energetic grounds. It now seems reasonable to suggest that the initial intermediate in this path is the silver hydride ion, AgH^+, which is formed through the homolytic splitting in the first (rate-determining) step of the sequence

$$2Ag^+ + H_2 \xrightarrow{k} 2AgH^+ \qquad (20)$$

$$AgH^+ + \text{substrate } (e.g., Cr_2O_7^{=}) \xrightarrow{\text{fast}} \text{reduced products} + Ag^+ \qquad (21)$$

This mechanism is similar to that which has been proposed for the activation of H_2 by cuprous salts in quinoline solution.[7] It has also been demonstrated[18] that the species CuH^+, which is electronically analogous to AgH^+, is formed as an intermediate in the activation of H_2 by cupric salts in aqueous solution. AgH^+ also has been proposed[19] as an intermediate in the Ag^+ catalyzed reduction of MnO_4^- by H_2, whose kinetics are of the form $k_c[Ag^+][MnO_4^-][H_2]$. It has been suggested that the rate-determining step of this reaction is

$$Ag^+ + MnO_4^- + H_2 \longrightarrow AgH^+ + MnO_4^{=} + H^+ \qquad (22)$$

where MnO_4^-, because of its high electron affinity, effectively replaces one of the Ag^+ ions in step 20.

Schematic potential energy diagrams depicting the two paths of activation of H_2 by Ag^+ and showing the quantities which determine the energetics of each path are given in Fig. 7. The intermolecular path (involving AgH^+) can compete with the bimolecular path (which is favored on statistical grounds) because of its considerably lower activation energy (14.7 *vs.* 24 kcal./mole) and becomes predominant at low temperatures and at high acidities, when the competing back reaction (−3) involving H^+, suppresses the contribution of the latter path. The termolecular path does not involve release of H^+ ions in a rate-determining step and hence should not be affected by variations in acidity; this is in agreement with observation. On the other hand, the bimolecular path should be favored in solvents which are more basic than water, because of the increased stabilization of the H^+ ion which is released in the rate-determining step; this would have the effect of increasing k_1 and decreasing k_{-1}. This affords an explanation of the fact that only the bimolecular path is observed in pyridine solution.[4,5] It also has been found[20] that a similar effect is achieved in aqueous solution by complexing Ag^+ with suitable basic ligands.

It is possible that similar factors determine the relative contributions of the bimolecular and termolecular paths for the activation of hydrogen by cuprous salts.

Acknowledgment.—Support of this work through a grant from the National Research Council of Canada is gratefully acknowledged.

[19] A. H. Webster and J. Halpern, *Trans. Faraday Soc.*, **53**, 51 (1951).

[20] A. H. Webster and J. Halpern, THIS JOURNAL, **61**, 1245 (1957).

HOMOGENEOUS CATALYTIC ACTIVATION OF MOLECULAR HYDROGEN IN AQUEOUS SOLUTION BY SILVER SALTS. III. PRECIPITATION OF METALLIC SILVER FROM SOLUTIONS OF VARIOUS SILVER SALTS

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Silver salts in aqueous solution are reduced by molecular hydrogen to metallic silver. The rate of reduction is determined by a homogeneous reaction between a hydrogen molecule and a silver ion or complex. Complexing with acetate or ethylenediamine greatly increases the rate of this reaction, while the addition of cyanide prevents reduction. These effects are interpreted in the light of earlier related studies.

Introduction

In a previous paper[2] a mechanism for the homogeneous activation of H_2 by Ag^+ was proposed, on the basis of a kinetic study of the silver ion-catalyzed reduction of dichromate. If a reducible substrate, such as dichromate, is not present in the solution, the silver salt is itself reduced to metallic silver. It appeared to be of interest to examine the kinetics of the precipitation of silver and to relate the precipitation reaction to the silver ion-catalyzed reduction of dichromate.

