[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Homogeneous Catalytic Hydrogenation. VII. The Rate of Hydrogenation of Various Silver Salts in Pyridine Solution[1]

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Exploratory studies of the homogeneous hydrogenation of various silver salts have been made in pyridine solution at temperatures of 25–65°. All data were obtained from a consideration of initial rates only, since the products of the reaction, metallic silver and acid, influence the rate of hydrogenation. A comparison of the various silver salts indicates that the reaction rates can be correlated directly with anion basicity. More detailed kinetic studies were carried out with the single salt, silver acetate. In pyridine the reaction is first order in both silver acetate and molecular hydrogen. The second-order rate constant is given by the expression, $k = 10^{7.64}e^{-12,500/RT}$ (moles/l.)$^{-1}$ sec.$^{-1}$. A mechanism has been proposed which is in agreement with the various observations. It is necessary to assume that a hydrogen-carrying intermediate is formed between the activated complex and the reaction products. An attempt has been made to deduce energetically plausible structures for the intermediate and the activated complex.

It was first reported by Calvin in 1938 that certain cuprous salts in quinoline solution catalyze the homogeneous hydrogenation of benzoquinone and a variety of cupric salts.[2] Since that time detailed kinetic studies of the hydrogenation of cupric acetate have been carried out in several laboratories.[3] The results indicate that the activation of hydrogen is achieved by the reaction of hydrogen and cuprous acetate leading to the reversible formation of a hydrogen-carrying intermediate which has been assigned the formula CuAc·H.[3b]

In the absence of reducible substrates the catalytic activity of a cuprous salt can be demonstrated by its capacity to catalyze the conversion of parahydrogen.[4] In this work it was demonstrated that with cuprous acetate the parahydrogen conversion and the hydrogenation proceed by a common mechanism involving the rate-determining formation of CuAc·H. In the presence of a reducible substrate the intermediate, CuAc·H, is completely consumed in the hydrogenation reaction; in the absence of such substrate the conversion is achieved by reaction of two molecules of CuAc·H to regenerate the reactants. Finally, it should be noted that the intermediate, CuAc·H, is thermodynamically unstable with respect to the formation of metallic copper and acetic acid, but carefully purified quinoline this reaction does not occur at an appreciable rate at temperatures below 110–120°.

The present paper deals with the reaction of silver acetate and hydrogen in pyridine solution. Some years ago it was discovered that metallic silver was produced rapidly at temperatures as low as 25°, but no kinetic studies were attempted at that time.[5] The experiments discussed below indicate that in this reaction silver acetate also forms a hydrogen-carrying intermediate. However, unlike the cuprous acetate intermediate, its principal and perhaps only reaction is its irreversible reaction with silver ion leading to the deposition of metallic silver.

Experimental

Materials.—C.P. pyridine was purified by first allowing it to stand in contact with anhydrous barium oxide for one week and then distilling it through a glass fifteen-plate Oldershaw bubble plate column at a reflux ratio of more than 15/1. All except the middle fraction of the distillate boiling at 115.3–115.4° (uncorrected) was discarded. When the solvent was purified in this manner no change in rate was observed with pyridine obtained from different sources. The rate was also unaffected by a further purification step which consisted of addition of excess silver acetate, followed by refluxing of the solution for 30 hours to remove reducing impurities, and then redistillation as indicated above.

Electrolytic hydrogen was passed slowly through a deoxo unit to remove oxygen and dried by passage through a phosphorus pentoxide tower and a liquid nitrogen trap.

Commercial C.P. silver acetate was recrystallized from water and dried over sulfuric acid *in vacuo*.

Anal. Calcd. for $AgC_2H_3O_2$: C, 14.38; H, 1.80. Found: C, 14.32; H, 2.06.

Silver fluoride was prepared by adding excess reagent grade silver oxide to a 10% hydrofluoric acid solution in a polyethylene beaker, filtering the resulting suspension, and evaporating the solution *in vacuo* over sulfuric acid until the solid silver fluoride precipitated.

