[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES]

# Homogeneous Catalytic Hydrogenation. V.[1] The Kinetics and Mechanism of Hydrogenation of Various Cupric Salts in Quinoline Solution

BY M. CALVIN AND W. K. WILMARTH[2]

RECEIVED JULY 5, 1955

The homogeneous hydrogenation of cupric salts of various organic acids has been studied in the solvent, quinoline, at 100°. The cupric salts alone do not hydrogenate under these conditions but, in a number of cases, the cuprous salt acts as a homogeneous catalyst for the hydrogenation reaction. When reaction does occur the cuprous salt and the organic acid are formed in quantitative yield. In the case of cupric acetate the rates of hydrogenation have been studied in sufficient detail to permit formulation of a satisfactory rate law. Here, after empirical correction for a slight inhibitory effect produced by the formation of acetic acid, it was found that the rate is second order in cuprous acetate, first order in hydrogen, and independent of the cupric acetate concentration. A mechanism compatible with these observations can be formulated in terms of a rate-determining homolytic rupture of the bond in the hydrogen molecule; energy for the process is provided mainly by the formation of two copper–hydrogen bonds at the transition state. The copper–hydrogen bonds remain intact in an intermediate which either reduces the cupric salt by hydrogen atom or electron transfer, or reacts with itself to regenerate the hydrogen molecule.

## Introduction

A preliminary study of the homogeneous catalytic hydrogenation of benzoquinone and several cupric salts was reported by Calvin in 1938.[1a] Since then several papers have clarified the gross features of the mechanism of this unusual reaction[1c,1d,3]; however, a number of questions regarding both the generality of the catalytic action of the cuprous salts and detailed features of the mechanism remain unanswered. The present paper deals with the kinetics of hydrogenation of cupric acetate at 100° in the solvent quinoline. It also includes an exploratory study of the cuprous-catalyzed hydrogenation of a variety of other cupric salts under the same experimental conditions.

## Experimental

**Apparatus and Procedure.**—The apparatus and procedure involved in this work were essentially the same as that previously described.[1a,1b] However, the reaction vessel was modified so that solid cuprous acetate could be dissolved in the quinoline *in vacuo*, thus avoiding partial oxidation of the cuprous salt by oxygen of the air. All of the values for hydrogen absorption are expressed as ml. of hydrogen measured at 25° and 360 mm.

**Preparation of Cuprous Acetate.**—Fifty grams of cupric acetate monohydrate was added slowly to a solution of 154 g. of ammonium acetate dissolved in 60 ml. of concentrated ammonium hydroxide; the final solution was cooled (heat is evolved upon addition of the ammonia) and diluted to 250 ml. The cupric ammonia complex ion was reduced to the cuprous oxidation state by the addition of 35 g. of the acetate salt of hydroxylamine in 75 ml. of water. During this operation the two solutions were kept at approximately 60°, and the mixing was carried out in a nitrogen atmosphere. The resulting solution, containing the cuprous ammonia complex ion, was cooled to 20° and slowly added to 1000 ml. of glacial acetic acid. Fine white crystals of cuprous acetate immediately precipitated. The product, which was contaminated with a small amount of the cupric salt, was repeatedly washed with acetic acid and ether in the absence of air until all traces of the blue color had disappeared. The white cuprous acetate was then dried in vacuum without further exposure to air. When completely dried it was rapidly separated into portions just sufficient for a single experiment. The separate portions were stored in individual evacuated glass tubes which were opened just before use. The net yield was 20 g.

*Anal.* Calcd. for $CuC_2H_3O_2$: C, 18.57; H, 2.45; Cu, 51.9. Found: C, 18.78; H, 2.45; Cu (residue), 50.03.

**Solutions of Cuprous Salts.**—In the case of cuprous acetate, all of the solutions were prepared by dissolving the solid cuprous salt as indicated above. In all other cases the solid cuprous salts were not readily available and were prepared directly in solution in the reaction vessel by reduction of the corresponding cupric salt with anhydrous gaseous hydrazine. This reaction occurs within a matter of seconds at room temperature, and the product, nitrogen, can be removed by evacuation before introduction of the hydrogen. An accurate measure of the volume of hydrazine could not be obtained directly, but the fraction of the cupric salt which was reduced could be calculated by difference from the known amount of cupric salt and the volume of hydrogen required to carry the hydrogenation to completion. In general, somewhat less than half of the cupric salt was reduced by the hydrazine, but, if hydrogenation was not observed after the first exposure to hydrazine, the reduction and attempted hydrogenation were repeated until the appearance of a clear red color in the solution indicated that all of the cupric salt had been reduced by the hydrazine.

