A KINETIC STUDY OF THE CATALYTIC ACTIVATION OF MOLECULAR HYDROGEN BY SILVER AMINE COMPLEXES

by

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ABSTRACT

The kinetics of the reduction of silver amine complexes in aqueous solutions were investigated and found to be second order overall, the rate being proportional to silver complex and hydrogen concentrations. These systems were studied under conditions of essentially complete complexing and therefore the rates were independent of amine concentration. The rates were also shown to be independent of amine perchlorate concentration and thus of pH within a limited range. Enthalpies and entropies of activation were determined for each system and an attempt was made to correlate kinetic data with information on complex stability constants and amine basicities. The most prominent trend in the results was the inverse dependence of rate on complex stability constant. Two mechanisms are proposed both involving heterolytic cleavage of the hydrogen molecule. In the first mechanism, the proton released in the rate determining step is taken up by the basic ligand directly. In the second mechanism, a water molecule replaces the amine ligand and acts as the proton acceptor. The strength of the silver-ligand bond and the difficulty of ligand replacement by water account for the inverse dependence of rate on complex stability for each mechanism respectively. Arguments are presented to support both mechanisms.

In general dibasic amine complexes activated hydrogen more readily and displayed a more negative entropy of activation than do the monoamine complexes. These observations are attributed to the presence of a free basic group in the ligand aiding the cleavage of the hydrogen molecule in the rate determining step. The proximity of the second basic group to the central silver atom also appears to be important. These effects and the possible role of the free basic group in the ligand are discussed.

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INTRODUCTION

Molecular hydrogen is a relatively inert substance as indicated by the high endothermicity of its uncatalysed reactions. The chain initiating step for the hydrogenation of ethylene;

$$H_2 + C_2H_4 \longrightarrow H + C_2H_5$$

has an activation energy of 60-70 kcal./mole (1), (2). The unreactive nature of this molecule has been attributed to the high bond energy of 103 kcal./mole and closed shell electronic configuration. However, on the surface of a catalyst an alternative reaction path requiring less energy is provided. Thus, while the apparent activation energy for the homogeneous hydrogenation of ethylene is 43 kcal./mole, the reaction takes place on a nickel surface with an apparent activation energy of only 11 kcal./mole (3).

The catalytic activation of hydrogen may be conveniently divided into two types; activation taking place on the surface of a solid and activation occurring homogeneously in solution.

HETEROGENEOUS CATALYSIS

Heterogeneous catalytic processes are widely known and extensively used. However, the mechanism by which hydrogen reacts on a surface with a lower energy requirement than in the gas phase remains to be adequately

explained. The activation of hydrogen is considered to occur through homolytic cleavage of the H-H bond with simultaneous formation of covalent bonds with the catalyst. Both crystal dimensions and electronic character of the metal have been employed in attempts to explain the heterogeneous activation of hydrogen but with only limited success.

Some experimental support for the relationship between activity and crystal dimensions and geometry has been provided by studies on the hydrogenation of ethylene (3) and benzene (4), (5) on surfaces of transition metals. A semiquantitative treatment of the variation of activation energy for chemisorption of hydrogen on carbon with lattice parameters by Sherman and Eyring (6) has lent theoretical support to this approach. However, several objections to this point of view have been raised; (a) metals such as Cu and Zn have optimum lattice spacing, yet show no catalytic activity and (b) catalysis on alloy surfaces bears no relationship to geometric factors (7), (8), (9). At present crystal dimensions appear to be of secondary significance and of greater importance in catalytic activation is the electronic character of the solid (10).

The ability of metals to catalyse hydrogen reactions has been related to incomplete filling of the metal d-bands (9). This is demonstrated by the catalytic activity of the transition metals and the reduction in activity caused by alloying with strong electron-donating metals such as those of group IB where electrons are donated into the d-bands of the transition metal (9). Similarly these metal catalysts are poisoned by electron-donating compounds such as the sulfides. The paramagnetic susceptibility of palladium decreases upon absorption of hydrogen indicating filling of metal d-bands (11). This indicates that hydrogen is activated through the

formation of an actual bond involving donation of electrons from the hydrogen into the metal d-bands.

Dowden has given a theoretical treatment to the electronic approach (12). He points out the proportionality between catalytic activity and the energy density of electron levels at the Fermi surface and the electronic work function of the transition metals. Some experimental evidence has been presented to support these ideas but at present quantitative application of the theory is difficult.

HOMOGENEOUS CATALYSIS

Calvin in 1938 was the first to demonstrate that hydrogen could be activated homogeneously (13) and since that time numerous similar systems have been discovered and studied (14), (15), (16). These systems are of particular interest in the study of the catalytic process because of their simplicity compared with the heterogeneous systems.

Calvin showed that cupric acetate and benzoquinone could be reduced homogeneously in the presence of cuprous acetate in quinoline at temperatures of about 100° C. He reported the process to be between first and second order dependent in Cu(I) concentration and it was proposed that the active species was a dimer of Cu(I) (13), (17). However, further study of this system has shown the Cu(I) dependence to be exactly second order (18), (19) and this along with other evidence (20) indicates that a single termolecular step involving homolytic splitting of hydrogen is rate determining:

$$2Cu(I) + H_2 \longrightarrow 2CuH$$

Cuprous acetate has also been shown to activate hydrogen at moderate temperatures in dodecylamine and pyridine (21) but in these solvents first order dependence on Cu(I) concentration was observed. The reason for the difference in order of dependence on Cu(I) concentration remains to be adequately explained. While cupric acetate was not noted to activate hydrogen in these solvents, this salt was reduced to Cu_2O in aqueous solution (22). Similarly cupric perchlorate was observed to catalyse reduction of substrates such as dichromate and iodate in aqueous solution (23). However cuprous salts were found to be inactive in aqueous medium (24). Both Cu(I) and Cu(II) heptanoates were found to activate hydrogen in heptanoic acid, biphenyl and octadecane (20) at 125° C. In all solvents except quinoline the kinetics were first order in the active copper species and the mechanisms proposed involve the formation of hydride intermediates with heterolytic splitting of hydrogen:

$$Cu(II) + H_2 \longrightarrow CuH^+ + H^+$$

$$Cu(I) + H_2 \longrightarrow CuH + H^+$$

The nature of the copper salt and its state of complexing affect the rate of hydrogen activation. This has been attributed to the difference in basicity of the ligand or anion but other evidence (16) and the results of the present work indicate that the stability of the activating species as defined by the degree to which the d-orbitals are filled by electrons from the ligand is of prime importance. Thus ethylenediaminetetra-acetic acid and ethylenediamine inhibit the rate of reaction in quinoline (25) and cuprion (2;2'-bisquinoline) appears to have the same effect on the catalytic activity of Cu(I) in heptanoic acid (20). A summary of previous work on

the effect of complexing Cu(II) in aqueous solution and information on complex stability are given in Table I.

The activation of hydrogen by Ag(I) salts has been studied in aqueous solution (26), pyridine and dodecylamine (21) and heptanoic acid (27). First order dependence on Ag(I) concentration was observed in all four solvents suggesting a mechanism similar to that for Cu(I) in pyridine and heptanoic acid involving heterolytic splitting of the hydrogen molecule:

$$Ag^+ + H \longrightarrow AgH + H^+$$

In aqueous solution a second activation path kinetically second order in Ag(I) concentration was also observed for which a mechanism similar to that for cuprous acetate in quinoline has been proposed. In this mechanism the hydrogen is split homolytically:

$$2Ag^+ + H_2 \longrightarrow 2AgH^+$$

Where the silver is activating hydrogen in a basic ligand environment the bimolecular mechanism is preferred.

Both Hg(I) and Hg(II) activate hydrogen in aqueous solution (28), (29) and Hg(II) undergoes reduction by hydrogen in both heptanoic acid and biphenyl (27). These reactions were all kinetically first order in the mercury salt and the mechanisms proposed are similar to those for Cu(II) and Ag(I) although thermodynamic considerations indicate that the formation of an hydride intermediate is unfavourable (30):

$$Hg^{++} + H_2 \longrightarrow Hg + 2H^+$$

$$Hg_2^{++} + H_2 \longrightarrow 2Hg + 2H^+$$

The effects of complexing Cu(II) (31), Hg(II) (32), (28) and Ag(I) (33) have been studied in aqueous solution and varying rates noted. This work is summarised in Table I with data on complex stability. The presence of a proton-accepting ligand in the heterolytic mechanism would tend to accelerate the rate of activation but in several instances marked slowing of the rate is observed even with strong basic ligands. These effects may be explained on the basis of an activated complex of the type:

$$\begin{matrix} {}^{n-1}X & - & M^{z+} & - & X \\ & & \vdots & & \vdots \\ & & {}^{\delta-}H & - & H^{\delta+} \end{matrix}$$

where X = ligand, M = metal cation, n = total no. of ligands and Z = total cation charge. In a complex of this type it is apparent that the rate will depend directly on the strength of the M-H and X-H bonds and inversely on the strength of the M-X bond. The strengths of all these bonds will depend on the character of the ligand, X. Donation of electrons from the ligand into the d-orbitals of the metal will reduce its ability to form the M-H bond, a process analogous to poisoning in heterogeneous catalysis, while increasing the basicity of the ligand should accelerate the reaction by strengthening the X-H bond. This explains the results of complexing with Ag(I), Cu(II), and Hg(II) where increasing complex stability reduces the rate of reaction while with the weak complexes, increasing ligand basicity accelerates the rate.