Silver trifluoroacetate was prepared by a procedure analogous to that used for the silver fluoride.

Anal. Calcd. for $AgC_2F_3O_2$: C, 10.87. Found: C, 11.15.

All other silver salts were of a C.P. grade and were used without further purification.

Apparatus and Procedure.—The hydrogenation apparatus and procedure will be published elsewhere.[3c] Parahydrogen conversion studies were carried out as described by Wilmarth and Barsh.[4] Their procedure was also used in obtaining the hydrogen solubility data of Table II. However, the apparatus was improved by substitution of a more sensitive manometer, all parts of the apparatus were thermostated, and the hydrogen was presaturated with pyridine vapor before the measurement was taken.

In each experiment the absorption of hydrogen at constant pressure was followed until approximately 5 ml. of gas had been consumed. The initial slope of a plot of hydrogen absorbed *versus* time was used to evaluate the rate data collected in Table I. For all salts except silver fluoride the slope was taken from a curve so nearly linear that no difficulty was involved in estimating the slope at zero time. In the experiments with silver fluoride the reaction rate decreased considerably, even during the first 10% of the reaction. As the discussion below will indicate, hydrogen fluoride might be expected to inhibit the reaction; however, the magnitude of the effect here was unusually large and the reported value of the reaction rate should be considered as provisional.

Molecular weight data for silver acetate in pyridine were obtained using a thermometric apparatus similar to that described by Müller and Stolten.[6] However, in our apparatus, the vacuum tube voltmeter in the Wheatstone Bridge circuit was replaced by a galvanometer. The ac-

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[1] This research was sponsored by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] M. Calvin, *Trans. Faraday Soc.*, **34**, 1181 (1938).

[3] (a) S. Weller and G. A. Mills, THIS JOURNAL, **75**, 769 (1953); (b) M. Calvin and W. K. Wilmarth, *ibid.*, **78**, 1301 (1956); (c) W. K. Wilmarth and Max K. Barsh, *ibid.*, **78**, 1305 (1956).

[4] W. K. Wilmarth and Max K. Barsh, *ibid.*, **75**, 2237 (1953).

[5] W. K. Wilmarth, Ph.D. dissertation, University of California, Berkeley, 1942.

[6] R. H. Müller and H. J. Stolten, *Anal. Chem.*, **25**, 1103 (1953).

curacy obtained using the galvanometer was somewhat less than that described in the original article, but it was sufficient to establish the monomeric state of aggregation of silver acetate. The apparatus was calibrated using *p*-dichlorobenzene which was assumed to be monomeric in pyridine. The calibration curve, a plot of ΔR *versus* mole fraction of solute, was linear with a zero intercept. For *p*-dichlorobenzene with a molecular weight of 147 calibration measurements at 0.050 M and at 0.104 M both yielded an experimental value of 147 ± 15. For silver acetate the theoretical value of 167 is to be compared with the experimental values of 157 ± 15 at 0.033 M and 179 ± 15 at 0.066 M.

Results and Discussion

In pyridine solutions which have been carefully purified so as to remove reducing impurities the hydrogenation of silver acetate ion can be studied without interfering side reactions

$$2\mathrm{AgAc} + \mathrm{H_2} \longrightarrow 2\mathrm{Ag} + 2\mathrm{HAc} \qquad (1)$$

Equation 1 then represents both the observed stoichiometry and, with the possible exception of the acetic acid, the actual state of aggregation of the molecules involved. Molecular weight data were not obtained for acetic acid since it was not required in formulating the rate law. However, a variety of evidence suggests that there would be little ionic dissociation under our experimental conditions.[7]

It was originally hoped that the rate law for the hydrogenation process might be established by following each experiment well along toward the completion of the reaction. However, this procedure was abandoned when it became clear that both of the products of the reaction markedly influenced the rate of hydrogenation. Experiments in Table I illustrate the effect of both the acetic acid and the metallic silver. An amount of acetic acid equivalent to the concentration of silver acetate depressed the rate by 30%.[8] By contrast, the presence of metallic silver in amounts equivalent to the silver acetate strongly catalyzes the reaction. The 13% increase in rate may represent only a minimum effect, since the silver produced in the previous experiment had been in contact with the solution for one day and a considerable decrease in surface area may have occurred during this interval.

