (3-28)$$

Using the data of the Expt. 7-f, $k_1 K_h$ was estimated to be $1 \times 10^5 \text{ mole}^{-2} \text{ l}^2 \text{ sec}^{-1}$. Although this is a very rough estimate, it agrees with that of ethylamine ($k K_h = 1.0 \times 10^5$), at least in order of magnitude.

A further expected feature of the kinetics in the observed

curvature of Arrhenius plot (Figure XI) of the apparent rate constant, k_{exp} , at $[L] = 0.100 \text{ mole} \cdot \text{l}^{-1}$. As can be seen from the several experiments at 40°C . (Table 8) the kinetics at this temperature were closer to the "standard" ones than at 25°C . However, at $[L] = 0.1$ and at 25°C . the kinetics appear to be close to those for ethylamine and the two other ethanolamine complexes and the apparent energy of activation under this condition and at this temperature is also very close to those for two other ethanolamines ($\Delta E^* \sim 18 \text{ Kcal. mole}^{-1}$).

This mechanism, comprising a sequence of (ii') and (iv), appears to give a satisfactory account of the kinetic behaviour of the triethylamine and triethanolamine complexes, although only a semi-quantitative discussion was possible for the latter. As mentioned previously, the necessary condition for this mechanism to hold is that either k_{-1} is abnormally large or k_2 abnormally small compared to those for ethylamine. This behaviour may be related to the fact that the dissociation constants (especially K_{d_1}) of the silver complex of tertiary amines are abnormally large (K_{d_1} is 70 times for triethylamine and 400 times for triethanolamine complex as large as that of ethylamine; Appendix I), that is, their bis-complexes seem to be abnormally unstable toward the loss of the second coordinated group. A similar instability of the intermediate complex $L\text{-Ag-COOH}$ toward decomposition could account for an abnormally large value of k_{-1} .

These observations provide some information about the

Fig. XI. Arrhenius Plots for Triethanolamine
 and Ethylenediamine Complexes

second step of the reaction, beyond that which could be deduced from the results of the ethylamine-type systems. In particular, they indicate that the second silver species which reacts with the intermediate complex is also a mono-complexed species. This point is to be discussed again later.

AMMONIA COMPLEX

The ammonia complex exhibited the slowest overall reaction rate of all the amine complexes investigated in this study. Most of the rate measurements for this system were made in an autoclave at 30°C. and at high CO pressure (up to 20 atm.). The experimental results are summarized in Table 9 and some typical rate plots are given in Figure XII. The dependence of the rate on the ammonium ion concentration was complex. The $\log k'$ vs. $\log [LH^+]$ plot in Figure XIII shows that the rate is inversely proportional to $[LH^+]$ at low ammonium ion concentrations but that at higher ammonium ion concentrations the inverse order increases to two or higher. This implies that the reaction mechanism may be different in the two regions or the rate is controlled by different steps.

The effects of silver ion concentration, CO pressure and free ammonia concentration were studied at both low (0.02 mole·l⁻¹) and high (0.1 mole·l⁻¹) NH_4^+ concentration and these results also are summarized in Table 9. In both NH_4^+ region, the reaction rate was first order in CO and only slightly

TABLE 9

RATE OF REACTION OF AMMONIA COMPLEX

Initial [Ag(I)] mole·l ⁻¹	CO Pressure atm.	Ammonia [L] mole·l ⁻¹	Ammonium [LH ⁺] mole·l ⁻¹	T°C.	k' mole ⁻¹ ·l sec ⁻¹	k _{exp} sec ⁻¹	Expt. No.
<u>Effect of Ammonium</u>							
0.010	9.2	0.180	0.0200	30	4.6x10 ⁻²	9.2x10 ⁻⁴	8a
0.010	9.2	0.180	0.0236	30	3.3x10 ⁻²	7.4x10 ⁻⁴	8b
0.010	9.2	0.180	0.0300	30	2.8x10 ⁻²	8.4x10 ⁻⁴	8c
0.010	9.2	0.180	0.0500	30	1.65x10 ⁻²	8.3x10 ⁻⁴	8d
0.010	9.2	0.180	0.0700	30	7.6x10 ⁻³	5.3x10 ⁻⁴	8e
0.010	9.2	0.180	0.0850	30	8.3x10 ⁻³	7.0x10 ⁻⁴	8f
0.010	9.2	0.180	0.100	30	5.5x10 ⁻³	5.5x10 ⁻⁴	8g
0.010	9.2	0.180	0.125	30	5.0x10 ⁻³	6.3x10 ⁻⁴	8h
0.010	9.2	0.180	0.150	30	3.1x10 ⁻³	4.7x10 ⁻⁴	8i
0.010	9.2	0.180	0.175	30	1.8x10 ⁻³	3.1x10 ⁻⁴	8j
0.010	9.2	0.180	0.200	30	1.2x10 ⁻³	2.4x10 ⁻⁴	8k
<u>Effect of CO Pressure</u>							
0.010	4.1	0.180	0.020	30	5.3x10 ⁻²	10.5x10 ⁻⁴	8l
0.010	9.2	0.180	0.020	30	4.6x10 ⁻²	9.2x10 ⁻⁴	8a
0.010	14.1	0.180	0.020	30	4.9x10 ⁻²	9.8x10 ⁻⁴	8n
0.010	19.2	0.180	0.020	30	5.0x10 ⁻²	10.0x10 ⁻⁴	8o
0.010	4.1	0.180	0.100	30	5.7x10 ⁻³	5.7x10 ⁻⁴	8l'
0.010	9.2	0.180	0.100	30	5.5x10 ⁻³	5.5x10 ⁻⁴	8g
0.010	14.1	0.180	0.100	30	5.7x10 ⁻³	5.7x10 ⁻⁴	8n'
0.010	19.2	0.180	0.100	30	7.2x10 ⁻³	7.2x10 ⁻⁴	8o'
<u>Effect of Initial Silver Ion</u>							
0.0047	9.2	0.180	0.020	30	4.2x10 ⁻²	8.5x10 ⁻⁴	8p
0.0047	9.2	0.180	0.020	30	4.6x10 ⁻²	9.2x10 ⁻⁴	8a
0.0195	9.2	0.180	0.020	30	4.8x10 ⁻²	9.6x10 ⁻⁴	8q
0.0048	9.2	0.180	0.100	30	2.6x10 ⁻³	2.6x10 ⁻⁴	8p'
0.0099	9.2	0.180	0.100	30	5.5x10 ⁻³	5.5x10 ⁻⁴	8g
0.0196	9.2	0.180	0.100	30	9.8x10 ⁻³	9.8x10 ⁻⁴	8q'