Several other systems have been noted to activate hydrogen homogeneously or cause deuterium exchange with the solvent. Chloropalladate (II) (34) and chlororhodate (II) (35) complexes both activate hydrogen as shown by the reduction of Fe(III) substrate in their presence. The kinetics are first order in each complex. Dicobaltoctacarbonyl has also been demonstrated

to activate hydrogen homogeneously (36). Hydrogen is apparently split homolytically through the mechanism:

$$Co_2(CO)_8 + H_2 \longrightarrow 2HCo(CO)_4$$

Similarly cobaltous cyanide solutions catalyse the reduction of substrates such as cinnamic acid homogeneously (37). The species $(CN)_4Co\text{-}CN\text{-}Co(CN)_4$ has been proposed as the catalyst by Winfield (38). Ethylene platinous chloride has been observed to catalyse addition of hydrogen to the ethylene double bond homogeneously at high ethylene concentrations and temperatures below 0° C. (39). It has been suggested that the reduction takes place through the sequence of steps:

$$(PtCl_2C_2H_4)_2 + C_2H_4 \rightleftharpoons 2PtCl_2(C_2H_4)_2$$

$$2PtCl_2(C_2H_4)_2 + 2H_2 \longrightarrow (PtCl_2C_2H_4)_2 + 2C_2H_6$$

The oxyanion MnO_4^- has also been shown to cause hydrogen oxidation (40) involving a bimolecular rate determining step of the type:

$$MnO_4^- + H_2 \longrightarrow HMnO_4^- + H^+$$

However, a solution of Ag(I) and MnO_4^- obeys kinetics of the form: rate = $k\,[H_2]\,[Ag^+]\,[MnO_4^-]$. $D_2\text{-}NH_3$ (41) and $D_2\text{-}H_2O$ (42), (43), (44) exchange reactions have been observed in basic medium and the reaction was found to be first order in NH_2^- and OH^- concentrations respectively. However, no reduction of dissolved substrate, $CrO_4^=$, was observed in the aqueous solution. The homogeneous activation process discussed above is unique in that it occurs at temperatures far below that required for uncatalysed hydrogenations. Several other metal cations including Ca^{++}, Mg^{++}, Zn^{++}, Mn^{++}, Ni^{++}, Cd^{++},

Pb^{++}, Al^{+++}, Cr^{+++}, Tl^{+++}, Ce^{++++} and $CrO_4^{=}$ have been studied up to temperatures of 150° C. and found to be inactive.

The purpose of the work on which this thesis is based was to study further the effect of complexing on the rate of hydrogen activation by Ag(I). A series of silver-amine complexes was chosen for study since information about the stability of these complexes is readily available. It was hoped that such a study would provide more information about the configuration of the activated complex and reveal the effects of ligand basicity and complex stability on the rate of catalytic activation.

TABLE I

Effect of Complexing on Activity

Complex (a)	Stability Constant (b)	Relative Activity
$HgSO_4$	22	1.8
Hg^{++}	--	1.0
$HgAc_2$	2.7×10^{8}	4×10^{-2}
$HgPr_2$	--	4×10^{-2}
$HgCl_2$	1.7×10^{13}	2.5×10^{-3}
$HgBr_2$	1.2×10^{15}	1.7×10^{-3}
$Hg(en)_2^{++}$	2.6×10^{23}	1.0×10^{-3}
AgAc	4.4	80
$Ag(en)_2^{+}$	5×10^{7}	25
Ag^{+}	--	1
$Ag(CN)_2^{-}$	6×10^{20}	inactive
$CuBu_2$	--	150
$CuPr_2$	--	150
$CuAc_2$	4×10^{2}	120
$CuSO_4$	2.2×10^{2}	6.5
$CuCl_4^{-}$	10^{5}	2.5
Cu^{++}	--	1
$CuGl_2^{-}$	4×10^{15}	< 0.5
$Cu(en)_2^{++}$	1×10^{20}	0.1

(a) Ligand designations: Bu^{-} = butyrate, Pr^{-} = propionate, Ac^{-} = acetate, Gl^{-} = glycinate, en = ethylenediamine.

(b) $K_n = [MX_n] / [M][X]^n$ (44).

EXPERIMENTAL

MATERIALS

Silver perchlorate used in this investigation was a G. F. Smith Reagent grade product. N,N,N',N'-tetramethylethylenediamine, N,N'-dimethylpiperazine, N,N-dimethylethylenediamine and 1,3-diaminopropane were products of K&K Laboratories. Distillation of these products had no effect on reaction rate and hence they were all used without further purification. Triethylamine, BDH Reagent grade, was redistilled before use. The Houdry Process Corporation triethylenediamine was used directly, since the rate of Ag(I) reduction was unaffected by using recrystallized amine. All other amines were Eastman Kodak White Label and except for methyl-, ethyl- and propylamine, were redistilled before use. All other chemicals were Baker and Adamson Reagent grade. Hydrogen and nitrogen gases were supplied by the Canadian Liquid Air Co. Distilled water was used in the preparation of all solutions. In the D_2O experiment, recovered D_2O (88.8%) was employed.

ANALYSIS

The normality of all the liquid amines was determined by direct titration using 0.1N $HClO_4$ or by back titration using 0.1N NaOH and $HClO_4$ solutions. These amines were used directly in making up the reaction mixtures. Aqueous solutions of the amino-acids of known normality were made up gravimetrically and were used to prepare reaction mixtures. Other solid amines were made up in aqueous solution and employed to prepare reaction

mixtures in this form.

The silver analysis was done by thiocyanate titration using ferric indicator. To avoid interference due to silver metal and insoluble amine salts the sample was filtered while warm, then diluted and acidified.

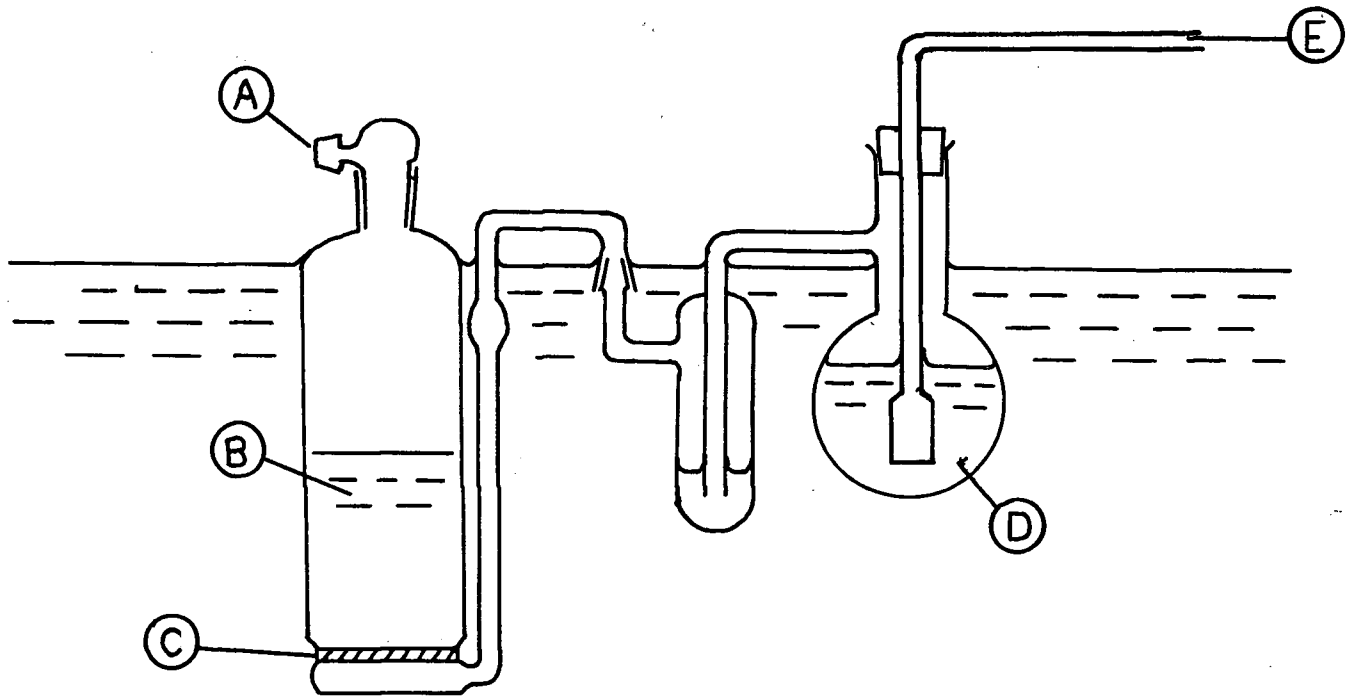
PROCEDURE

For rates that could be determined at atmospheric pressure and in the temperature range 50° C. to 85° C., the glass apparatus depicted in Figure I. was used. A presaturator filled with aqueous solution of the same ionic strength as the reaction mixture was employed to prevent volume changes in the mixture. The whole apparatus was immersed in a constant temperature bath thermostated to within $\pm$ 0.03° C. A 250 ml reaction mixture was made up from stock solutions and placed in the reaction vessel. Nitrogen was run into the mixture, entering the reaction vessel through a glass sinter at the bottom, for periods of up to an hour. Samples were taken during this time to establish the stability of the mixture. Hydrogen was then introduced and, when the mixture became saturated with hydrogen, samples were taken at appropriate intervals and analysed for silver content. The uncertainty of the reaction starting time was of the order of a minute during which time the solution was becoming saturated with hydrogen. A high rate of hydrogen flow was used to insure complete saturation of the reaction mixture and to provide adequate mixing.

For rates of reaction requiring more severe conditions an autoclave was used. The apparatus used was of Parr manufacture (series 4500) with a stainless steel reaction vessel provided with a stirrer, gas inlet, sampling

tube, pressure gauge and thermowell, surrounded by a 250 watt electric heating mantle controlled by a rheostat. A glass liner was used in all the present work. Fine temperature control was achieved by use of an auxillary 5 watt heater placed directly in the reaction mixture through the thermowell. It was controlled by a Thermistemp Temperature Controller (model 71) and probe placed in the reaction mixture through as opening originally provided for a cooling coil. This arrangement gave temperature control of $\pm$ 0.3° C.

A 500 ml reaction mixture was made up from stock solutions and placed in the reaction vessel. Nitrogen gas was run into the mixture at atmospheric pressure, the vessel was sealed and brought to temperature. Samples were taken over a one hour period to establish the stability of the solution. One of two procedures was then used to introduce the hydrogen. With the less volatile amines the solution was flushed with hydrogen and then brought to the desired pressure. With the volatile amines the desired hydrogen partial pressure was established directly and was determined by correcting the total gauge pressure for the contribution made by the nitrogen. Samples were then taken at appropriate times and analysed for silver content. The stirrer was rotated at 600 rpm. It has previously been established that these reactions are independent of stirring rate.



A. Gas Outlet
B. Reaction Mixture
C. Sintered Glass Plate
D. Presaturator Solution
E. Gas Inlet

Fig. 1. Apparatus for Experiments from 50°C. to 85°C. at Atmospheric Pressure.