Also, it has been found that the rates of reaction of molecular hydrogen with cupric[3,4] and mercuric[5] salts in aqueous solution are profoundly affected by complexing the metal ions with ligands such as chloride, acetate and amines. An investigation of such effects in the Ag(I)–H_2 system was therefore undertaken using acetate and ethylenediamine as representative of carboxylate and amine type complexing reagents. The activation of H_2 by the acetate complex could not be investigated by the dichromate method because of the insolubility of Ag_2CrO_4 at *p*H's where silver acetate complexes are stable; the reaction was followed, therefore, by observing the precipitation of silver.

Experimental

Eastman Kodak "white label" grade ethylenediamine was used; all other chemicals were Baker and Adamson or B.D.H. reagent grade products. Hydrogen gas was supplied by the Canadian Liquid Air Co. The reactions were carried out in a titanium lined autoclave described previously.[2] Silver ion concentrations were determined by

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[2] A. H. Webster and J. Halpern, THIS JOURNAL, **61**, 1239 (1957).

[3] E. Peters and J. Halpern, *Can. J. Chem.*, **34**, 554 (1956).

[4] E. Peters and J. Halpern, *ibid.*, **33**, 356 (1955).

[5] G. J. Korinek and J. Halpern, *ibid.*, **34**, 1372 (1956).

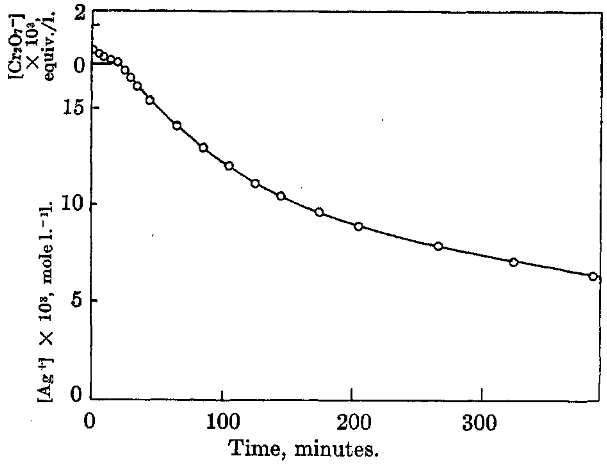

Fig. 1.—Rate plot showing the reduction of dichromate followed by the precipitation of silver at 110° 4 atm. H_2, from a solution containing initially 0.00013 *M* $K_2Cr_2O_7$, 0.0173 *M* $AgClO_4$, 0.102 *M* $HClO_4$.

KCNS titration in acid solution using a ferric indicator.

Results and Discussion

(1) **Perchlorate Solution.**—The reduction of Ag^+ by H_2 is represented by

$$2Ag^+ + H_2 \longrightarrow 2Ag + 2H^+ \quad (1)$$

In accord with this equation it was found that Ag^+ was consumed and H^+ was produced in equimolar quantities.

A rate plot for silver precipitation at 110° is shown in Fig. 1. Initially 0.77×10^{-3} equiv./liter $Cr_2O_7^=$ was present in the solution. No precipitation of the silver occurred until all of the dichromate had disappeared. It is seen that the rate of precipitation of silver is greater than the limiting rate of dichromate reduction as $[Cr_2O_7^=] \rightarrow 0$. This probably indicates that the reactive intermediates, which would otherwise take part in back reactions,[2] become stabilized on the surface of the silver crystals. It is apparent from Fig. 1 that any induction period, due to nucleation of the metallic phase, in the precipitation of silver must be very small.

In Table I, observed and calculated rates of silver precipitation are compared. The observed rates were determined by drawing tangents to the rate plots; this procedure is at best crude, giving errors of the order of ±15%. For comparison, rates were calculated on the basis of the previously determined rates of H_2 activation by Ag^+ as determined by the Ag^+-catalyzed reduction of $Cr_2O_7^=$ in the region where the rates were independent of $Cr_2O_7^=$ concentration.[2] The acid concentrations used in these calculations were estimated from the initial concentrations, applying corrections for the acid produced during the course of the reaction. The rates of precipitation and of hydrogen activation (as measured by $Cr_2O_7^=$ reduction) follow the same trends, decreasing with increasing acid concentration. However, the calculated rates are in all cases higher (by 20 to 60%) than the observed rates.