TABLE 9 (Continued)

Initial [Ag(I)] mole·l ⁻¹	CO Pressure atm.	Ammonia [L] mole·l ⁻¹	Ammonium [LH ⁺] mole·l ⁻¹	T°C.	k' mole ⁻¹ .l sec ⁻¹	k _{exp} sec ⁻¹	Expt. No.
<u>Effect of Free Ammonia</u>							
0.010	9.2	0.080	0.020	30	3.9x10 ⁻²	7.8x10 ⁻⁴	8r
0.010	9.2	0.180	0.020	30	4.6x10 ⁻²	9.2x10 ⁻⁴	8a
0.010	9.2	0.280	0.020	30	3.1x10 ⁻²	6.2x10 ⁻⁴	8s
0.010	9.2	0.080	0.030	30	2.7x10 ⁻²	8.2x10 ⁻⁴	8r''
0.010	9.2	0.180	0.030	30	2.8x10 ⁻²	8.4x10 ⁻⁴	8c
0.010	9.2	0.280	0.030	30	2.2x10 ⁻²	6.6x10 ⁻⁴	8s''
0.010	9.2	0.080	0.100	30	7.6x10 ⁻³	7.6x10 ⁻⁴	8r'
0.010	9.2	0.180	0.100	30	5.5x10 ⁻³	5.5x10 ⁻⁴	8g
0.010	9.2	0.280	0.100	30	5.1x10 ⁻³	5.1x10 ⁻⁴	8s'
<u>Effect of Temperature</u>							
0.010	9.2	0.180	0.050	25	1.06x10 ⁻²	5.3x10 ⁻⁴	8t
0.010	9.2	0.180	0.050	30	1.4x10 ⁻²	7.2x10 ⁻⁴	8d
0.010	9.2	0.180	0.050	35	2.0x10 ⁻²	10.2x10 ⁻³	8u
0.010	9.2	0.180	0.050	40	3.1x10 ⁻²	1.5x10 ⁻³	8v
0.010	9.2	0.180	0.050	50	6.6x10 ⁻²	3.3x10 ⁻³	8w

dependent on the free NH₃ concentration. No trend, however, was discernible in the latter dependence. The dependence on [Ag(I)] was first order at low [NH₄⁺] and second order at high [NH₄⁺] (i.e., k' was proportional to [Ag(I)]). This suggests that at high [NH₄⁺] the rate is controlled in part by the second step in which the second silver (I) species takes part. The high inverse order dependence on [NH₄⁺] in this region further suggests that the second silver species also is hydrolyzed.

Fig. XII. Typical Rate Plots for Ammonia Complex

— See Table 9 for experimental conditions.