RESULTS AND DISCUSSION

The stoichiometry of the reduction of silver amine complexes by hydrogen reported in this thesis is probably the same as that reported by Webster (26) in the absence of substrate such as $Cr_2O_7^{=}$:

$$2Ag^+ + H_2 \longrightarrow 2Ag + 2H^+$$

It was not possible to follow the reaction using $Cr_2O_7^{=}$ in the basic medium in which the reactions reported here were studied due to the preferential reduction of Ag^+. Webster observed that at high temperatures and in basic solutions the reaction was predominantly first order in Ag^+ concentration and in the perchlorate system first order dependence on H_2 was observed (26), (33). Similar results are reported in this work.

The disappearance of Ag^+ at constant H_2 pressure for all the silver amine complexes studied in the present investigation obeyed first order kinetics as is shown by the linear plots given in Figures 2 - 6 inclusive. This dependence was verified by the fact that the same rate constant was obtained for two different silver concentrations in the study of each of several complexes. Results are given in Tables II - VI inclusive. In several instances, notably diethylamine, triethylamine, ammonia, ethylenediamine, 1,3-diaminopropane, β-alanine, methyl-, ethyl- and propylamine, an increase to higher order of Ag^+ dependence was observed as the reaction proceeded. This was attributed to autocatalysis on the surface of the precipitated silver metal. The onset of autocatalysis could normally be delayed by buffering the reaction mixture at a lower pH. In those instances

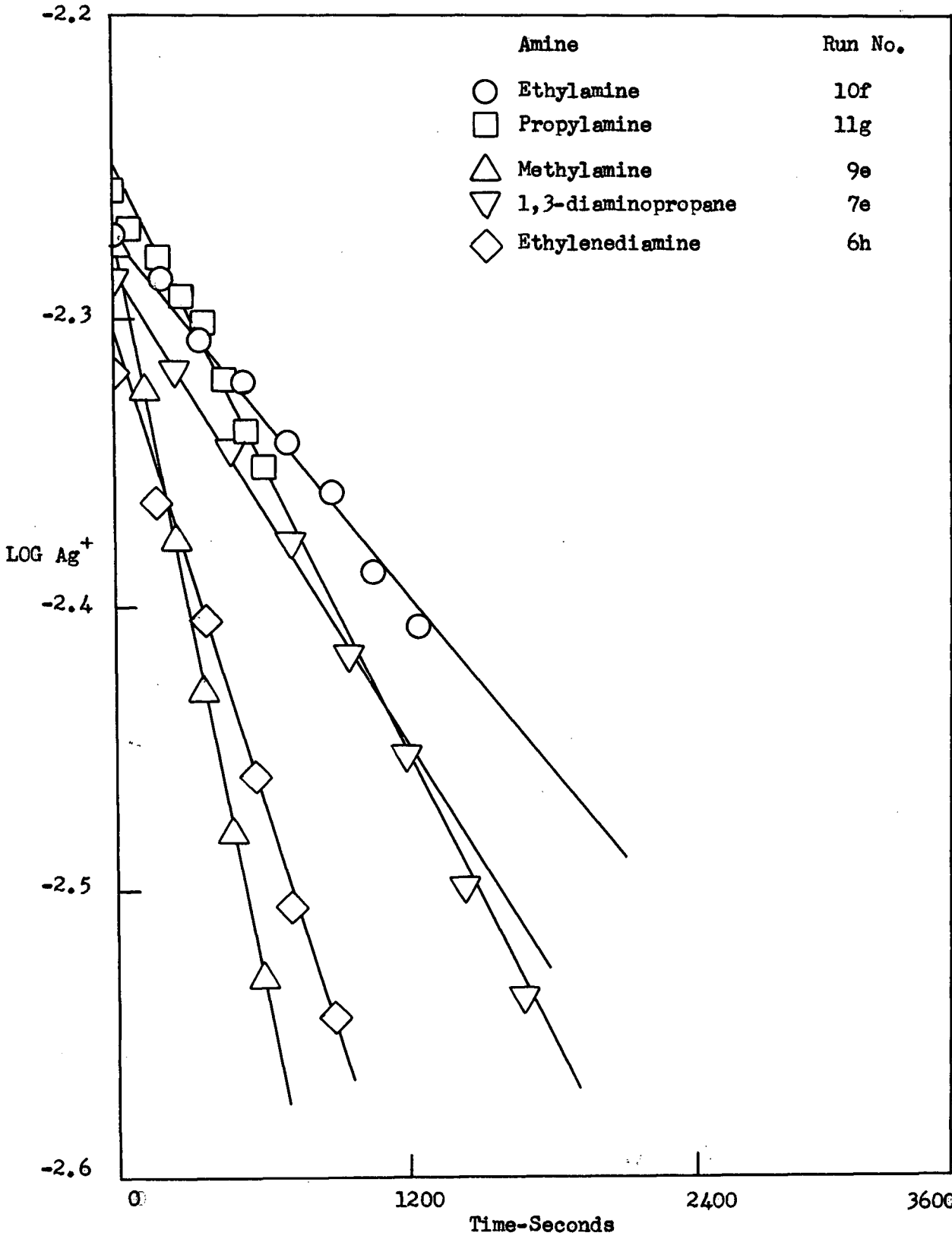


Figure 2

Typical Rate Plots for the Reduction of Silver Complexes of Methyl-, Ethyl-, Propylamine, Ethylenediamine and 1,3-Diaminopropane

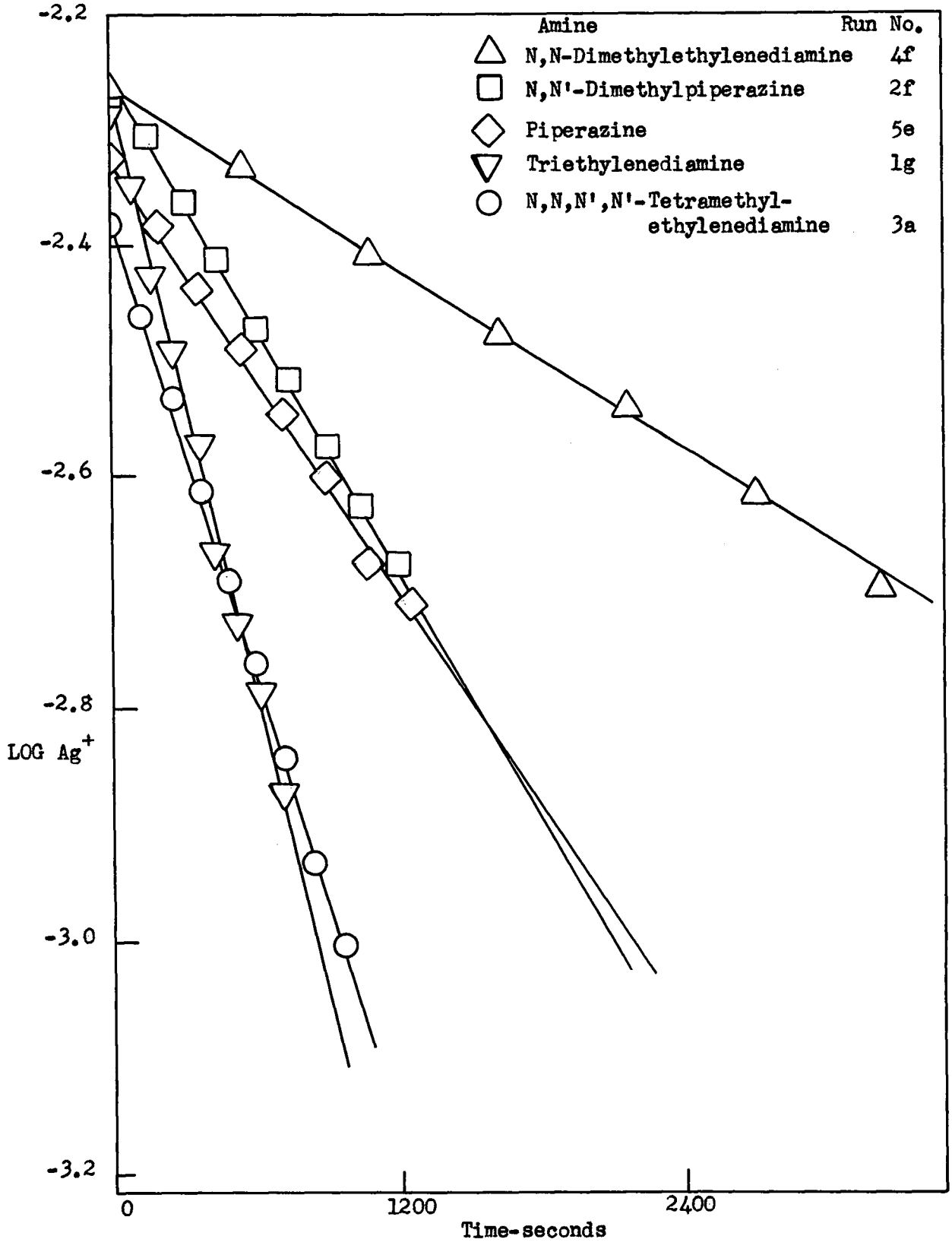


Figure 3

Typical Rate Plots for the Reduction of Silver Complexes of N,N-Dimethylethylenediamine, N,N'-Dimethylpiperazine, Piperazine, Triethylenediamine and N,N,N',N'-Tetramethylethylenediamine