The precipitate produced was identified as metallic silver by X-ray diffraction. When formed in acid solution the precipitate consisted mainly of pellets about 0.5 to 2 mm. in diameter, which were composed of very small particles, about 5 μ in diameter.

TABLE I

COMPARISON OF RATES OF SILVER PRECIPITATION FROM PERCHLORATE SOLUTIONS AT 110°, 4 ATM. H_2, WITH RATES CALCULATED ON THE BASIS OF THE Ag^+-CATALYZED REDUCTION OF $Cr_2O_7^=$ (REF. 2)

Initial conditions			$(-d[Ag^+]/dt) \times 10^6$, mole l.$^{-1}$ sec.$^{-1}$		
$[Ag^+] \times 10^2$, *M*	$[HClO_4]$, *M*	$[Ag^+] \times 10^2$, *M*	Obsd.	Calcd.	Calcd./obsd.
2.48	0.003	2.3	5.1	6.3	1.2
		1.4	2.0	3.0	1.5
		0.8	0.8	1.2	1.4
1.54	.031	1.4	1.8	2.4	1.3
		0.95	0.9	1.2	1.3
		0.7	0.4	0.7	1.6
2.61	.031	2.0	3.1	3.7	1.2
		1.4	1.7	2.0	1.2
		0.8	0.6	0.7	1.2
1.73	.102	1.6	1.2	1.6	1.3
		1.2	0.7	0.9	1.3
		0.8	0.3	0.5	1.6

The results of this cursory examination of the precipitation of silver are consistent with the view that both the precipitation reaction and the catalyzed reduction of dichromate proceed by essentially the same mechanism. Complications in the case of the precipitation process appear to arise from the presence of some back reaction, possibly similar to that observed in the reduction of $Cr_2O_7^=$ at low $Cr_2O_7^=$ concentration. The extent of this back reaction may be governed by the presence of silver crystals. Similar discrepancies between observed rates of metal precipitation and rates of activation of hydrogen have been found in the Cu^{++}–H_2 system.[6]

(2) **Acetate Solution.**—Rate plots for the precipitation of silver at 70° from solutions containing acetate are shown in Fig. 2; the plots indicate apparent first-order behavior to the extent of at least 85% reaction. If it is assumed that the rates are proportional to the partial pressure of H_2 (as is the case for uncomplexed silver ions[2] and for cupric[3,4] and mercuric[5] complexes), the rate equation becomes

$$-\frac{d[H_2]}{dt} = -\frac{1}{2}\frac{d[Ag(I)]}{dt} = k[Ag(I)]\,[H_2] \quad (2)$$

No change in the rate was produced by a threefold increase in the acetic acid concentration at constant sodium acetate. On the other hand an increase in sodium acetate concentration produced a marked increase in rate, as shown in Fig. 3.

With perchlorate solutions it was noted that the rate of reaction of hydrogen in the precipitation process was smaller than in the dichromate reduction. This discrepancy, if due to a back-reaction, involving, H^+, would probably not be so serious in this case because of the much lower H^+ concentration and because of proton stabilization by the basic acetate ligands. The absence of any effect due to such a back-reaction is supported by the observation that the rate is unaffected by variation of the acetic acid concentration.

A complete interpretation of the kinetics in this system would require a knowledge of the concen-

[6] E. R. Macgregor and J. Halpern, *J. Metals*, in press.