Fig. XIII. Dependence of Rate on Ammonium Ion Concentration at 30° for Ammonia Complex; $[\text{L}] = 0.200 \text{ mole l}^{-1}$

The following mechanism is consistent with these observations:

where two processes with rate constants k_{-1} and k_2 are competing for intermediate complex, L-Ag-COOH. The kinetics, assuming steady state concentration of L-Ag-COOH, are thus of the following type.

$$\begin{aligned} -\frac{d[\text{CO}]}{dt} &= -\frac{1}{2} \frac{d[\text{Ag(I)}]}{dt} = \frac{k_{\text{exp}}}{2} [\text{Ag(I)}][\text{CO}]/[\text{LH}^+] \\ &= \frac{k_1 k_2 K_h^2 K_b^2 K_{d1}^2 [\text{Ag(I)}]^2 [\text{CO}]}{[\text{LH}^+]^2 \{k_{-1} + k_2 K_h K_b K_{d1} [\text{Ag(I)}]/[\text{LH}^+]\}} \end{aligned} \quad (3-29)$$

At low $[\text{NH}_4^+]$ where $k_{-1} \ll k_2 K_h K_b K_{d1} [\text{Ag(I)}]/[\text{LH}^+]$, the kinetics approach those for ethylamine while at high $[\text{NH}_4^+]$ where $k_{-1} \gg k_2 K_h K_b K_{d1} [\text{Ag(I)}]/[\text{LH}^+]$, the reaction is second order on $[\text{Ag(I)}]$ and inverse second order on $[\text{LH}^+]$, i.e.,

$$\text{Low } [\text{LH}^+] : -\frac{d[\text{CO}]}{dt} = k_1 K_h K_b K_{d1} \frac{[\text{Ag(I)}][\text{CO}]}{[\text{LH}^+]} \quad (3-30)$$

$$\text{High } [\text{LH}^+] : -\frac{d[\text{CO}]}{dt} = \frac{k_1 k_2}{k_{-1}} K_h^2 K_b^2 K_{d1}^2 \frac{[\text{Ag(I)}]^2 [\text{CO}]}{[\text{LH}^+]^2} \quad (3-31)$$

From the experiments at low $[\text{LH}^+]$ (0.020 mole l^{-1})

$$k_{\text{exp}} = 2k_1 K_h K_b K_{d1} = 9 \times 10^{-4} \text{ sec}^{-1} \quad (3-32)$$

Using the values for K_b and K_{d1} at 30°C . in Appendix I,

$$k_1 K_h = \frac{k_{\text{exp}}}{2K_b K_{d1}} = 1.6 \times 10^5 \text{ mole}^{-2} \cdot \text{l}^2 \cdot \text{sec}^{-1} \quad (3-33)$$

On the other hand at high (LH^+) k_{exp} corresponds to:

$$k_{\text{exp}} = \frac{2k_1 k_2}{k_{-1}} K_h^2 K_b^2 K_{d1}^2 \frac{[\text{Ag(I)}]}{[\text{LH}^+]} \quad (3-34)$$

The experimental rate constant k_{exp} at $(\text{LH}^+) = 0.100 \text{ mole} \cdot \text{l}^{-1}$ (Expt's. 8p', 8g, 8q') exhibits a good first order dependence on $[\text{Ag(I)}]$ and gives a constant value for $k_{\text{exp}} / [\text{Ag(I)}]$ (5.4, 5.6 and $5.0 \times 10^{-2} \text{ mole}^{-1} \cdot \text{l} \cdot \text{sec}^{-1}$, respectively), i.e.,

$$\text{at } (\text{LH}^+) = 0.100 \text{ mole} \cdot \text{l}^{-1}$$

$$\frac{k_{\text{exp}}}{[\text{Ag(I)}]} = \frac{2k_1 k_2}{k_{-1}} \frac{K_h^2 K_b^2 K_{d1}^2}{(\text{LH}^+)} = 5 \times 10^{-2} \text{ mole}^{-1} \cdot \text{l} \cdot \text{sec}^{-1} \quad (3-35)$$

Substituting $(\text{LH}^+) = 0.100 \text{ mole l}^{-1}$ and using (3-32) and the values for K_b and K_{d1} again we get

$$\frac{k_2 K_h}{k_{-1}} = 2 \times 10^9 \text{ mole}^{-2} \cdot \text{l}^2 \quad (3-36)$$

All these results are for 30°C . This temperature was chosen for the most of kinetic studies instead of 25°C . because of difficulty in controlling the autoclave temperature at 25°C . To compare the rate constant with those of other systems, it is necessary to correct it to 25°C . Arrhenius plot at $(\text{LH}^+) = 0.050 \text{ mole l}^{-1}$ given in Figure XIV also reflects the complex nature of the kinetics of this system. It was difficult to measure the temperature effect at lower (LH^+) than this because

Fig. XIV. Arrhenius Plot for Ammonia Complex

$[L] = 0.200$, $[LH^+] = 0.0500 \text{ mole l}^{-1}$, $P_{\text{CO}} = 9.20 \text{ atm}$.

of the fast rates and poor rate plots. The Arrhenius plot in Figure XIV is linear at high temperature but is concave upwards at low temperatures. This indicates that the linear portion represents the temperature dependence of the apparent rate constant of the form given by (3-34) and not (3-32). The apparent energy of activation calculated for linear portion of the Arrhenius plot is 13.7 Kcal. mole⁻¹, which is very close to the values for k_{exp} ($=2kK_h K_b K_{d_1}$) for other systems (14-18 Kcal. mole⁻¹, Table 6). It thus seems reasonable to calculate the rate constant given by (3-32) for 25°C. using a temperature coefficient corresponding to $\Delta H^* = 14-18$ Kcal. mole⁻¹. Because the temperature interval involved is small (5°C.), the error involved in the extrapolation can hardly be very large. Thus, from (3-32)

$$k_{\text{exp}} = 2kK_h K_b K_{d_1} = 6 \times 10^{-3} \text{ sec}^{-1} \text{ (at } 25^\circ\text{C.)} \quad (3-37)$$

Again, using the values for K_b and K_{d_1} for 25°C. in Appendix I.

$$k_1 K_h = 1.4 \times 10^5 \text{ mole}^{-2} \cdot \text{l}^2 \cdot \text{sec}^{-1} \quad (3-38)$$

This is very close to the values previously found for ethylamine and related systems (1.0×10^5).