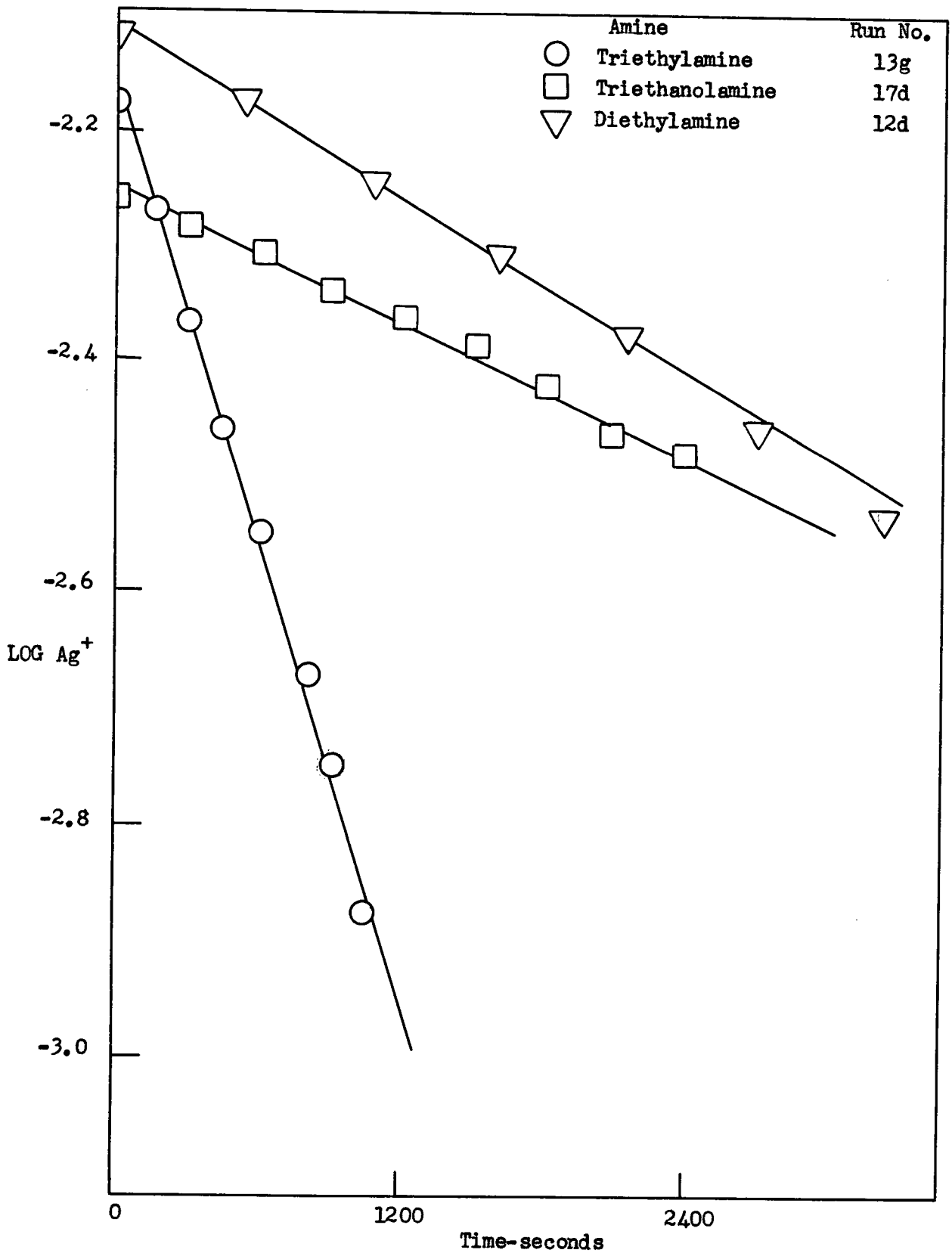


Figure 4

Typical Rate Plots for the Reduction of Silver Complexes of Triethylamine, Triethanolamine and Diethylamine