In order to avoid the complexities associated with the build-up of reaction products, all of the data of Table I were obtained from initial rates extrapolated to zero time. It is believed that there is no appreciable error involved in this procedure, since the amount of reaction products is then negligibly small, and there is no evidence for an inhibition period or other irregularities in the initial stages of a hydrogenation.

TABLE I

RATE CONSTANTS FROM INITIAL RATES OF HYDROGENATION

25°		25°		44.7°	
Concn. (moles/1.)	k (1./mole sec.)	Concn. (moles/1.)	k (1./mole sec.)	Concn. (moles/1.)	k (1./mole sec.)
0.020	0.025	0.050[c]	0.032	0.010	0.110
.025	.028	.099[a]	.031	.025	.111
.050	.029	.099	.031	.040	.110
.050[a]	.028	.100[a]	.030	.050	.111
.050	.028	.100[d]	.031		
.053[b]	.018	.150	.030		

[a] Solvent repurified as described in Experimental section. [b] Initial acetic acid concentration, 0.026 M. [c] Contained 0.02 g. finely divided silver from previous run. [d] $P_{\mathrm{H_2}}$ = 260 mm. Hg. In all other experiments $P_{\mathrm{H_2}}$ = 502 mm. Hg.

TABLE II

SOLUBILITY OF HYDROGEN IN PYRIDINE

T, °C.	Solubility[a]
25	0.0467
44.7	.0545

[a] Ml. of H_2 measured at 25° per ml. of pyridine.

The values of the rate constant k listed in Table I were calculated by utilizing the solubility data of Table II and assuming in the initial stages of the reaction that the complete rate law has the form

$$\frac{-\mathrm{d(AgAc)}}{\mathrm{d}t} = 2k(\mathrm{AgAc})(\mathrm{H_2})$$

When the unit of time is seconds k has the values 0.030 and 0.111 for the two temperatures 25 and 44.7°, respectively. If the usual assumption is made that the activation energy is approximately constant over the temperature region under consideration, the temperature dependence of k is given by the expression

$$k = 10^{7.64}\, e^{-12{,}500/RT}\ (\mathrm{moles/l.})^{-1}\ \mathrm{sec.}^{-1}$$

The kinetics of hydrogenation can be understood in terms of the following simple mechanism

$$\mathrm{AgAc} + \mathrm{H_2} \xrightarrow{k} \mathrm{AgH} + \mathrm{HAc}\ \text{rate-determining} \qquad (2)$$

$$\mathrm{AgH} + \mathrm{AgAc} \longrightarrow 2\mathrm{Ag} + \mathrm{HAc}\ \text{rapid} \qquad (3)$$

AgH is postulated as existing, at least momentarily, as a monomeric soluble species, and both it and silver acetate should probably be regarded as pyridine complexes. Equation 3 is not meant to represent the detailed mode of deposition of metallic silver. It seems quite possible that this step of the reaction is actually heterogeneous, since the formation of isolated silver atoms or even diatomic silver molecules[9] would probably be endothermic. Fortunately as far as this kinetic study is concerned, the deposition of the silver follows the rate-determining step, and any minor irregularities in reaction 3 would not be reflected in the observed rate.

The rate law signifies that the rate-determining step involves only the predominant silver-containing species in the solution, undissociated silver acetate[10]; the activated complex must therefore have the chemical composition $\mathrm{AgAc{\cdot}H_2}$. To the extent that the rate constants at 25° increase with increasing silver acetate concentration, it could be argued that there is a second reaction path leading to an activated complex containing more than one silver acetate molecule. A reaction path second order in silver acetate would not be unexpected in view of the kinetic behavior in the cuprous acetate–quinoline system.[3] However, the trend in rate constant is small, and it has not been estab-

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(7) L. F. Audrieth and J. Kleinberg, "Non-aqueous Solvents," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 123-129.