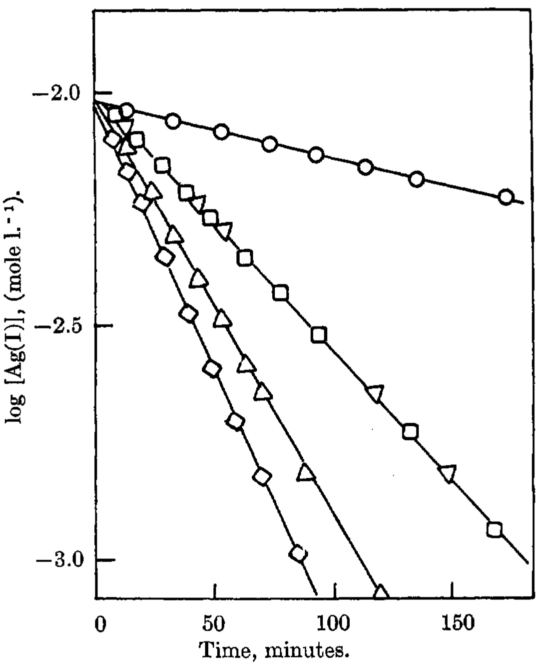

Fig. 2.—First-order rate plots for the precipitation of silver at 70°, 4 atm. H_2, from acetate solutions containing initially 0.01 *M* AgOAc: ○, 3.4 × 10^{-5} *M* HOAc; ▽, 0.3 *M* HOAc, 0.1 *M* NaOAc; □, 0.1 *M* HOAc, 0.1 *M* NaOAc; △, 0.2 *M* HOAc, 0.2 *M* NaOAc; ◇, 0.3 *M* HOAc, 0.3 *M* NaOAc.

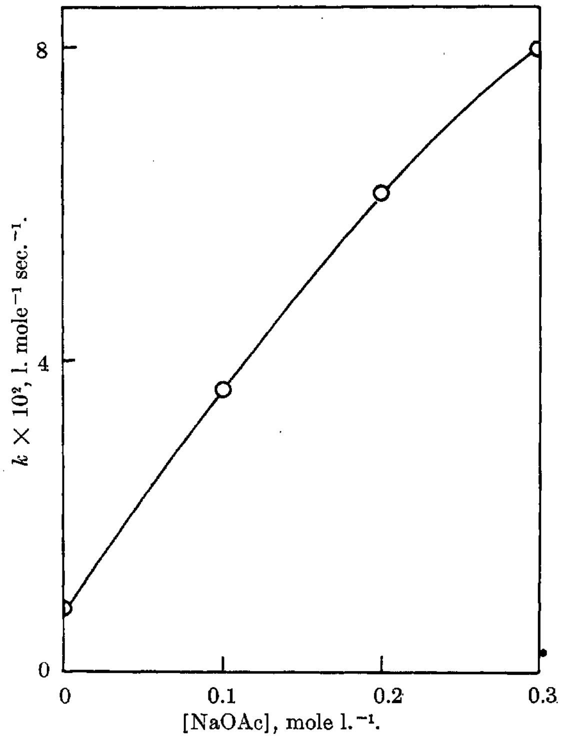

Fig. 3.—Dependence of the rate at 70° on the acetate concentration.

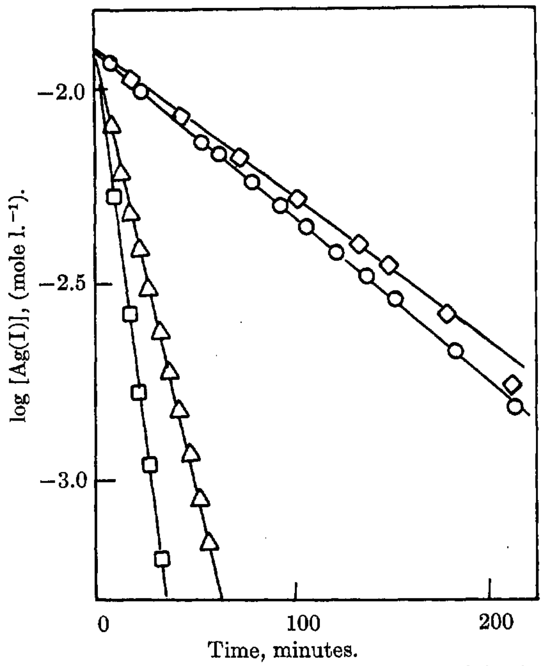

Fig. 4.—First-order rate plots for the precipitation of silver at 70°, 4 atm. H_2 from solutions containing initially 0.012 *M* $AgClO_4$ and (◇) 0.18 *M* EDA, (○) 0.36 *M* EDA, (△) 0.21 *M* EDA, 0.047 *M* NaOH, (□) 0.21 *M* EDA, 0.093 *M* NaOH.