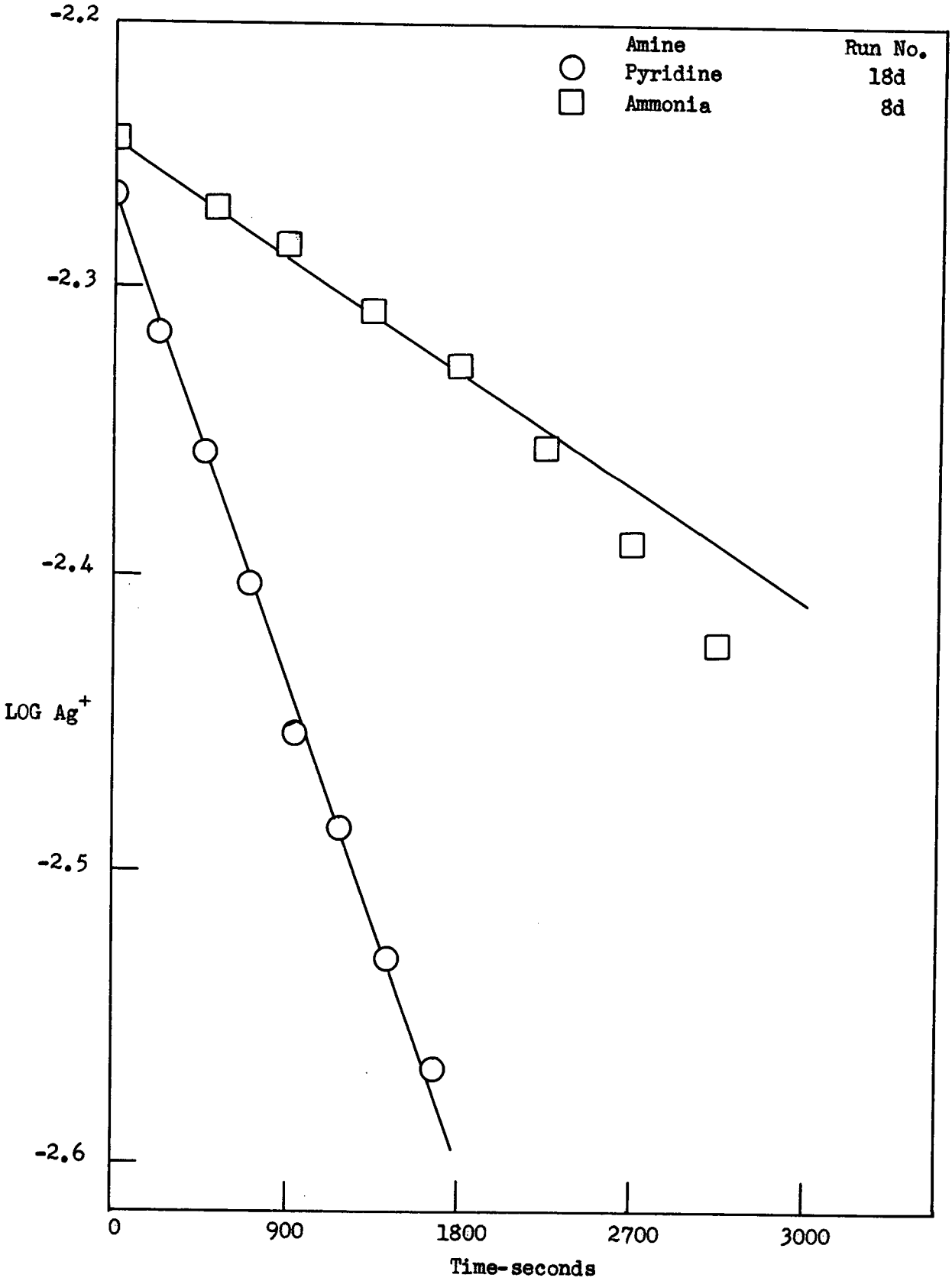


Figure 5

Typical Rate Plots for the Reduction of Silver Complexes of Pyridine and Ammonia

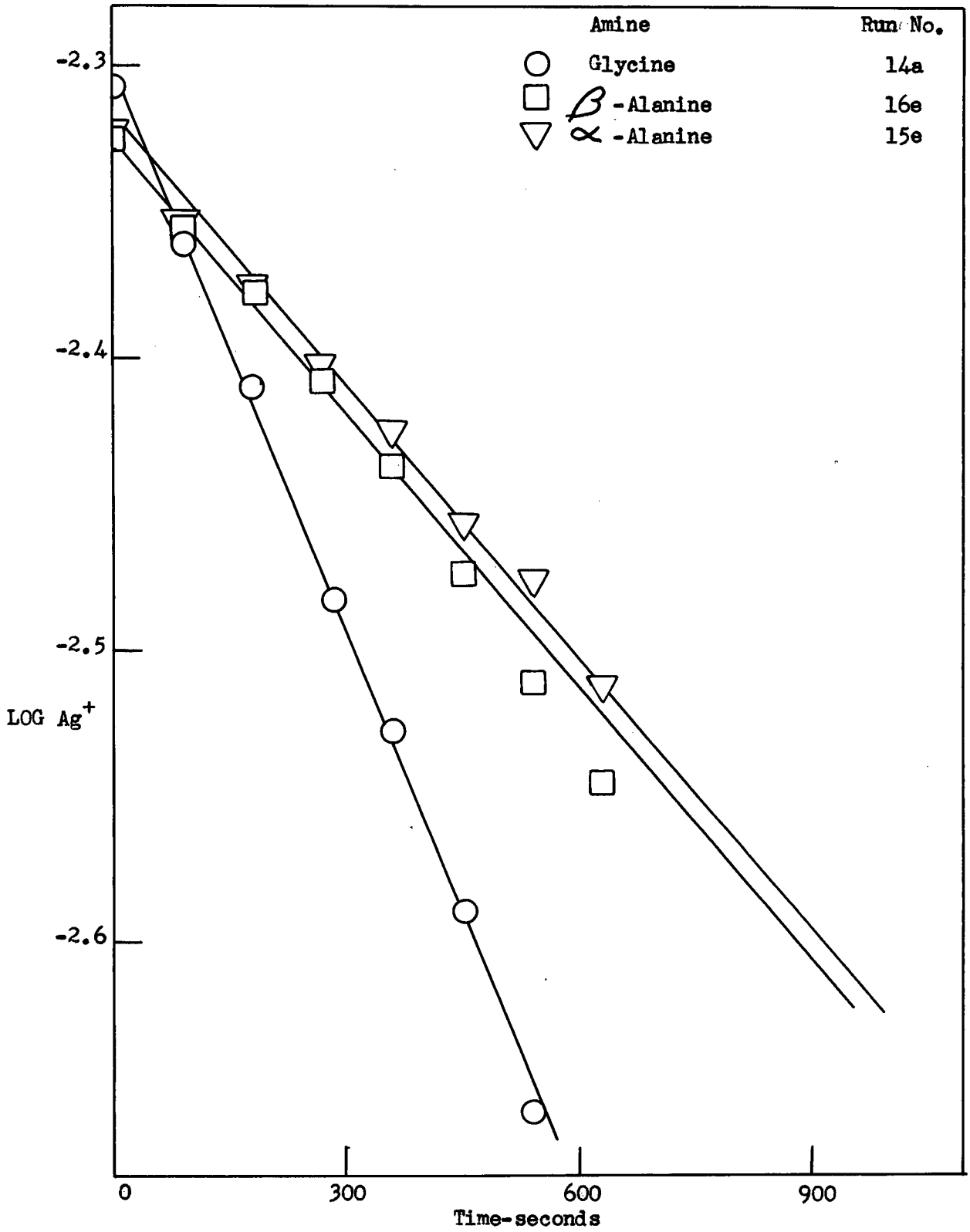


Figure 6

Typical Rate Plots for theReduction of Silver Complexes of Aminoacids

Table II

Rates of Reaction with Silver-Tertiary Diamine Complexes

Amine Name	Initial $AgClO_4$ M. x 10^3	H_2 Pressure atm.	Amine M.	Amine Perchlorate M.	T°C	k M^{-1} sec^{-1}	No.
Triethylenediamine	2.7	0.803	0.18	0.060	60	0.83	1a
	5.5	0.803	0.18	0.060	60	0.87	1b
	5.5	0.803	0.13	0.022	60	0.81	1c
	5.5	0.803	0.13	0.135	60	0.82	1d
	5.5	0.803	0.09	0.030	60	0.87	1e
	5.5	0.755	0.09	0.030	65	1.22	1f
	5.5	0.691	0.09	0.030	70	1.86	1g
	5.5	0.879	0.09	0.030	50	0.42	1h
	5.5	0.848	0.09	0.030	55	0.62	1i
N,N'-Dimethylpiperazine	2.7	0.803	0.09	0.030	60	0.40	2a
	5.5	0.803	0.09	0.030	60	0.40	2b
	5.5	0.803	0.13	0.045	60	0.43	2c
	5.5	0.803	0.13	0.022	60	0.43	2d
	5.5	0.755	0.09	0.030	65	0.57	2e
	5.5	0.691	0.09	0.030	70	0.81	2f
	5.5	0.879	0.09	0.030	50	0.17	2g
	5.5	0.848	0.09	0.030	55	0.27	2h
N,N,N',N'-Tetramethylethylenediamine	5.5	0.691	0.13	0.045	70	1.48	3a
	5.5	0.691	0.18	0.060	70	1.44	3b
	5.5	0.691	0.13	0.022	70	1.48	3c
	5.5	0.755	0.13	0.045	65	1.02	3d
	5.5	0.803	0.13	0.045	60	0.72	3e
	5.5	0.848	0.13	0.045	55	0.50	3f
	5.5	0.879	0.13	0.045	50	0.34	3g
N,N-Dimethylethylenediamine	5.5	0.532	0.18	0.060	80	0.72	4a
	5.5	0.532	0.24	0.080	80	0.71	4b
	5.5	0.532	0.18	0.030	80	0.70	4c
	5.5	0.429	0.18	0.060	85	0.95	4d
	5.5	0.620	0.18	0.060	75	0.47	4e
	5.5	0.691	0.18	0.060	70	0.30	4f
	5.5	0.755	0.18	0.060	65	0.22	4g
	5.5	1.74	0.18	0.060	65	0.18	4h
	5.5	2.75	0.18	0.060	65	0.21	4i
	5.5	3.75	0.18	0.060	65	0.18	4j

Table III

Rates of Reaction with Silver-Diamine Complexes

Amine Name	Initial $AgClO_4$ M. x 10^3	H_2 Pressure atm.	Amine M.	Amine Perchlorate M.	T°C	k M^{-1} sec^{-1}	No.
Piperazine	5.5	9.53	0.075	0.150	80	0.097	5a
	5.5	9.53	0.150	0.300	80	0.093	5b
	5.5	9.53	0.075	0.300	80	0.100	5c
	5.5	9.75	0.075	0.150	65	0.031	5d
	5.5	9.69	0.075	0.150	70	0.051	5e
	5.5	9.62	0.075	0.150	75	0.069	5f
	5.5	9.43	0.075	0.150	85	0.135	5g
Ethylenediamine	5.5	10.69	0.180	0.060	70	0.017	6a
	5.5	10.69	0.270	0.090	70	0.017	6b
	5.5	10.69	0.180	0.180	70	0.016	6c
	5.5	7.69	0.180	0.180	70	0.016	6d
	5.5	5.09	0.180	0.180	70	0.015	6e
	5.5	10.75	0.180	0.180	65	0.010	6f
	5.5	10.62	0.180	0.180	75	0.024	6g
	5.5	10.53	0.180	0.180	80	0.039	6h
	5.5	10.43	0.180	0.180	85	0.059	6i
1,3-diamino-propane	5.5	10.69	0.180	0.180	70	0.0082	7a
	5.5	10.69	0.270	0.270	70	0.0090	7b
	5.5	10.69	0.180	0.360	70	0.0088	7c
	5.5	10.62	0.180	0.360	75	0.014	7d
	5.5	10.53	0.180	0.360	80	0.020	7e
	5.5	10.43	0.180	0.360	85	0.029	7f
	5.5	10.31	0.180	0.360	90	0.045	7g

Table IV

Rates of Reaction with Silver-Simple Monoamine Complexes

Amine Name	Initial $AgClO_4$ M. x 10^3	H_2 Pressure atm.	Amine M.	Amine Perchlorate M.	T°C	k M^{-1} sec^{-1}	No.
Ammonia	5.5	31.31	0.045	0.360	90	0.0034	8a
	5.5	31.31	0.090	0.720	90	0.0035	8b
	5.5	31.31	0.045	0.720	90	0.0034	8c
	5.5	31.43	0.045	0.360	85	0.0021	8d
	5.5	31.17	0.045	0.360	95	0.0061	8e
	5.5	31.00	0.045	0.360	100	0.0096	8f
	5.5	30.85	0.045	0.360	104	0.0174	8g
Methylamine	5.5	16.43	0.045	0.360	85	0.054	9a
	5.5	16.43	0.090	0.720	85	0.051	9b
	5.5	16.43	0.045	0.720	85	0.051	9c
	5.5	16.62	0.045	0.360	75	0.022	9d
	5.5	16.53	0.045	0.360	80	0.041	9e
	5.5	16.31	0.045	0.360	90	0.086	9f
	5.5	16.17	0.045	0.360	95	0.121	9g
Ethylamine	5.5	16.43	0.090	0.360	85	0.015	10a
	5.5	16.43	0.180	0.720	85	0.016	10b
	5.5	16.43	0.090	0.720	85	0.016	10c
	5.5	16.69	0.090	0.720	70	0.0040	10d
	5.5	16.62	0.090	0.720	75	0.0059	10e
	5.5	16.53	0.090	0.720	80	0.0095	10f
	5.5	16.31	0.090	0.720	90	0.022	10g
Propylamine	5.5	16.62	0.045	0.360	75	0.0085	11a
	5.5	16.62	0.090	0.720	75	0.0084	11b
	5.5	16.62	0.045	0.720	75	0.0085	11c
	5.5	16.80	0.045	0.360	60	0.0020	11d
	5.5	16.75	0.045	0.360	65	0.0032	11e
	5.5	16.69	0.045	0.360	70	0.0048	11f
	5.5	16.53	0.045	0.360	80	0.0154	11g
Diethylamine	11.0	10.69	0.180	0.180	70	0.044	12a
	11.0	10.69	0.270	0.270	70	0.044	12b
	11.0	10.69	0.180	0.360	70	0.041	12c
	11.0	10.80	0.180	0.180	60	0.019	12d
	11.0	10.75	0.180	0.180	65	0.027	12e
	11.0	10.62	0.180	0.180	75	0.067	12f
	11.0	10.53	0.180	0.180	80	0.114	12g

Table IV (continued)

Amine Name	Initial $AgClO_4$ M. x 10^3	H_2 Pressure atm.	Amine M.	Amine Perchlorate M.	T°C	k M^{-1} sec^{-1}	No.
Triethylamine	11.0	7.92	0.180	0.360	40	0.053	13a
	11.0	7.92	0.270	0.540	40	0.049	13b
	11.0	7.92	0.270	0.270	40	0.053	13c
	11.0	7.96	0.270	0.540	30	0.017	13d
	11.0	7.94	0.270	0.540	35	0.028	13e
	11.0	7.90	0.270	0.540	45	0.079	13f
	11.0	7.88	0.270	0.540	50	0.130	13g
	11.0*	7.90	0.270	0.540	45	0.079	13h

* - rate determined in 88.8% D_2O

Table V

Rates of Reaction with Silver-Aminoacid Complexes

Amino-Acid Name	Initial $AgClO_4$ M. x 10^3	H_2 Pressure atm.	Amine -acid M.	NaOH M.	T°C	k_{-1} M^{-1} sec^{-1}	No.
Glycine	5.5	9.53	0.107	0.107	80	0.104	14a
	5.5	9.53	0.214	0.214	80	0.106	14b
	5.5	9.80	0.107	0.107	60	0.0176	14c
	5.5	9.75	0.107	0.107	65	0.030	14d
	5.5	9.69	0.107	0.107	70	0.048	14e
	5.5	9.62	0.107	0.107	75	0.076	14f
	11.0	9.80	0.107	0.107	60	0.0178	14g
	11.0	9.80	0.107	0.240	60	0.161	14h
	11.0	9.80	0.107	0.190	60	0.127	14i
	5.5	9.80	0.107	0.130	60	0.050	14j
	5.5	9.80	0.107	0.090	60	0.0084	14k
	5.5	19.80	0.107	0.090	60	0.0086	14l
	5.5	19.80	0.107	0.065	60	0.0055	14m
	5.5	19.80	0.107	0.050	60	0.0051	14n
α-Alanine	5.5	9.62	0.120	0.120	75	0.0305	15a
	5.5	9.62	0.240	0.240	75	0.0309	15b
	5.5	9.75	0.120	0.120	65	0.0173	15c
	5.5	9.69	0.120	0.120	70	0.0250	15d
	5.5	9.53	0.120	0.120	80	0.0491	15e
	5.5	9.43	0.120	0.120	85	0.0699	15f
β-Alanine	5.5	9.62	0.120	0.120	75	0.040	16a
	5.5	9.62	0.240	0.240	75	0.039	16b
	5.5	9.75	0.120	0.120	65	0.015	16c
	5.5	9.69	0.120	0.120	70	0.029	16d
	5.5	9.53	0.120	0.120	80	0.051	16e
	5.5	9.43	0.120	0.120	85	0.075	16f

Table VI

Rates of Reaction with Miscellaneous Silver Complexes

Amine Name	Initial $AgClO_4$ M.x10^3	H_2 Pressure atm.	Amine M.	Amine Perchlorate M.	T°C	k M^{-1} sec^{-1}	No.
Triethanolamine	5.5	0.691	0.180	0.720	70	0.47	17a
	5.5	0.691	0.225	0.900	70	0.45	17b
	5.5	0.691	0.180	0.360	70	0.49	17c
	5.5	0.803	0.180	0.720	60	0.19	17d
	5.5	0.755	0.180	0.720	65	0.30	17e
	5.5	0.620	0.180	0.720	75	0.68	17f
	5.5	0.532	0.180	0.720	80	0.96	17g
Pyridine	5.5	9.53	0.270	0.270	80	0.019	18a
	5.5	9.53	0.540	0.540	80	0.018	18b
	5.5	9.53	0.270	0.135	80	0.020	18c
	5.5	9.43	0.270	0.135	85	0.029	18d
	5.5	9.31	0.270	0.135	90	0.043	18e
	5.5	9.17	0.270	0.135	95	0.060	18f
	5.5	9.00	0.270	0.135	100	0.093	18g

in which autocatalysis interfered to a large extent, reproducible rates could be determined from the first 5% of reaction.