(8) Acetic acid also inhibits the activation of molecular hydrogen by cuprous acetate (Reference 3b). Presumably in both systems acetic acid converts the metal ions to inactive acetate complexes.

(9) B. Kleman and S. Lindkvist, *Arkiv. Fys.*, **9**, 385 (1955).

(10) It must be recognized that the silver acetate may exist in various states of solvation as un-ionized molecules, ion pairs, or both. The referee has suggested that the abnormally small bimolecular frequency factor for the reaction may signify that the reactive species is one present at only a very low concentration.

lished well enough to justify a minor correction in the parameters of the Arrhenius equation listed above.

In order to satisfy the kinetic requirements and the over-all stoichiometry of the reaction, it is also necessary that a reducing intermediate of appreciable lifetime be formed between the transition state and reaction products. In equation 2 the formula AgH has been assigned to this intermediate; other formulations which will be considered below are also possible but seem somewhat less plausible. The formula for the intermediate was arrived at on the grounds that the activated complex, $AgAc{\cdot}H_2$, would represent a molecule unstable with respect to formation of AgH and acetic acid. In the absence of thermochemical data this conclusion cannot be proven, but it would seem valid unless AgH has a basicity quite unlike other silver salts, or unless formation of acetic acid from $AgAc{\cdot}H_2$ requires a quite appreciable interval of time.

Fortunately there are sufficient thermochemical data to permit us to draw some conclusions about the possible stability of solvated monomeric silver hydride. If the reasonable assumption is made that the heat of solution in pyridine of solid silver acetate and liquid acetic acid do not differ greatly, then the enthalpy change for the following reaction serves as a guide in estimating the required heat of solution of AgH from the gas phase.

$$AgAc(c) + H_2(g) \longrightarrow AgH(g) + HAc(l) \quad \Delta H = 35 \text{ kcal.}$$

It would thus appear that AgH might be postulated as an intermediate if its heat of solution were as great as 30–35 kcal./mole. Since the known thermochemical data and the relatively high solubility would lead to an estimated value of perhaps 50 kcal./mole for gaseous silver chloride, it would seem that, as far as energetics are concerned, AgH might reasonably be postulated as an intermediate. This conclusion is of interest, in spite of the fact that the kinetics cannot define the formula of the intermediate, because the calculation also serves as a guide in the consideration of the activated complex, a molecule whose formula can be specified.

Before considering the structure of the activated complex, it is profitable to consider the effect of variation of solvent and of anion. As the data in Table III indicate, silver acetate, silver sulfate and possibly silver fluoride all hydrogenate at approximately the same rate, whereas silver trifluoroacetate, silver perchlorate and silver chloride are all unreactive under our experimental conditions. For silver nitrate in pyridine at 60° it has been established that the unreactivity extends to parahydrogen conversion, thus indicating that the reaction is blocked at the step involving hydrogen activation. As a limiting value it can be said that the latter group of salts react at least one-three thousandth as rapidly as silver acetate. Since the most striking difference in acetate ion and trifluoroacetate ion is that of basicity, and since the other pairs of anions under comparison have similar electronic structures but widely different basicities, it would seem that a valid generalization might be drawn relating anion basicity and rate of hydrogenation.