**Anhydrous Cupric Acetate.**—Anhydrous cupric acetate was used in all of the experiments since preliminary studies indicated that the monohydrate hydrogenated at a somewhat slower rate. The anhydrous salt was prepared according to the directions of Späth.[4]

*Anal.* Calcd. for $CuC_4H_6O_4$: C, 26.40; H, 3.30; Cu, 35.0. Found: C, 26.4; H, 3.40; Cu, 33.0.

**Cupric Salts of Salicylaldehyde and Derivatives.**—These salts were prepared according to the directions of Pfeiffer, Breith, Lubbe and Tsumaki.[5] Several compounds were prepared by Dr. R. H. Bailes of this Laboratory.

**Quinoline.**—The Eastman Kodak Co. quinoline was first crudely purified by distillation. It was then cooled with ice and enough hydrochloric acid added to form the acid salt. The aniline impurity was removed by diazotization and the diazo compound broken down by warming the solution to 60°. Non-basic impurities were removed by ether extraction. The quinoline hydrochloride was then neutralized with sodium hydroxide, the quinoline dried over potassium hydroxide and fractionated through an efficient column at a pressure of approximately 10 cm. It was first believed that this procedure would be sufficient, but subsequent work indicated that very small amounts of active substances were introduced by the nitrous acid treatment and were not removed by the above procedure. These impurities were found to be catalytically reduced, the reduction products appearing as a blue-green coloration in the

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[1] (a) Paper I, M. Calvin, *Trans. Faraday Soc.*, **34**, 1181 (1938); (b) Paper II, M. Calvin, THIS JOURNAL, **61**, 2230 (1939); (c) Paper III, W. K. Wilmarth, M. K. Barsh and S. S. Dharmatti, *ibid.*, **74**, 5035 (1952); (d) Paper IV, W. K. Wilmarth and M. K. Barsh, *ibid.*, **75**, 2237 (1953).

[2] (a) Taken in part from the dissertation of W. K. Wilmarth submitted in June, 1942, in partial fulfillment of the requirements for the Ph.D. degree; (b) the part of this work carried out by W. K. Wilmarth at the University of Southern California was sponsored by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[3] (a) S. Weller and G. A. Mills, THIS JOURNAL, **75**, 769 (1953); (b) L. W. Wright and S. Weller, *ibid.*, **76**, 3345 (1954).

[4] E. Späth, *Monatsh.*, **33**, 235 (1911).

[5] P. Pfeiffer, E. Breith, E. Lubbe and T. Tsumaki, *Ann.*, **503**, 84 (1933).

otherwise orange colored quinoline solutions of cuprous acetate. To eliminate these impurities, approximately 7 g. of cuprous acetate was dissolved in each liter of quinoline in a vacuum and shaken with hydrogen at 100° for 12 hours. The hydrogen was then pumped off and the quinoline removed from the reduced impurities by a bulb-to-bulb distillation. The quinoline was then fractionated, b.p. 112° at 16.5 mm.

**Hydrogen.**—The hydrogen was prepared electrolytically in this laboratory and purified by liquefaction. It contained less than 0.01 mole per cent. impurities.

Other reagents were used as purchased without further purification.

## Results

**The Hydrogenation of Cupric Acetate.**—In the solvent quinoline at 100° cupric acetate does not react directly with hydrogen. However, in the presence of cuprous acetate the catalyzed hydrogenation proceeds readily with the production of equivalent amounts of cuprous acetate and acetic acid.

$$CuAc_2 + H_2 \longrightarrow CuAc + HAc \qquad (1)$$

In a given experiment an autocatalytic reaction is observed because of the continuous production of the catalyst, cuprous acetate. Figure 1 indicates that the accumulation of the other product, acetic acid, must appreciably reduce the reaction rate below what it would have been in the absence of the acid.