At (NH_4^+) exceeding $0.1 \text{ mole} \cdot \text{l}^{-1}$, the dependence of the rate on (NH_4^+) seems to exceed inverse second order (Figure XIII). However, in this region the actual rate of the reaction was extremely slow so that the measurements are considered unreliable.

The mechanism involved here is substantially the same as that

derived previously for the two tertiary amines, triethylamine and triethanolamine, apart from a difference in the nature of the Ag(I) species participating in the second step of the reaction (L-Ag-OH and LAg^+ , respectively). No explanation for this difference is available. Recently, Peters and McAndrew (5) reported the kinetics of the reduction of silver in perchlorate media at 70°C . to be

$$-\frac{d(\text{Ag}^+)}{dt} = k(\text{Ag}^+)^2(\text{OH}^-)(\text{CO}) \quad (3-39)$$

which was interpreted by the following mechanism

In this case the second silver (I) species reacting with the intermediate complex is an unhydrolyzed ion analogous to LAg^+ in the tertiary amine cases.

The slowness of the second step in the case of the ammonia complex which leads to the departure from the simple ethylamine-type kinetics may be due to the much lower basicity of ammonia (i.e., to a smaller L-Ag-OH concentration). However, the failure of diethanolamine, which is even less basic, to exhibit the same type of kinetics as ammonia, throws some doubts on this.

DIAMINE COMPLEXES

In addition to the above monoamines, three primary diamines, ethylenediamine, 1,3-diaminopropane and 1,4-diaminobutane were examined. The experimental results are summarized in Table 10

TABLE 10

RATE OF REACTION OF DIAMINE COMPLEXES

Amine	Initial [Ag(I)] mole.l ⁻¹	CO Pres- sure mmHg	Amine [L] mole.l ⁻¹	Amine Per- chlorate mole.l ⁻¹	Temp. °C.	k ⁱ mole ⁻¹ .l. sec ⁻¹	k ^{exp} sec ⁻¹	No.
Ethylene- diamine	0.013	705	0.300	0.100	40	0.34	0.034	9a
	0.013	705	0.300	0.300	40	0.112	0.034	9b
	0.013	705	0.100	0.100	40	0.34	0.034	9c
	0.012	705	0.200	0.200	40	0.17	0.034	9d
	0.020	705	0.200	0.100	40	0.34	0.034	9e
	0.020	508	0.200	0.100	40	0.34	0.034	9f
	0.020	239	0.200	0.100	40	0.34	0.034	9g
	0.010	741	0.200	0.100	15	0.132	0.0132	9h
	0.010	742	0.200	0.100	20	0.193	0.0193	9i
	0.010	730	0.200	0.100	25	0.216	0.0216	9j
	0.010	728	0.200	0.100	30	0.220	0.0220	9k
	0.010	712	0.200	0.100	35	0.228	0.0228	9l
	0.010	699	0.200	0.100	40	0.354	0.0354	9m
	0.010	683	0.200	0.100	45	0.480	0.0480	9n
	0.010	664	0.200	0.100	50	0.668	0.0668	9o
1,3-Diamino- propane	0.010	736	0.183	0.100	25	7.1x10 ⁻²	7.1x10 ⁻³	10a
	0.010	736	0.183	0.050	25	1.6x10 ⁻¹	8.2x10 ⁻³	10b
	0.010	736	0.183	0.025	25	2.8x10 ⁻¹	7.1x10 ⁻³	10c
	0.005	736	0.192	0.100	25	7.1x10 ⁻²	7.1x10 ⁻³	10d
	0.010	736	0.0356	0.025	25	1.7x10 ⁻¹	4.2x10 ⁻³	10e
	0.010	736	0.0643	0.025	25	2.2x10 ⁻¹	5.5x10 ⁻³	10f
	0.010	736	0.0840	0.025	25	2.5x10 ⁻¹	6.1x10 ⁻³	10g
	0.010	736	0.183	0.025	25	2.8x10 ⁻¹	7.1x10 ⁻³	10h
	0.010	736	0.282	0.025	25	3.0x10 ⁻¹	7.6x10 ⁻³	10i
1,4-Diamino- butane	0.010	736	0.190	0.0177	25	4.3x10 ⁻¹	7.6x10 ⁻³	11a
	0.010	736	0.190	0.0250	25	3.2x10 ⁻¹	8.1x10 ⁻³	11b
	0.010	736	0.190	0.0354	25	2.3x10 ⁻¹	8.3x10 ⁻³	11c
	0.010	736	0.090	0.0250	25	3.3x10 ⁻¹	8.3x10 ⁻³	11d
	0.010	736	0.050	0.0250	25	3.4x10 ⁻¹	8.4x10 ⁻³	11e
	0.010	736	0.010	0.0250	25	2.6x10 ⁻¹	6.4x10 ⁻³	11f
	0.010	736	0.005	0.0250	25	2.4x10 ⁻¹	6.0x10 ⁻³	11g

and some typical rate plots are given in Figure XV. The ethylene-diamine complex was first investigated at 40°C. and found to