TABLE III

RELATIVE RATES OF HYDROGENATION OF VARIOUS SILVER SALTS

Solute	Concn. (moles/l.)	T, °C.	Rate[a]
	Pyridine solutions		
Silver acetate	0.01–0.100	25–45	1
Silver trifluoroacetate	0.01	75	Non-reactive[b]
Silver fluoride	.01	25	5
Silver chloride	.01	75	Non-reactive[b]
Silver sulfate	.01	50	~1
Silver perchlorate	.01	75	Non-reactive[b]
Silver nitrate	.06	60	Non-reactive[b]
	Aqueous solutions		
Silver acetate	0.07	65	1/100
Silver dipyridine[c] acetate	.10	65	1/300
Silver diammine[c] acetate	.10	65	Non-reactive[b]

[a] Relative to silver acetate in pyridine at the temperature and concentration specified; extrapolated values used at temperature above 45°. [b] Rates are at most 1/3,000 that of silver acetate. [c] Ammine concentration was ten times that of the silver concentration.

The last three entries in Table III represent experiments in aqueous solution carried out to explore the effect of ionic dissociation and further variation of the groups bonded to the silver ion. In the presence of the ammine ligands the complex silver salts should be completely dissociated, but there remains the possibility that on reaction the acetate ion returns to participate at the transition state. For the pyridine complex the decrease in rate compared to the pyridine solution is perhaps no more than might be expected for the lesser efficiency in utilization of the acetate ion under these conditions of complete dissociation. However, the further decrease in the presence of ammonia suggests that, in contrast to the correlation noted for anions, an increase in ammine basicity decreases the rate of the reaction. In view of the sparsity of the data, this conclusion should be regarded as tentative. Unfortunately the experiment involving aqueous silver acetate does not further clarify the question. The partial association of silver ions and acetate ions, which probably occurs under our experimental conditions, prevents the results from being directly comparable to the solution containing only strong electrolytes.[11] However, the experiment does show that the presence of the pyridine, while helpful, is not essential for the hydrogenation process.

The nature of the activated complex can best be visualized by considering the change in bonding which has occurred somewhere midway between the reactants and the reaction intermediate. At this point the bond in the hydrogen molecule has been greatly weakened, and something approaching nascent silver hydride and acetic acid is being formed. Recently, experiments in this laboratory have demonstrated that strong bases catalyze the exchange of dissolved molecular hydrogen and protonic solvents, presumably through the reversible heterolytic fission and subsequent reformation of the hydrogen molecule.[12] In the early

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(11) F. H. MacDougall and L. E. Topol, *J. Phys. Chem.*, **56**, 1090 (1952).

(12) (a) W. K. Wilmarth, J. C. Dayton and J. M. Flournoy, THIS JOURNAL, **75**, 4549 (1953); (b) W. K. Wilmarth and June C. Dayton, *ibid.*, **75**, 4553 (1953).

stages of the present work, Dr. Sol Weller of the Houdry Corporation suggested to the authors that the hydrogenation of silver acetate might involve a similar heterolytic fission process with silver ions and acetate ions engaging opposite ends of the hydrogen molecule in a concerted attack.

The relatively small pre-exponential factor, $10^{7.64}$ (mole/l.)$^{-1}$ sec.$^{-1}$, offers support for this model of the activated complex, since it is consistent with the low values frequently obtained in four center reactions.[10] The observed correlation of rate with both basicity of anion and basicity of the ammine liquid would also be understandable. Increased basicity of the anion would tend to favor reaction rate, since proton extraction is occurring at the transition state; alternately, decreased basicity of the ammine would render the silver ion more electronegative and facilitate hydride ion extraction by the silver ion.[13]

While the conclusion reached above regarding the instability of second silver–hydrogen bond is probably correct, the structure cannot be completely ignored for the energy-rich activated complex. Judging from the considerable stability of $(H_3)^+$, $(AgH_2)^+$ might well exist as a stable ion in the gas phase.[14] Unfortunately little can be said about the stability of the ion when associated with acetate ion and pyridine in the solution phase.

The kinetics of hydrogenation of mercuric acetate[15] and cupric acetate[16] have recently been studied in aqueous solution; activation energies of 20.7 and 24.6 kcal., respectively, were observed for the two salts.