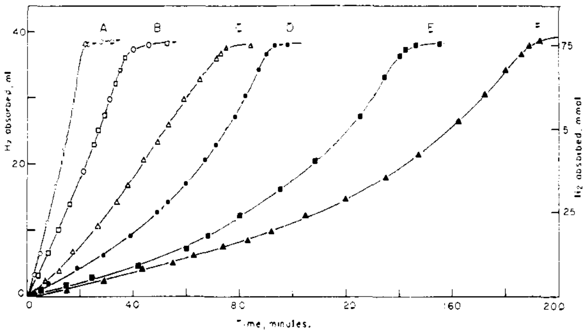


Fig. 1.—Effect of acetic acid upon the rate of hydrogenation. All six runs at 100° using 50 ml. of solution and a hydrogen pressure of 360 mm. In runs A, B and C the initial cuprous acetate concentration was 0.05 *M* and the initial acetic acid concentration was 0.00, 0.21 and 0.42 *M*, respectively. In runs D, E and F the initial cuprous acetate concentration was 0.01 *M* and the initial acetic acid concentration was 0.00, 0.07 and 0.14 *M*, respectively.

It is possible to make an empirical correction for the accumulation of the acetic acid. Rates of hydrogenation at various acetic acid concentrations, obtained by taking slopes of the curves in Fig. 1, were plotted against the acetic acid concentration and the curves extrapolated to zero acetic acid. These corrected values for the rates of hydrogenation are plotted against the square of the cuprous acetate concentration in Fig. 2.

Throughout the concentration range covered in our studies variation in the concentration of cupric acetate did not influence the rate of the reaction. In typical comparative experiments at 0.04 *M* cuprous acetate the rate of hydrogenation was constant over the range 0.002–0.02 *M* cupric acetate.

It has been established previously and it has been confirmed in this work that the rate is directly proportional to the pressure of hydrogen and hence to the concentration of dissolved hydrogen.[1a,b]

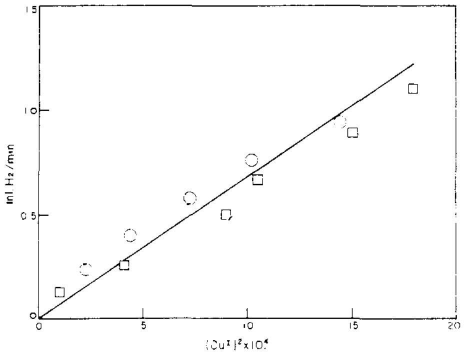
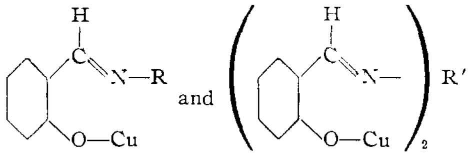


Fig. 2.—The second-order dependence of rate upon cuprous acetate concentration: ○, direct measurement; □, calculated from parahydrogen conversion. All measurements at 100°; rate in ml. of $H_2$/min. (at 360 mm. pressure of hydrogen) refers to 50 ml. of solution.

**The Catalytic Hydrogenation of Other Cupric Salts.**—None of the cupric salts considered in this paper react directly with hydrogen under the experimental conditions employed. However, as Table I indicates, a number of them can be catalytically hydrogenated in the presence of their cuprous salts. All of the cupric salts of carboxylic acids yielded curves analogous in shape to those of Fig. 1; comparative rates of hydrogenation are listed in Table I.

TABLE I

CATALYTIC ACTIVITY OF CUPROUS SALTS OF VARIOUS ORGANIC ACIDS AT 100°

| | Rate[a] |
|---|---|
| Carboxylic acids | |
| Acetic | 0.31 |
| Stearic | .18 |
| Benzoic | .09 |
| 4-Nitrobenzoic | Inactive |
| 2-Nitrobenzoic | Inactive |
| Salicylaldehyde derivatives | |
| Salicylaldehyde | 0.31 |
| 4-Hydroxysalicylaldehyde | .32 |
| 4-Hydroxyacetophenone | .54 |
| 5-Chlorosalicylaldehyde | .06 |
| 5-Nitrosalicylaldehyde | Inactive |
| 3-Nitrosalicylaldehyde | Inactive |
| Schiff bases | |
|  | |
| R = $CH_3$ | 0.32 |
| R = $C_6H_4$ | Inactive |
| R' = $C_2H_4$ | Inactive |
| R' = O-$C_6H_4$ | Inactive |
| R' = absent[b] | Inactive |

[a] Rate measured in 50 ml. of solution containing 0.02 *M* cuprous salt; pressure of hydrogen 360 mm. [b] Salicylaldehyde azine.