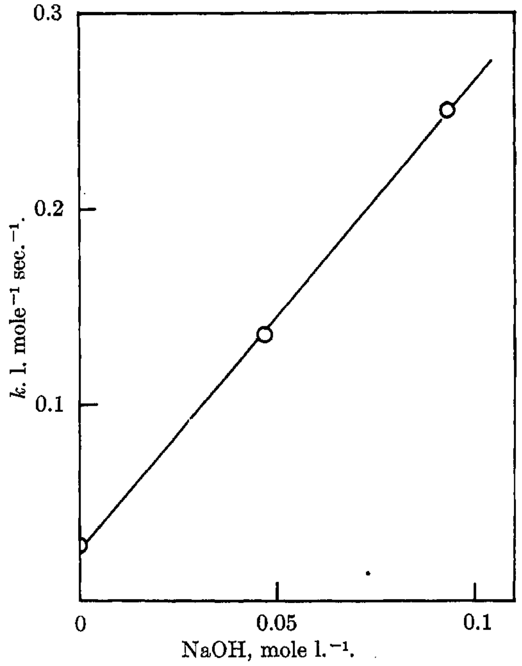

Fig. 5.—Dependence of the rate of reaction between H_2 and $Ag(EDA)_2^+$ at 70° on the OH^- concentration.

trations of the various species present in solution. Unfortunately silver acetate complexity constants have been determined only at room temperature, hence the following discussion can at best be only semi-quantitative. Furthermore the room temperature data[7] indicate that the solutions studied all contained appreciable concentrations of at least two of the species Ag^+, AgOAc and $Ag(OAc)_2^-$. However, even at the lowest acetate concentrations used, it is probable that not more than 15% of the observed rate could be due to activation of H_2 by uncomplexed Ag^+. As the NaOAc concentration is

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(7) F. H. MacDougall and L. F. Topol, THIS JOURNAL, **56**, 1090 (1952).

increased, the formation of the complexed species is favored; it may therefore be concluded that the reactivities of the silver acetate complexes are much higher than that of the uncomplexed silver ion. Using room temperature equilibrium data, the rate constant, k, for the reaction of AgOAc with H_2 at 70° was estimated to be approximately $(9 \pm 2) \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$. A similar accelerating effect due to acetate ligands was observed in the case of cupric ions.[4b] In the silver system, as in the mercuric system[5] the reactivity of the diacetate complex seems to be greater than that of the monoacetate complex.

(3) **Ethylenediamine Solution.**—The kinetics of reduction of the silver–ethylenediamine (EDA) complex were found to be essentially first order in Ag(I) as shown in Fig. 4. The effects on the rate of varying the concentrations of EDA and OH^- are depicted in Figs. 4 and 5. It is seen that increasing the EDA:Ag(I) ratio from 15 to 30 produced only a small change in rate, suggesting that in this range the Ag(I) is fully complexed. Increasing the OH^- concentration, however, produced a very marked increase in rate as shown by the plot in Fig. 5, which is fitted by the equation

$$k = k_0 + k_c[OH^-] \qquad (3)$$

where k_0 is the rate constant at pH 10.5, *i.e.*, 0.026 l. mole^{-1} sec.$^{-1}$ and $k_c = 2.4$ l.^{2} mole^{-2} sec.$^{-1}$.

The silver precipitate in this case was darker in color than that from acetate solution; it consisted of very fine particles, smaller than those formed from perchlorate solution.