Fig. XV. Typical Rate Plots for Diamine Complexes

— See Table 10 for experimental conditions.

exhibit kinetics similar to those of the ethylamine complex as can be seen from Table 10. However, the study of the temperature dependence of the rate revealed more complicated behaviour at lower temperature and the results failed to yield a linear Arrhenius plot (Figure XVI). Attempts to elucidate the kinetics at 25°C. and obtain directly the rate constant at this temperature for comparison with the other amine complexes were unsuccessful. Thus the rate of this system at this temperature exhibited a very complicated dependence on amine, amine perchlorate and silver ion concentration which was not altogether reproducible. At higher temperature, however, (above 35°C.) the system appeared to be well behaved.

Extrapolation of the linear portion of the Arrhenius plot in this region yielded a value of $1.07 \times 10^{-2} \text{ sec}^{-1}$ for k_{exp} at 25°C. Using the values for K_b and K_{d1} of ethylenediamine in Appendix I, we get

$$kK_h = \frac{k_{\text{exp}}}{2K_b K_{d1}} = 0.30 \times 10^5 \text{ mole}^{-2.12} \cdot \text{sec}^{-1} \quad (3-40)$$

This is only about one-third of the value for ethylamine and related amine complexes.

The silver complex of 1,3-diaminopropane has an abnormally large first stability constant ($K_{01} = 8.9 \times 10^5$) as can be seen in Appendix I, and there has not been reported any data on its second stability constant. This is due to stabilization of

Fig. XVI. Dependence of Rate on Free Amine Concentration
at 25° for 1,3-Diamino propane Complex

the mono-complex by chelation, with the result that there is little tendency to add a second amine molecule to form the bis-complex. This great stability of the monochelate complex is reflected in the extremely large first stability constant, the second stability constant, K_{12} , presumably being very small, so that the approximation, $[Ag(I)] = [AgL_2^+]$ is obviously invalid in this case. Therefore, equation (3-41) (as in the case of triethanolamine, which also has a small K_{12} , i.e., large K_{d1}) must be used for the concentration of AgL^+ . Assuming

$$[AgL^+] + [AgL_2^+] = [Ag(I)] \quad (3-22)$$

$$\frac{[AgL_2^+]}{[AgL^+][L]} = K_{12} = K$$

$$[AgL^+] = \frac{[Ag(I)]}{1+K[L]} \quad (3-41)$$

where K is the second stability constant of the silver complex. Then if ethylamine-type behaviour applies also in this case, the overall kinetics will be as follows:

$$\begin{aligned} - \frac{d[CO]}{dt} &= \frac{1}{2} \frac{d[Ag(I)]}{dt} = \frac{k_{exp}}{2} \frac{[Ag(I)][CO]}{[LH^+]} \\ &= kK_h K_b \frac{[Ag(I)][L][CO]}{(1+K[L])[LH^+]} \end{aligned} \quad (3-41)$$

Then

$$k_{exp} = 2kK_h K_b \frac{[L]}{1+K[L]} \quad (3-42)$$

Taking the reciprocal of k_{exp}

$$\frac{1}{k_{exp}} = \frac{1}{2kK_h K_b} \left(\frac{1}{[L]} + K \right) \quad (3-43)$$

The experimental free amine concentration was first calculated assuming $[Ag(I)] = [AgL^+]$, and on this basis the experimental results for different $[L]$ were plotted as $1/k_{exp}$ vs. $1/[L]$. The resulting plot, which was not quite linear but slightly concave upwards, was used to obtain a rough estimate of K , which in turn was used to improve the free amine concentration. This procedure was repeated to self-consistency and yielded a good linear plot of $1/k_{exp}$ vs. $1/[L]$ shown in Figure XVI. The constants derived from this, using the value of K_b in Appendix I are

$$kK_h = 5.1 \times 10^2 \text{ mole}^{-2} \cdot \text{l}^2 \cdot \text{sec}^{-1} \quad (3-44)$$

$$K = 26 \text{ mole}^{-1} \cdot \text{l} \quad (3-45)$$

This value of kK_h is only 1/200 of the "normal" value for ethylamine, etc. ($kK_h = 1.0 \times 10^5$).

The much lower reactivity of this complex presumably reflects blocking of the reaction site by chelation, i.e.