As in the acid perchlorate medium, the rate was directly dependent on hydrogen concentration as is shown in Figures 7 and 8. At different hydrogen pressures a constant k' was also obtained for glycine complexes (Table V). Thus, the overall rate law may be expressed as:

$$\frac{-d[H_2]}{dt} = -\frac{1}{2}\frac{d[Ag^+]}{dt} = k'[Ag^+]p_{H_2}\alpha = k[Ag^+][H_2]$$

where p_{H_2} is the hydrogen pressure and α is Henry's constant. In the region of pressures investigated, Henry's law is obeyed. The values taken for hydrogen solubility at different temperatures were those of Weibe and Gaddy (46). It was assumed that the hydrogen solubilities in the solutions used in the present study were, within the limits of experimental error, the same as for pure water.

These kinetics suggest a mechanism of the type:

$$Ag^+ + H_2 \xrightarrow{\text{slow}} AgH + H^+$$

$$AgH + Ag^+ \xrightarrow{\text{fast}} H^+ + 2Ag$$

which has been justified on thermodynamic grounds (30).

Except for triethylamine, all experiments were made under conditions in which the silver was completely complexed by the amine. Limitations due to the insolubility of triethylamine in water allowed only 95% complexing in this case but, since the rate with this amine is 1000 times that for uncomplexed silver, the error in true rate for triethylamine complex is small.

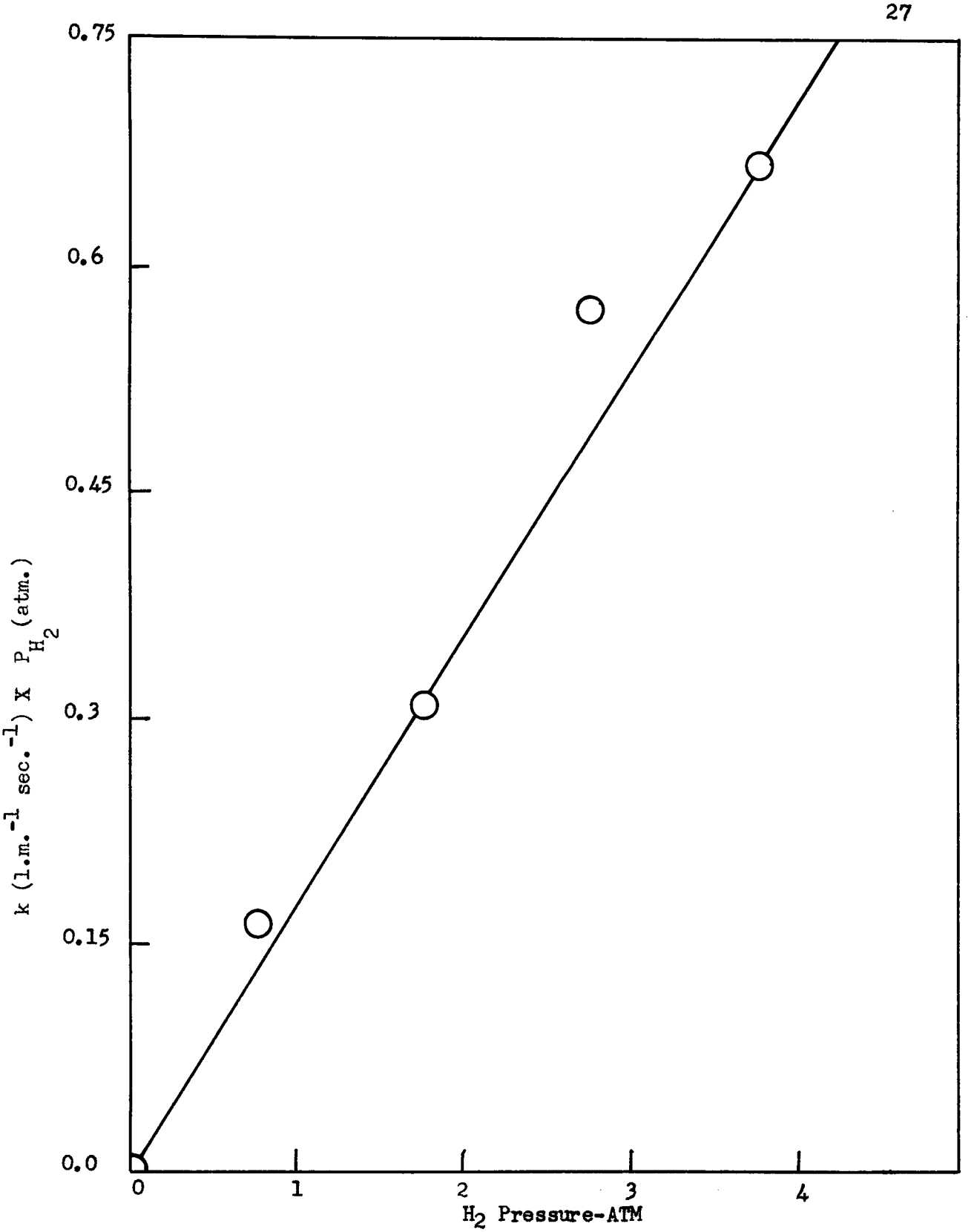


Figure 7

Dependence of Rate on Hydrogen Partial Pressure at 65° C. for N,N-Dimethylethylenediamine Complex

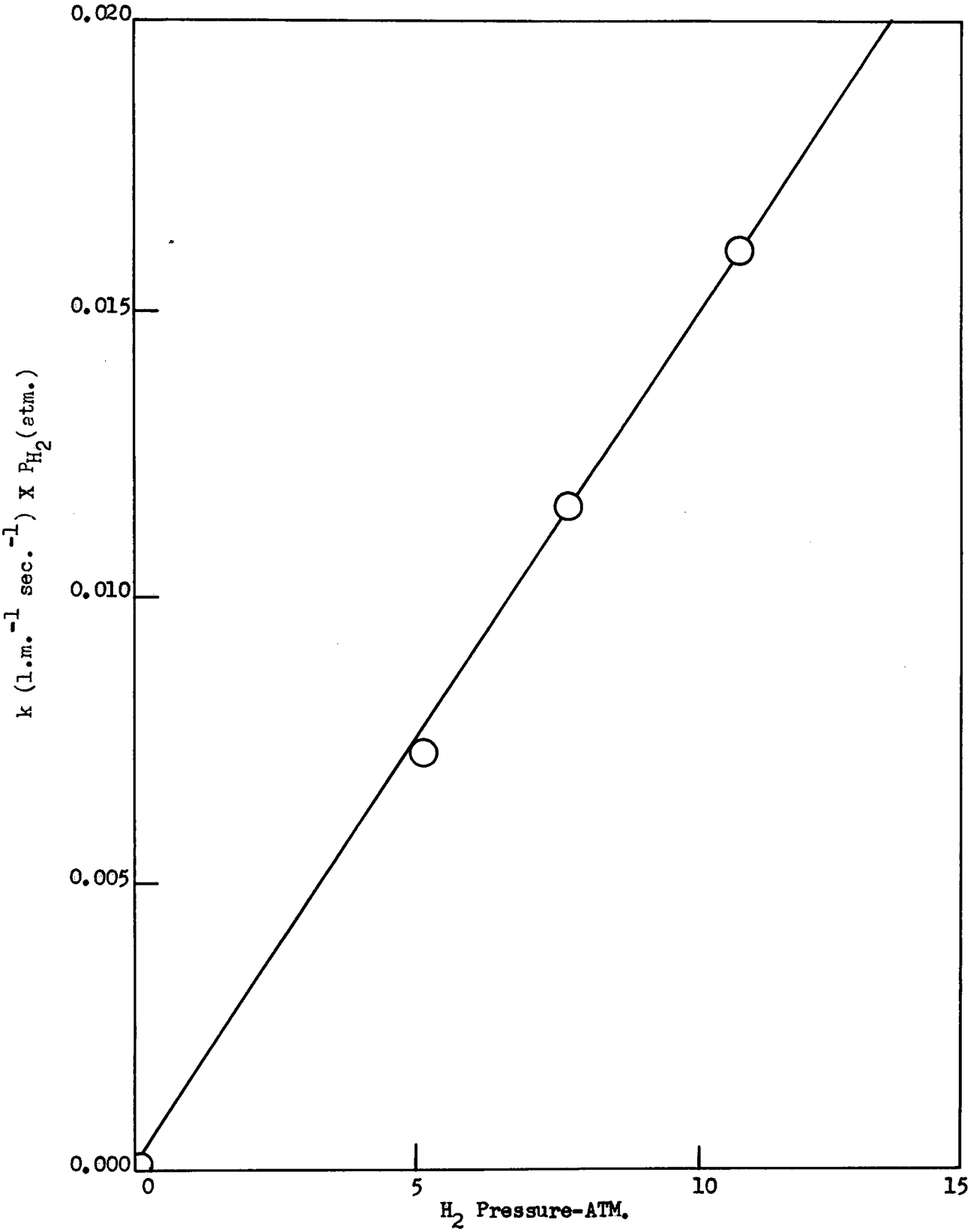


Figure 8

Dependence of Rate on Hydrogen Partial Pressure at 70° C.
for Ethylenediamine Complex

That the rate is independent of amine concentration is shown in Tables II-VI. All the reaction mixtures were buffered with an amine-amine perchlorate system to prevent large changes in pH. The rate was shown to be independent of amine perchlorate concentration in a limited range. This is shown in Tables II-VI. It is consequently independent of pH within the pH change caused by the protons liberated in the complete reduction of the Ag^+.

The agreement between rates obtained in the glass apparatus and those determined in the autoclave is shown in the results for N,N-dimethylethylenediamine (Table II).