Room temperature complexity constants for the silver–ethylenediamine system[8] indicate that there is essentially complete complexing of the silver as $Ag(EDA)_2^+$ in the solutions considered here. Unlike the ethylenediamine complexes of cupric and mercuric ions, $Ag(EDA)_2^+$ is reduced more rapidly than the uncomplexed Ag^+ ion.

It was found that the $Ag(CN)_2^-$ complex is not reduced at a measurable rate by 4 atm. H_2 at 70°.

These results indicate that the order of reactivities toward H_2 of the silver species examined is

$$AgOAc > Ag(EDA)_2^+ > Ag^+ >> Ag(CN)_2^-$$

At 70°, the relative rates of activation of H_2 by these species, reflected in the relative magnitude of k (k_1 in the case of Ag^+ [3]), are approximately 80:25:1: << 1.

As in the case of the cupric complexes,[9] the acceleration of the reaction by basic ligands (B) may be attributed to the stabilization of the proton released in the rate-determining step of the reaction, *i.e.*

$$AgB^+ + H_2 \longrightarrow AgH + BH^+ \qquad (4)$$

However unlike the ethylenediamine complexes of cupric and mercuric ions, $Ag(EDA)_2^+$ is reduced more rapidly by hydrogen than the uncomplexed Ag^+ ion. This difference possibly is due to the relatively lower stability of the silver complex, reflecting a lesser degree of electron displacement from the ligands to the silver ion.[5]

The promoting influence of OH^- on the reactivity of $Ag(EDA)_2^+$ parallels the effect observed for $Hg(EDA)^{++}$. It may be due to equilibria of the type

$$Ag(EDA)_2^+ + OH^- \rightleftarrows (EDA)\,Ag(NHCH_2CH_2NH_2) + H_2O \qquad (5)$$

or

$$Ag(EDA)_2^+ + OH^- \rightarrow Ag(EDA)^+_2.OH^- \qquad (6)$$

which lead to the formation of silver complexes in which a more basic group than EDA or H_2O (*i.e.*, $NH_2CH_2CH_2NH_2^-$ or OH^-) is present to serve as acceptor for the proton which is released in the reaction with H_2. While equilibria of this type have not been demonstrated for $Ag(EDA)_2^+$, they are well recognized[10–13] for amine or ethylenediamine complexes of more highly charged cations such as $Co(NH_3)_6^{+++}$, $Au(EDA)_2^{+++}$, $Pt(NH_3)_5Cl^{+++}$, $Co(NH_3)_5Cl^{++}$, etc., and account for certain kinetic aspects of the substitution reactions of such ions.[12]

The cyanide complex of silver is much more stable than the acetate or ethylenediamine complexes. Its low reactivity probably is due to the fact that the Ag^+ orbitals which are involved in the formation of AgH are used already in forming strong covalent bonds with CN^-. A similar explanation has been suggested[3–5,9] for the observation that the reactivities toward H_2 of the very stable covalent complexes of Cu^{++} and Hg^{++} are also much lower than those of the simple ions or their weak ionic complexes.

Acknowledgment.—Support of this work through a grant from the National Research Council of Canada is gratefully acknowledged.

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(8) G. Schwarzenbach, H. Ackermann, B. Maissen and G. Andregg, *Helv. Chim. Acta*, **35**, 2337 (1952).

(9) J. Halpern, *Quart. Rev.* (*London*), **10**, 463 (1956).

(10) F. Basolo in "Chemistry of the Coördination Compounds," ed. by J. C. Bailar, Jr., Reinhold Publ. Corp., New York, N. Y., 1956, p. 416.

(11) J. A. Caton and J. E. Prue, *J. Chem. Soc.*, 671 (1956).

(12) R. G. Pearson and F. Basolo, *J. Am. Chem. Soc.*, **78**, 4878 (1956).

(13) B. P. Block and J. C. Bailar, Jr., *ibid.*, **73**, 4722 (1951).