The rate constant of ethylenediamine is also smaller than that of ethylamine, etc., but the reduction factor is only 1/3 in this case. Presumably this also is attributable to chelation but in this case the chelation tendency is much smaller than 1,3-diaminopropane, because of the preference of Ag^+ for linear coordination which, for steric reason, is more readily realized with 1,3-diaminopropane than with ethylenediamine. This is

reflected also in the corresponding stability constants of the complexes. Thus the first stability constant of ethylenediamine silver complex, while larger than that of ethylamine, is much smaller than that of 1,3-diaminopropane. These data are summarized in Table 11.

TABLE 11

RATE OF DIAMINE COMPLEXES AND THEIR STABILITY CONSTANTS

	Log K_{01}	Log K_{12}	Log K_{02}	$kK_h \times 10^5$ mole^{-2} sec^{-1}
$\text{CH}_3\text{CH}_2\text{NH}_2$	3.37	3.93	7.30	1
$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	4.62	2.92	7.54	0.3
$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	5.77	$1.42^{1)}$	$7.19^{1)}$	0.005

1) Results from the present study. Other stability constants are from Appendix I.

It is seen that K_{12} and kK_h both of which should reflect (inversely) the chelating tendency of the mono-complex indeed follow closely parallel trends.

1,4-diaminobutane which also has an abnormally large K_{01} value, similar to that for 1,3-diaminopropane, was expected to show the same type of behaviour as the latter. However, the rate in this case was almost independent of the amine concentration and the kinetics were similar to those for ethylamine, although the actual overall rate of reaction (k_{exp}) was almost

the same as for 1,3-diaminopropane (cf. Table 10). The significance of this behaviour is not understood.

GENERAL DISCUSSION

A common feature of the systems examined in the course of this study is that in every case CO apparently reacts with a species of the composition L-Ag-OH. The initial reaction in each case can be represented as

The rate constant, k , of this process could not be measured directly, but the data yielded values of kK_h . In some cases, the back reaction of (ii) was sufficiently fast to compete with the subsequent reaction of the intermediate, L-Ag-COOH, with another silver ion.

All the values of kK_h (or k_1K_h) for various amine complexes investigated in this study are summarized in Table 12, together with the values of K_b , K_{d1} and $kK_hK_bK_{d1}$. The value of the latter is identical to $\frac{1}{2}k_{\text{exp}}$ in the case of ethylamine-type "standard" amine complexes. For all the mono-dentate amines it is seen that kK_h is substantially independent* of the nature of the amine.

* Triethylamine is the only case where the deviation of the value of kK_h from the "standard" value of 1×10^5 appears to lie outside experimental error. For this amine the values of K_{d1} and K_{d2} , both of which were used for the determination of kK_h were less precise than those for the other amines; only one significant figure was available from the literatures. Furthermore, in this system it was necessary to use high $[\text{LH}^+]$ in most of the experiments so that ionic strength effects which have not been taken into account may be important.

TABLE 12

SUMMARY OF KINETIC AND RELATED THERMODYNAMIC DATA

Amine	$kK_h K_b K_{d1}$ $\times 10^2$ sec^{-1}	K_{d1} $\times 10^4$ $\text{mole} \cdot \text{l}^{-1}$	K_b $\times 10^4$ $\text{mole} \cdot \text{l}^{-1}$	$K_b K_d$ $\times 10^8$ $\text{mole}^2 \cdot \text{l}^{-2}$	kK_h $\times 10^{-5}$ $\text{mole}^{-2} \cdot \text{l}^2 \cdot \text{sec}^{-1}$
NH_3	0.03	1.2	0.18	0.22	1.4
CH_3NH_2	1.43	2.9	5.2	15	0.9
$\text{C}_2\text{H}_5\text{NH}_2$	0.78	1.2	6.5	7.6	1.0
$\text{HOC}_2\text{H}_4\text{NH}_2$	0.14	2.8	0.55	1.5	1.0
$(\text{C}_2\text{H}_5)_2\text{NH}$	4.3	5.0	9.1	46	1.0
$(\text{HOC}_2\text{H}_4)_2\text{NH}$	0.16	16	0.10	1.6	1.0
$(\text{C}_2\text{H}_5)_3\text{N}$	120	80	5.9	470	2.5
$(\text{HOC}_2\text{H}_4)_3\text{N}$	0.36	460	0.0079	3.6	1
$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	0.5	12	1.5	18	0.30
$\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}_2$	0.4	380	4.4	1700	0.0025

The constancy of kK_h over a 2,000 fold variation of $K_b K_{d1}$ (and hence of $kK_h K_b K_{d1}$) is striking.

The constant kK_h may be identified with the rate constant of the alternative and kinetically equivalent representation of (ii), i.e., with the rate constant of the termolecular process (ii"),

It seems likely that K_h also is insensitive to the nature of

L, and indeed probably does not differ greatly from the hydrolysis constant of the free Ag^+ ion whose value is about $2 \times 10^2 \text{ mole l}^{-1}$ (11). Using this value for K_h , k is estimated to be about $5 \times 10^2 \text{ mole}^{-1} \cdot \text{l} \cdot \text{sec}^{-1}$.