A variety of substituted salicylaldehyde derivatives was also found to undergo autocatalytic hydrogenation in quinoline solution at 100°. The results presented in Fig. 3 show that unlike the carboxylic acid derivatives the hydrogenation curves are S-shaped because of a decrease in reaction rate in the latter stages of the reaction.

When impure quinoline was used as a solvent metallic copper appeared almost immediately after the cuprous oxidation state had been reached.[1a] However, with the carefully purified quinoline used in these experiments, metallic copper did not appear at 100° in times less than 30 minutes after the cupric salt had been completely hydrogenated.

Although the experimental results are not presented here, the monohydrate of cupric acetate was used instead of the anhydrous salt in some of the early experiments. For these experiments the hydrogenation curves qualitatively resembled those in Fig. 1, but the actual rates of hydrogenation were approximately 10% slower for the hydrated salt.

## Discussion

In his exploratory studies of the hydrogenation Calvin originally postulated that the rate-determining step involved the interaction of a dimeric form of the cuprous salt with the hydrogen molecule.[1a,b] More recently Weller and Mills have re-examined the kinetics of hydrogenation of cupric acetate.[3a] They concluded Calvin's original mechanism was correct, and on the basis of their data they calculated an equilibrium constant of 11.2 for the dimerization of cuprous acetate. However, detailed conclusions drawn from either of these studies are subject to error as the monohydrate of cupric acetate was used, and no correction was made for the inhibitory effect of water or of the acetic acid generated during the reaction. In addition, the evidence for the dimerization of cuprous acetate was based upon measurements made at high cuprous acetate concentrations where, at least in our studies, ordinary methods of agitation were not sufficient to maintain the steady state concentration of dissolved hydrogen at its equilibrium value. On examining their data, it appears likely that Weller and Mills did not achieve solubility equilibrium, since their reported rates, even after correction to 50 ml. of solution, are less than half of those observed in this Laboratory.[6]

At 100° and at cuprous acetate concentrations below 0.04 $M$ the rate of hydrogenation of cupric acetate was not affected either by change in method of agitation from shaking to stirring or by a 30% decrease in rate of agitation. Under these conditions the rate is proportional to the pressure of hydrogen gas, independent of the cupric acetate concentration, and to the extent that the plot in Fig. 2 is linear, proportional to the square of the cuprous acetate concentration. The following simple mechanism is compatible with all of these observations.

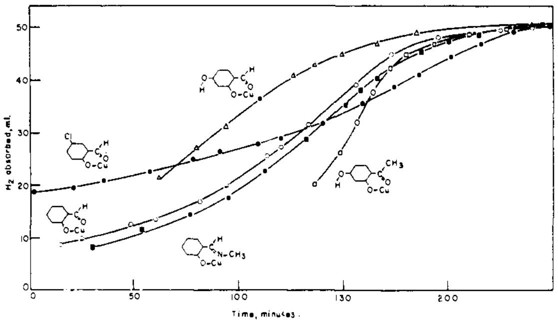


Fig. 3.—Catalytic hydrogenation of various cupric salts. All measurements at 100° using 0.04 $M$ cupric salt in 50 ml. of quinoline and a $H_2$ pressure of 360 mm. Final volume reading represents quantitative reduction.

$$2\mathrm{Cu}^{\mathrm{I}} + \mathrm{H}_2 \underset{k_1'}{\overset{k_1}{\rightleftarrows}} 2\mathrm{Cu}^{\mathrm{I}}\cdot\mathrm{H} \qquad (2)$$

$$\mathrm{Cu}^{\mathrm{I}}\cdot\mathrm{H} + \mathrm{Cu}^{\mathrm{II}} \xrightarrow{k_2} 2\mathrm{Cu}^{\mathrm{I}} + \mathrm{H}^+ \qquad (3)$$

Cuprous acetate, cupric acetate and acetic acid, represented by $\mathrm{Cu}^{\mathrm{I}}$, $\mathrm{Cu}^{\mathrm{II}}$, and $\mathrm{H}^+$ above, would be weak electrolytes in the solvent quinoline, and, judging from the color of the solutions, both copper ions are solvated. The kinetic studies require that $k_2 \gg k_1' \gg k_1$.