The activity of the silver-glycinate complex was studied in solutions containing excess base (NaOH) and excess glycine (Table V, runs 14g-14n inclusive). The reaction mixtures containing excess base were unstable, silver being reduced in the absence of hydrogen. However, by subtracting this background rate from the observed rate with hydrogen, semi-quantitative rate constants could be determined. The large increase in rate with increasing OH^- concentration has been observed before for silver ethylenediamine and mercury (II) ethylenediamine complexes (26), (32) and may be explained in one of two ways. The OH^- may participate directly in the rate determining step:

$$+Ag(H_2NCH_2COO^-)_2 + OH^- + H_2 \longrightarrow AgH + H_2O + 2H_2NCH_2COO^-$$

or an equilibrium of the type observed with Co amine complexes by Pearson and Basolo (47) may be responsible:

$$^-OOCCH_2NH_2\overset{+}{A}gNH_2CH_2COO^- + OH^- \longrightarrow {}^-OOCCH_2NH_2\overset{+-}{A}gNNHCH_2COO^- + H_2O$$

where $^{-}NHCH_2COO^{-}$ is a much stronger base than $H_2NCH_2COO^{-}$. The decrease in rate in the region of constant total glycine plus glycinate concentration with decreasing glycinate concentration is anomalous in as much as sufficient glycinate is present to complex fully the silver in all cases and the rate has been shown to be independent of glycinate concentration in this region. This effect remains to be explained.

A 10,000-fold variation in rate for the silver complexes studied was observed, ranging from 3.3×10^{-4} l.moles^{-1}sec.$^{-1}$ for $Ag(NH_3)_2^{+}$ to 1.84 l.moles^{-1}sec.$^{-1}$ for the triethylenediamine complex at 70°C. A complete resumé of thermodynamic values, complex stability constants, amine basicities and rates is given in Table VII. In general the differences in rates are reflected primarily in the activation energies. The activation entropies are normal for the simple bimolecular mechanism suggested, although with the exception of triethanolamine, pyridine and glycine, those for the dibasic ligands are somewhat more negative (-7 to -19 eu.) than those for the monoamines (7 to -6 eu.). These differences suggest differences in the rate determining step for the dibasic amines and the monobasic amines.

Table VII contains evidence of two different trends: (a) a decrease in catalytic activity with increasing complex stability and decreasing amine basicity and (b) a generally greater activity for the dibasic amines than the monobasic. These two trends will be discussed separately in this order.

On the basis of the rate determining step:

$$R_3N\overset{+}{A}gNR_3 + H_2 \longrightarrow AgH + R_3NH^{+} + R_3N$$

Table VII

Summary of Kinetic Data Stability Constants and Basicities

Amine Name	Amine Basicity[a] pK_a	Stability Constants[b] log K_1	log K_2	log β_2	$\Delta H^{\ddagger}$ kcal. mole	$\Delta S^{\ddagger}$ eu.	log k(70°)
Ammonia	9.25	3.37	3.78	7.15	28.3	+7.6	-3.48
Methylamine	10.72	3.15	3.53	6.68	22.3	-2.8	-1.91
Ethylamine	10.61	3.37	3.93	7.30	21.6	-7.1	-2.42
Propylamine	10.58	-	-	7.39	23.3	-1.5	-2.26
Diethylamine	10.98	-	-	6.36	20.5	-5.4	-1.33
Triethylamine	10.77	-	-	4.76	18.8	-4.8	-0.13
Ethylenediamine	10.18	4.62	2.92	7.54	20.8	-6.7	-1.80
1,3-Diamino-propane	10.72	5.77	-	-	18.9	-13	-2.00
Piperazine	9.81	3.32	-	-	16.8	-16	-1.32
N,N-Dimethyl-ethylenediamine	9.53	-	-	-	17.1	-11	-0.49
N,N,N',N'-Tetra-methylethylene-diamine	9.30	-	-	-	15.1	-14	0.17
N,N'-Dimethyl-piperazine	8.30	-	-	-	17.9	-7.2	-0.07
Triethylenediamine	8.19	1.57	-	-	17.1	-8.1	0.26
Glycine	9.78	3.51	3.38	6.89	21.5	-2.5	-1.33
α-Alanine	9.87	3.64	3.54	7.18	16.2	-19	-1.61
β-Alanine	10.19	-	-	-	18.3	-13	-1.63
Triethanolamine	7.90	2.30	1.34	3.64	17.5	-9.7	-0.36
Pyridine	5.45	2.04	2.18	4.22	19.3	-12	-2.09

(a) $K_a = \frac{[A][H^+]}{[AH^+]}$, Values taken from (45)

(b) $K_1 = \frac{[AgNR_3^+]}{[Ag^+][NR_3]}$, $K_2 = \frac{[Ag(NR_3)_2^+]}{[Ag^+NR_3][NR_3]}$, $\beta_2 = K_1K_2$ Values taken from (45)

corrected where necessary to 25° C., using temperature coefficient for

$Ag(NH_2C_2H_5)_2^+$ = d log K_1/dt = d log K_2/dt = -0.016 (48)

an activated complex of the type:

$$R_3N - \overset{+}{Ag} - NR_3$$
$$\delta- H - H\delta+$$

may be postulated for the monoamines (R may represent an alkyl group or H). On the basis of such a configuration the rate of hydrogen activation by the complex should depend directly on the strength of the Ag-H and H-NR_3 bonds and inversely on the strength of the Ag-NR_3 bond. Therefore, since the pK_a is a measure of the strength of the H-NR_3 bond and log K_2 a measure of the strength of the Ag-NR_3 bond being cleaved, one might expect a correlation between the rate of activation of hydrogen and a function involving these parameters of the type:

$$\log k \propto (pK_a - \log K_2)$$

A comparison of log k at 70° C. and the function (pK_a - log K_2) for simple monoamines is given in Table VIII and the dependence is clearly shown. Pyridine and triethanolamine are monoamines but their characters are different from that of the simple monoamine and they should be considered in their own homologous series.

The diamines follow a similar pattern (Table VIII) but because for most of these amines only information on the first stability constant is known, log K_1 is used. The relative correlation between the first stability constant and the overall stability constant is good and the use of log K_1 should not detract from the relationship drawn. For the dibasic amines it was felt appropriate to use the logarithm of the first basicity

Table VIII

Relationship between Rate of Activation and a Function of Amine Basicity and Complex Stability

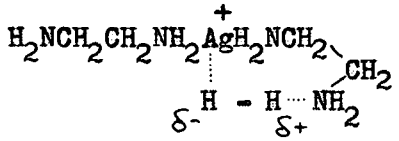
Monoamine Name	Function (pK_a - log K_2)	log k
Ammonia	5.47	-3.48
Ethylamine	6.68	-2.42
Methylamine	7.19	-1.91
Diethylamine	7.68	-1.33
Triethylamine	8.61	-0.13

Diamine Name	Function (pK_a - log K_1)	log k
1,3-Diaminopropane	4.95	-2.00
Ethylenediamine	5.56	-1.80
Piperazine	6.49	-1.32
Triethylenediamine	7.41	0.26

constant in as much as the ligand accepts one proton in the rate determining step. Table VIII shows the relationship between log k and (pK_a - Log K_1).

In the dibasic amines (including amino-acid anions) the presence of the second basic group may increase the rate. A comparison of the rates of ethylamine and ethylenediamine complexes and of diethylamine and piperazine complexes shows that the rate for the diamines is greater. Whether this is due to ligand basicity and complex stability effects or the presence of the second basic group is not clear. The proximity of the second basic group appears to be important. The logarithm of the stability constant for the Cu(II) glycine complex is greater than that for the Cu(II) β-alanine complex. This relationship is likely to hold for the Ag(I) complexes as well and if this is the case the faster rate with the glycine complex may be attributed to the proximity of the carboxyl group.

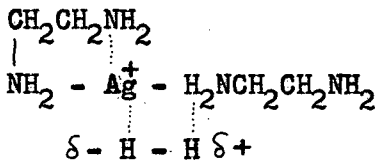
The tendency for chelation in silver complexes is small. In the solutions studied the silver complex would carry two monocoordinated dibasic ligands e.g. $H_2NCH_2CH_2NH_2\overset{+}{A}gH_2NCH_2CH_2NH_2$. A rate determining step involving direct acceptance of the proton by the non-bonded basic group in the ligand suggests an activated complex of the form:



The greater negative entropy change noted above for the diamine complexes may be indicative of an activated complex different from that suggested for the monoamine complexes. The acceptance of the released proton at a different site in the activated complex for the diamine mechanism may require a greater

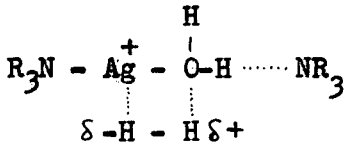
degree of solvation for these complexes than for the monoamine complexes. This greater degree of 'freezing out' of solvent molecules for the diamine complexes may be the cause of the greater negative entropy change.

A second configuration deserving consideration is:



However, if the formation of the Ag-H bond is dependent upon vacant d-orbitals in the silver as has been suggested earlier (16), coordination with the second amino group of one ligand would be expected to hinder this process and this type of activated complex would be unlikely.

All previous discussion has depended upon a mechanism in which the ligand accepts the proton in the rate determining step directly. However, certain general considerations and evidence would suggest a mechanism in which water acts as the proton acceptor or as a bridge between the proton and the ligand. This would give rise to an activated complex of the type:



A similar configuration may be postulated for the dibasic complexes. In as much as the electrons responsible for the basicity of an amine would be donated to the silver in the formation of the covalent bond in the complex

it would appear difficult for the ligand amine to accept a proton in the rate determining step. If this were true, it seems reasonable that water as a ligand may act more readily as the proton acceptor in that it has two coordinative positions. Evidence which would favour such a mechanism is the possible proton accepting role of OH^-, CO_3^-, acetate and propionate suggested by Korinek to explain the acceleration of hydrogen activation noted with Hg(II)-ethylenediamine complexes when these anions were added (32).

Support for this point of view is found in the measurement of rates of proton transfer for methylamines and ammonia by NMR techniques. Meiboom and co-workers by observing the broadening of the water and amine proton signals have been able to distinguish and measure the rates of the two separate paths of proton transfer; one employing an intervening water molecule and one by direct transfer:

$$R_3NH^+ + NR_3 \xrightarrow{k_1} R_3N + H^+NR_3$$

$$R_3NH^+ + \underset{H}{O}\text{-}H + NR_3 \xrightarrow{k_2} R_3N + H\text{-}\underset{H}{O} + H^+NR_3$$

They have observed that the second path is preferred by the methylamines (k_2/k_1 = 1.4, 14 and >10 for methylamine, dimethylamine and trimethylamine respectively) but not by ammonia (k_2/k_1 = 0.085) (49).