This participation of hydroxide ion in the reaction (base catalysis) accounts for the low reactivity of Ag^+ toward CO in acidic media. The insensitiveness of the reactivity of L-Ag-OH to the nature of L, suggests that the amine molecule in L-Ag-OH is acting only to solubilize AgOH and prevent precipitation of silver oxide. The enhancement of reactivity in these amine-buffered systems would appear to be due mainly to the high pH, rather than to specific complexing effects.

On the other hand, the rate of the back reaction of step (ii) and the rate and nature of the second step of the reaction do appear to vary with the nature of amine, L. This is shown particularly by a comparison of the ammonia and triethylamine complexes.

The apparent enthalpy and entropy of activation, ΔH_{exp}^* and ΔS_{exp}^* for $k_{\text{exp}} = kK_hK_bK_{d1}$ for "standard" amine complexes listed in Table 6 correspond to

$$\Delta H_{\text{exp}}^* = \Delta H^* + \Delta H_h + \Delta H_b + \Delta H_{d1} \quad (3-46)$$

$$\Delta S_{\text{exp}}^* = \Delta S^* + \Delta S_h + \Delta S_b + \Delta S_{d1} \quad (3-47)$$

where ΔH^* and ΔS^* correspond to the enthalpy and entropy of activation of the bimolecular process (ii) and the other terms with subscripts h, b and d_1 correspond to enthalpy and entropy

changes of the following equilibrium processes.

Few thermodynamic data relating to these processes are available.

Only in the case of ethylamine, has it been possible to obtain

fairly reliable values of ΔH_b , ΔH_{d_1} , ΔS_b and ΔS_{d_1} , using

available data (11, 12). The values of ΔH_b and ΔH_{d_1} thus

obtained for ethylamine are 0.7 and 6.4 Kcal. mole⁻¹ and ΔS_b

and ΔS_{d_1} are -12.2 and 3.6 e.u. respectively. The values of

ΔH_h and ΔS_h as well as that of K_h can be approximated to that

for the free Ag^+ ion as pointed out previously, which are esti-

mated to be about -2 Kcal. mole⁻¹ and 4 e.u., respectively.

Hence, the enthalpy and entropy of activation of the bimolecular

process (ii) are estimated to be $\Delta H^* \sim 9 \text{Kcal. mole}^{-1}$ and

$\Delta S^* \sim -15 \text{ e.u.}$ (the bimolecular rate constant being $k \sim 5 \times 10^2$

$\text{mole}^{-1} \cdot \text{sec}^{-1}$ at 25°C.). Although reliable values for ΔH_b ,

ΔS_{d_1} , etc. for other amines are not available, it is expected

that ΔH^* and ΔS^* for these systems will not differ greatly

from those for ethylamine.

Peters and McAndrew (5) have recently reported the following

kinetics for the reaction of aqueous silver acetate with CO in

acetate-buffered acidic media at 90°C. and high CO pressure.

$$\begin{aligned}
 -\frac{d[\text{CO}]}{dt} = & k_1[\text{AgOAc}][\text{CO}] + k_2K_c \frac{[\text{Ag}^+]^2[\text{CO}]}{[\text{H}^+]} \\
 & + k_3K_c \frac{[\text{Ag}^+][\text{AgOAc}][\text{CO}]}{[\text{H}^+]}
 \end{aligned} \quad (3-48)$$

and interpreted these in terms of the following mechanism,

In this case there appears to be a contribution to the reaction, not only from AgOH but also from AgOAc. The process (viii) which corresponds to (ii), (ii') or (ii'') in the case of amine complexes, is faster than the subsequent steps and thus corresponds to a pre-equilibrium. Hence, it is not kinetically distinguishable whether this is a base-catalyzed process as in the case of amine complexes or rather an acid-inhibited process; in other words, whether the silver species which is directly reactive toward CO molecule is a hydrolyzed species, AgOH, or an unhydrolyzed ion Ag^+ . In the case of amine-buffered solution L-Ag-OH was seen to be the only reactive species. It is of great interest, therefore, to see if the contribution of unhydrolyzed Ag^+ is detectable in the acetate-buffered solution.

It can easily be seen that rate constants and equilibrium constants of these two processes, base-catalyzed (ii'') and acid-inhibited (viii) are related as follows.

$$\frac{k_1}{k_{-1}} = \frac{K_c}{K_h K_w} \quad (3-49)$$

Suppose the base-catalyzed process (ii'') is the only process contributing to equilibrium (viii), then the kinetics observed by Peters and McAndrew requires that

$$\frac{k_2 [Ag^+]}{k_{-1}} \ll 1 \quad (3-50)$$

and hence

$$\frac{k_1 K_h k_2 [Ag^+]}{k_{-1}} \ll k_1 K_h \quad (3-51)$$

From the data of Peters and McAndrew the value of $k_1 K_h k_2 [Ag^+]/k_{-1}$ ($= k_2 K_c [Ag^+]/K_w$) can be estimated to be about $10^6 \text{ mole}^{-2} \cdot \text{l} \cdot \text{sec}^{-1}$ at 90°C . On the other hand the insensitiveness of the kK_h (rate constant of the base-catalyzed process (ii'')) for amine complex to the nature of L over a 1,000-fold variation in its basicity suggests that the reactivity of uncomplexed Ag^+ for the same type of process should also be close to that of amine-complexed species. Using the value of kK_h^* at 25°C . and the previously determined temperature coefficient, the value of kK_h at 90°C . can be estimated to be $9 \times 10^5 \text{ mole}^{-2} \cdot \text{l}^2 \cdot \text{sec}^{-1}$. These results are not in accord with (3-51). This suggests that in the case of