The zero-order dependence of rate upon cupric acetate concentration requires that a reducing intermediate be formed between the transition state and the final products. The kinetic studies do not specify the formula of the intermediate, so that the choice of the formula $\mathrm{Cu}^{\mathrm{I}}\cdot\mathrm{H}$ is somewhat arbitrary. However, in terms of simplicity and plausibility $\mathrm{Cu}^{\mathrm{I}}\cdot\mathrm{H}$ is somewhat arbitrary. $\mathrm{Cu}^{\mathrm{I}}\cdot\mathrm{H}$ would seem to be preferable to $\mathrm{Cu}_2^{\mathrm{I}}\cdot\mathrm{H}_2$, the formula previously used, since the latter species, formed at the transition state, would probably be unstable with respect to dissociation to the monomeric unit.

Figure 2 also contains points representing predicted rates of hydrogenation calculated from the data of Wilmarth and Barsh for the conversion of parahydrogen by quinoline solutions of cuprous acetate.[1d] Since the parahydrogen conversion is believed to occur through the forward and reverse steps of reaction 2, the rate-determining step should be the same as that of the hydrogenation reaction and a quantitative comparison of the two processes should be possible. To a first approximation the calculated rates have the expected values, but they are somewhat smaller than those directly observed, especially at the lower cuprous acetate concentrations. While the discrepancy between the two sources of data should be somewhat outside of the limit of error, the difference is not large, nor is it easily explained by assuming different mechanisms for the hydrogenation and conversion processes.[7]

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(6) For 0.075 $M$ cuprous acetate, in an initial rate presumably uninhibited by acetic acid, Weller and Mills report a rate of 0.66 ml. per minute, while our value for comparable conditions would be 2.0. In this region of concentration, agitation by shaking produced lower rates than agitation by stirring, and decrease in stirring speed led to a decrease in rate. At lower concentrations Weller and Mills only report their data in graphical form, but in all cases the values seem to be much less than ours.

(7) The simplest explanation of this discrepancy would involve the assumption that there is a second hydrogenation path of minor importance which does not lead to conversion. However, the zero order dependence of rate of hydrogenation upon cupric acetate concentration would require that the second hydrogenation path also proceed through a cuprous-hydrogen intermediate, and an intermediate which would not involve rupture of the hydrogen bond, and hence parahydrogen conversion, is somewhat improbable.

In addition it is also known that at 60°, where the hydrogenation experiments are believed to be more accurate and a greater range of concentration is available before hydrogen solubility difficulties are encountered, there is strong evidence for a strict second-order dependence of rate upon cuprous acetate concentration. On the basis of these considerations the rate constant has been evaluated by drawing the best straight line through all of the points in Fig. 2.

For acetic acid to inhibit the reaction, it must interact with the cuprous acetate, since interaction with cupric acetate would produce no effect, and reaction with molecular hydrogen is extremely unlikely. Qualitatively, the interaction with cuprous acetate furnishes a ready explanation of the inhibition. Silver acetate complexes of the form $AgAc_2^{-1}$ are well known, and analogous complexes with cuprous ion may reasonably be postulated. The cuprous complex should probably be formulated as $HCuAc_2$ in quinoline, since the low dielectric constant would favor association of the ions. The structure of the complex could be visualized as an un-ionized dimer, perhaps similar in structure to the ring dimer formed by acetic acid, or as an undissociated ion pair containing the $CuAc_2^{-1}$ anion and the conjugate acid of quinoline.