In a review of this work Halpern and Peters have summarized their views regarding the mechanism of hydrogenation of cations in aqueous solution. In a mechanism consistent with the rate law discussed above, their formulation of the structure of the intermediate is somewhat different than ours. However, they also conclude that the metal ions which readily hydrogenate will be characterized by having a strong attraction for electrons. While from our viewpoint high electronegativity is a prerequisite for rapid hydrogenation, of perhaps even greater importance is the ability of the metal ion to make use of an unoccupied orbital in forming a bond with a hydrogen atom or hydride ion. In this regard the dicoördinate silver and cuprous ions are especially favored, since they contain low-lying, non-bonding, p-orbitals which can be utilized in the activated complex. In cupric ion, and probably even in mercuric ion, the corresponding orbitals are used for bonding in the ground state, and the activated complex under consideration can be formed only at the expense of a considerable loss in solvation energy.

[13] In a solution where the anion is a very poor base it is to be expected that the hydrogenation will proceed by an alternate path less sensitive to anion basicity, if such a path exists. In a private communication A. H. Webster and J. Halpern of the University of British Columbia indicate that they have found this situation to occur in aqueous solutions of silver perchlorate. Here the rate of the relatively slow hydrogenation varies with the second power of the silver ion concentration. In the work summarized in Table IV, especially in those experiments where the rate is very slow, it is possible that alternate paths are contributing to the hydrogenation, and we are overestimating the contribution to the reaction by the path under consideration.

[14] Only semiquantitative information is available regarding the stability of $(H_3)^+$. A calculation by Joseph O. Hirschfelder, *J. Chem. Phys.*, **6**, 795 (1938), yields a value of approximately −80 kcal. for the heat of formation from molecular hydrogen and the proton.

[15] J. Halpern, G. K. Korinek and E. Peters, *Research* (*London*), **7**, S61 (1954).

[16] J. Halpern and E. Peters, *J. Chem. Phys.*, **23**, 605 (1955).

LOS ANGELES, CALIFORNIA

[CONTRIBUTION NO. 962 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Kinetics of the Reaction of Lithium Aluminum Hydride with Some Primary Alkyl Bromides[1]

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The kinetics of the reaction of lithium aluminum hydride, $LiAlH_4$, with *n*-butyl or *n*-amyl bromide in ether solutions was found to be second order for the reaction of the first hydride. Subsequent reaction is very slow; a precipitate, likely $(AlH_3)_x$, separates and redissolves.

Introduction

Substitution reactions with lithium aluminum hydride are usually believed to be SN2 reactions. This belief is supported by the following evidence: the reactivity of organic halides decreases in the order primary > secondary > tertiary.[3,4] Inversion occurs in the reduction of bicyclic epoxides.[4]

Conductivity measurements[5] indicate that lithium aluminum hydride is ionized in ethereal solutions, and Raman and infrared spectra give evidence of the presence of a tetrahedral AlH_4^- ion.[6] It is often assumed that this ion is the reacting species. However, Paddock[5] suggests that the increase in reactivity with increasing basicity of solvent is evidence for the equilibrium

$$AlH_4^- \rightleftharpoons H^- + AlH_3$$

and that the reactivity entity is the H^- ion.

Since no kinetics studies for lithium aluminum hydride reactions were found in the literature, and since the evidence cited above does not indicate the order of the rate-determining step, it seemed desirable to determine the kinetics of a simple substitution reaction. Accordingly, the kinetics

[1] Abstracted from a portion of the M.S. thesis of D. J. M., University of Pittsburgh, 1955.

[2] The authors wish to thank the Research Corporation for partial support of this work.

[3] J. E. Johnson, R. H. Blizzard and H. W. Carhart, THIS JOURNAL, **70**, 3664 (1948).

[4] L. W. Trevoy and W. G. Brown, *ibid.*, **71**, 1675 (1949).

[5] N. L. Paddock, *Nature*, **167**, 1070 (1951).

[6] E. R. Lippincott, *J. Chem. Phys.*, **17**, 1351 (1949).