The above considerations explain the observed variation in rates with different complexes. A water mediated mechanism seems plausible for the alkylamine complexes at least and the observed inverse variation of rate with complex stability constant may be due to the difficulty of replace-

ment of the ligand by a water molecule in the activated complex. The abnormally low rate constant for ammonia complex may be the result of direct proton transfer to the ligand in preference to the water mediated mechanism. Such a direct transfer would account for the anomalously high activation energy and positive entropy change for this complex in that the ligand removal would not be compensated for by replacement with a water molecule.

In order to determine whether the direct transfer mechanism was in operation for all the complexes or whether a water mediated mechanism was used, an experiment was made in D_2O with the triethylamine complex which should activate hydrogen by the water mediated mechanism if these ideas are correct. It would be expected that if a water mediated mechanism were in operation the difference in basicity of water and D_2O would be reflected in the rate. No such difference in rate was observed (Table IV) which would appear to substantiate the mechanism suggested earlier of direct proton transfer to the ligand. However, in as much as it is not clear whether the difference in basicity of the solvents is the only effect, this evidence is not conclusive.

CONCLUSION

The rate of activation of hydrogen by silver amine complexes was observed to be first order dependent on both complex and hydrogen concentration. This is in agreement with Webster's observations on the silver system at high temperatures and in the presence of basic ligands. Heterolytic splitting of the hydrogen molecule is suggested in the rate determining step (26), (33). The rate of activation was seen to vary inversely with complex stability in a manner similar to that reported for Cu(II), Hg(II) and some silver complexes (31), (32), (33). Two possible mechanisms can be used to explain these results; the first involves direct transfer of the proton released in the rate determining step:

$$H_2 + Ag^{+}(R_3N)_2 \longrightarrow R_3N - Ag^{+} - NR_3 \longrightarrow AgH + R_3NH^{+} + R_3N$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad \delta- H \; - \; H \delta-$$

In the other water acts as the main proton acceptor in all cases except that of the ammonia complex:

$$H_2 + Ag^{+}(R_3N)_2 + H_2O \longrightarrow R_3N - Ag^{+} - \overset{H}{\underset{|}{O}}-H \cdots NR_3 \longrightarrow R_3N + AgH + R_3NH^{+} + H_2O$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad \delta- H \; - \; H \delta+$$

The first mechanism finds support in the reasonable correlation drawn between the rate of reaction and the function (pK_a - $\log K_2$) for the simple monoamines. Since amine basicity should be a measure of the strength of the incipient H - NR_3 bond and the complex stability a measure of the strength of the Ag - NR_3 bond, the reaction rate should increase with increasing magnitude of this function. In addition the rate of activation by silver - triethylamine complex in D_2O and H_2O is the same suggesting that

solvent molecules are not involved in the rate determining step and that the proton is accepted directly by the ligand amine. However, this evidence is not conclusive since it is not clear whether the use of D_2O in place of H_2O would introduce only a solvent basicity difference.

A water mediated mechanism appears plausible in that the ability of a ligand such as an amine with its one coordinative position bonding to silver would be hindered from accepting a proton. A water ligand having one free coordinative position would be able to accept the proton in the rate determining step. The inverse dependence of rate on complex stability would reflect the difficulty of replacing the amine ligand by a water molecule. A recent study of proton transfer between amines in aqueous medium indicates two mechanisms: the first, preferred by the alkylamines, involves proton transfer through an intervening water molecule. The second, used by ammonia, involves transfer of the proton directly between ammonia molecules. The anomalously low rate observed for the silver-ammonia complex (slower than for the water complexed species) compared to those rates observed for the other monoamines may be explained by the difficulty in effecting a direct proton transfer to the ammonia ligand in the rate determining step. The abnormally high activation energy and positive entropy change for the ammonia complex appears reasonable in that, unlike the alkylamine complexes, release of the proton accepting ligand would be uncompensated by coordination of a water molecule.

The dibasic complexes displayed a greater activity and were observed to have a greater negative entropy change than the monoamine complexes. This suggests an accelerating effect due to the presence of the

second basic group possibly by accepting the proton released or by coordinating with the silver in the position vacated by the proton-accepting ligand in the rate determining step. The participation of the free basic group in the activation is further substantiated by the fact that the rate decreases as the second basic group becomes more distant from the silver atom in the complex. A water mediated mechanism may occur with these complexes as well.

It would appear reasonable that the presence of a basic ligand is responsible for the generally faster rates observed with silver amine complexes than the water coordinated silver species. Unlike similar Cu(II) and Hg(II) complexes, donation of electrons from the ligand into the silver d-orbitals does not have a great effect on the formation of a bond between hydrogen and the activating species.

REFERENCES

1. Rice, F. O. and Herzfeld, K.F., J.Am.Chem.Soc., 56, 284 (1934).
2. Varnerin, R. E. and Dooling, J. S., J.Am.Chem.Soc. 78, 1119 (1956).
3. Beeck, O., Rev.Mod.Phys., 17, 61 (1945).
4. Balandin, A. A., Zeit.fur physik. Chem., 2B, 289 (1929), ibid,3B, 167 (1929).
5. Beeck, O. and Ritchie, A. W., Disc. Farad. Soc., 8, 159 (1950).
6. Sherman, A. and Eyring, H., J.Am.Chem.Soc., 54, 2661 (1932).
7. Reynolds, P. W., J.Chem.Soc., 265 (1950).
8. Dowden, D. A. and Reynolds, P. W., Disc.Farad.Soc., 8, 184 (1950).
9. Couper, A. and Eley, D. D., Disc.Farad.Soc., 8, 172 (1950).
10. Beeck, O., Disc.Farad.Soc., 8, 118 (1950).
11. Mott, N. F. and Jones, H., 'The Theory of the Properties of Metals and Alloys', Oxford University Press, London (1936).
12. Dowden, D. A., Research, 1, 239 (1948), J.Chem.Soc., 242 (1950).
13. Calvin, M., Trans.Farad.Soc., 34, 1181 (1938). J.Am.Chem.Soc., 61, 2230 (1939).
14. Halpern, J., Quart.Rev., 10, 463 (1956).
15. Weller, S. W. and Mills, G. A., Advances in Catalysis, 8, 163 (1956).
16. Halpern, J., J.Phys.Chem., 63, 398 (1959).
17. Weller, S. W. and Mills, G. A., J.Am.Chem.Soc., 75, 769 (1953).
18. Calvin, M. and Wilmarth, W.K., J.Am.Chem.Soc., 78, 1301 (1956).
19. Wilmarth, W. K. and Barsh, M.K., J.Am.Chem.Soc., 78, 1305 (1956).
20. Chalk, A. J. and Halpern, J., J.Am.Chem.Soc., 81, 5846 (1959).
21. Wright, L. W., Weller, S. W. and Mills, G. A., J.Phys.Chem. 59, 1060 (1955).
22. Dakers, R. G. and Halpern, J., Can.J.Chem., 32, 969 (1954).
23. Peters, E. and Halpern, J., J.Phys.Chem., 59, 793 (1955).

24. MacGregor, E. R. and Halpern, J., Trans.Met.Soc.A.I.M.E., 212, 244 (1958)

25. Wright, L. W. and Weller, S., J.Am.Chem.Soc., 76, 3345 (1954).

26. Webster, A. H. and Halpern, J., J.Phys.Chem., 60, 280 (1956).

27. Chalk, A. J., Halpern, J. and Harkness, A. C., J.Am.Chem.Soc., 81, 5854 (1959).

28. Korinek, G. F. and Halpern, J., J.Phys.Chem., 60, 285 (1956).

29. Halpern, J., Korinek, G. J. and Peters, E., Research, 7, 615 (1954).

30. Halpern, J., Advances in Catalysis, 9, 302 (1957).

31. Peters, E. and Halpern, J., Can.J.Chem., 34, 554 (1956).

32. Webster, A. H. and Halpern, J., Can.J.Chem., 34, 1372 (1956).

33. Webster, A. H. and Halpern, J., J.Phys.Chem. 61, 1239 (1957), ibid, 1245 (1957).

34. Halpern, J., Harrod, J. F. and Potter, P. E., Can.J.Chem., 37, 1446 (1959).

35. Harrod, J. F. and Halpern, J., Can.J.Chem., 37, 1933 (1959).

36. Adkins, H. and Kresk, G., J.Am.Chem.Soc., 70, 383 (1948), ibid, 71, 3051 (1949).

37. Iguchi, M., J.Chem.Soc.Japan, 63, 634 (1942), ibid, 1752 (1942).

38. Winfield, M.E., Rev.Pure Appl.Chem. (Australia), 5, 217 (1955).

39. Flynn, J. H. and Hulburt, H. M., J.Am.Chem.Soc., 76, 3393 (1954), ibid, 3396 (1954).

40. Webster, A. H. and Halpern, J., Trans.Farad.Soc., 53, 51 (1957).

41. Wilmarth, W.K. and Dayton, J.C., J.Am.Chem.Soc., 75, 4553 (1953).

42. Wirtz, K. and Bonheffer, K.F., Zeit.fur Physik.Chem., A177, 1 (1936).

43. Claeys, Y. M., Dayton, J. C. and Wilmarth, W. K., J.Chem.Phys., 18, 759 (1950).

44. Wilmarth, W. K., Dayton, J. C. and Flournoy, J. M., J.Am.Chem.Soc., 75, 4549 (1953).

45. "Stability Constants", Chemical Society Special Publication No. 6, London, 1957.

46. Wiebe, R. and Gaddy, V. L., J.Am.Chem.Soc., 56, 76 (1934).

47. Basolo, F. and Pearson, R. G., 'Mechanisms of Inorganic Reactions', John Wiley and Sons Inc., New York, N. Y., p. 386.

48. Buehlman, R. J. and Verhoek, F. H., J.Am.Chem.Soc., 70, 1401 (1948).

49. Grunwald, E., Lowenstein, A. and Meiboom, S., J.Chem.Phys., 27, 630 (1957).
Lowenstein, A. and Meiboom, S., J.Chem.Phys. 27, 1067 (1957).
Meiboom, S., Lowenstein, A. and Alexander, S., J.Chem.Phys., 29, 969 (1958).