* The value of K_h and ΔH_h are not reliable so that kK_h is to be used for comparison. The value for $\Delta H^* + \Delta H_h$ ethyl-amine has been estimated to be $7.2 \text{ Kcal. mole}^{-1}$. This temperature coefficient being small and fairly reliable, the resulting kK_h for 90°C . is also fairly reliable.

acetate-buffered solution there may indeed be a reaction path involving direct reaction between unhydrolyzed Ag^+ and CO represented by (viii). However, the rate constant of this process is not obtainable from these data.

This possibility that the unhydrolyzed Ag^+ ion, may also be reactive toward CO is not altogether unexpected, since, as mentioned earlier, it has already been found that in acidic solutions the reduction of Hg^{2+} by CO proceeds through reaction with the unhydrolyzed ion (3). That such a path (i.e., OH^- -independent) is not observed in the case of the silver amine complex may simply be due to the high pH of the solutions, resulting in enhancement of the OH^- -dependent path.

Another interesting result of Peters and McAndrew's work is the evidence suggesting that AgOAc is also reactive toward CO, presumably through an intermediate complex analogous to L-Ag-COOH , i.e., Ag-COOAc . In this reaction the first step (vi) is rate-determining with a rate constant at 90°C . estimated to be

$$k_1 = 3.6 \times 10^{-2} \text{ mole}^{-1} \cdot \text{l} \cdot \text{sec}^{-1}.$$

This compares with a value of $2.5 \times 10^3 \text{ mole}^{-1} \cdot \text{l} \cdot \text{sec}^{-1}$ estimated for the corresponding rate constant of L-Ag-OH toward CO, i.e., L-Ag-OH appears to be about 10^5 times as reactive toward CO as AgOAc . The activation energy of the process (vi) has been determined to be $15 \text{ Kcal} \cdot \text{mole}^{-1}$ while that for the process (ii) is $9 \text{ Kcal} \cdot \text{mole}^{-1}$.

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APPENDIX I
SELECTED THERMODYNAMIC PROPERTIES OF AMINES
AND SILVER-AMINE COMPLEXES

Amine	*1 pKa	Stability Constants*3			*2 K _b x10 ⁴	*4 K _{d1} x10 ⁴
		LogK ₀₁	LogK ₁₂	LogK ₂		
NH ₃	9.25	3.31	3.92	7.23	0.174	1.2
*6	(9.09)	(3.24)	(3.81)	(7.05)	(0.182)	(1.5)
CH ₃ NH ₂	10.72	3.15	3.53	6.68	5.2	2.9
C ₂ H ₅ NH ₂	10.81	3.37	3.93	7.30	6.5	1.2
(C ₂ H ₅) ₂ NH	10.96	3.06	3.30	6.36	9.1	5.0
(C ₂ H ₅) ₃ N	10.77	2.6	2.1	4.76	5.9	80
HOC ₂ H ₄ NH ₂	9.74	3.13	3.55	6.68	0.55	2.8
(HOC ₂ H ₄) ₂ NH	9.00	2.69	2.79	5.48	0.10	16
(HOC ₂ H ₄) ₃ N	7.90	2.30	1.34	3.64	7.9x10 ⁻³	460
H ₂ NCH ₂ CH ₂ NH ₂	10.18	4.62	2.92	7.54	1.5	12
H ₂ N(CH ₂) ₃ NH ₂	10.64	5.77	1.42*5	7.19*5	4.4	380
H ₂ N(CH ₂) ₄ NH ₂	10.82	5.9			6.6	

*1 $[L][H^+]/[LH^+] = K_a$

*2 $[LH^+][OH^-]/[L] = K_b = K_w/K_a$

*3 $[AgL^+]/([Ag^+][L]) = K_{01}$, $[AgL_2^+]/([Ag^+L][L]) = K_{12}$, $K_{02} = K_{01} \cdot K_{12}$

*4 $[AgL^+][L]/[AgL_2^+] = K_{d1}$

These data are from "Stability Constants of Complex Salts", special publication of the Chemical Society, corrected, where necessary, to 25°C. using the known temperature coefficient for $Ag(NH_2C_2H_5)_2^+$ ($d \log K_{01}/dt = d \log K_{12}/dt = -0.016$)

* 5 Estimated from the result of the present work (cf. p. 62).

* 6 Values in parentheses are for 30°C.