The results summarized in Table I list the other cuprous salts whose catalytic activity is roughly comparable to that of cuprous acetate. In addition, a number of cuprous salts are listed whose catalytic activity is so small that it could not be detected under comparable conditions. These latter salts, which are designated as "inactive," must activate hydrogen, if at all, at a rate roughly one-hundredth that of cuprous acetate. Small differences in rate for the various salts listed in Table I are probably not very significant as the studies are at a single temperature and no correction was applied for the possible inhibitory effect of the organic acid produced during the reaction. In addition, when the hydrogenation curves were S-shaped the relative rates change considerably during the course of the reaction. However, it is believed that the more extreme differences in rate could not be caused by these complications and therefore represent real differences in behavior.

Among the salts which are catalytically active, the rates of hydrogenation differ in one interesting respect. In the case of the carboxylic acid anions the maximum rate occurs just before completion of the reaction, whereas with all the salicylaldehyde derivatives a continuous decrease in rate is observed during the last 25–50% of the reaction. The decrease in rate arises from the regeneration of molecular hydrogen from the intermediate $Cu^{I}{\cdot}H$ by the reversal of eq. 2. When this process begins to compete seriously with the hydrogenation of the cupric salt (eq. 3) a maximum in reaction rate will be observed. Since the position of the maximum will depend upon the ratio $k_2(Cu^{II})/k_1'$ and individual values of $k_2$ and $k_1'$ cannot be evaluated, it is impossible to determine whether the salicylaldehyde derivatives differ from the carboxylic acid derivatives with respect to the reversal of reaction 2, reaction 3, or both.

Before discussing further the relative rates of hydrogenation, it should be noted that apparent catalytic inactivity might arise either from the failure of the cuprous salt to form the intermediate $Cu^{I}{\cdot}H$, or from the inability of the cupric salt to react with $Cu^{I}{\cdot}H$; only the first of these two possibilities would really represent catalytic inactivity. In a single case, that of cuprous salicylaldehyde anil, it has been established by parahydrogen conversion experiments that the inactivity actually represents a failure to form $Cu^{I}{\cdot}H$. However, it is quite possible that this result does not represent a general behavior.

Turning now to the relative catalytic activity of various cuprous salts, it would seem profitable to consider first the data for the substituted salicylaldehyde derivatives listed in Table I. In this series of compounds the functional acidic center containing the phenolic and carboxyl oxygen atoms is held constant, and the effect of substituents should be primarily one of changing the basicity of the oxygen atoms. A definite trend is observed here with a continuous decrease in rate through the series 5-nitro-, 5-chloro- and 4-hydroxysalicylaldehyde. If a generalization is to be drawn, it would seem that an increase in basicity increases the catalytic activity. A corresponding trend among the salts of the carboxylic acids serves to strengthen the validity of the generalization. Here the order of decreasing acidity, 4-nitrobenzoic acid, benzoic acid, stearic acid, is again the order of increasing catalytic activity.

As a tentative explanation for the effect of various substituents, it might be assumed that an increase in basicity of the anion bonded to the cuprous atom would render the cuprous atom more electropositive and decrease the energy required for promotion of an electron from its full 3-*d* shell to an empty upper orbital. A decreased energy of promotion might be expected to lower the activation energy for the hydrogenation process, since such a promotion must occur before the copper–hydrogen bonds can be formed at the transition state.

The Schiff bases formed from salicylaldehyde and various amines represent a more complex structural change than that posed by substitution in the aromatic ring. In addition to inductive and resonance effects, the presence of a bulky alkyl or aryl group attached to the doubly bonded nitrogen may be expected to produce steric effects as well. Experimentally, it would appear that small alkyl groups in this portion of the molecule do not cause serious steric hindrance. The cuprous salt of acetophenone is even more reactive than salicylaldehyde, and the Schiff base prepared from salicylaldehyde and methylamine also yields an active cuprous salt. However, the presence of the larger phenyl ring in the anil definitely renders the cuprous salt inactive in both the hydrogenation and parahydrogen conversion processes. In addition, all of the Schiff bases prepared from diamines form inactive salts. The latter result is particularly interesting, since these Schiff bases have two phenolic hydroxyl groups, and thus contain within a single molecule the two cuprous atoms required at the transition state. Evidently the geometry of the molecule is such that either hydrogen activation cannot occur or the hydrogen carrying intermediate is unable to react with the cupric salt; parahydrogen conversion experiments will distinguish between these two alternatives.

The conclusion that steric effects are important is also consistent with the over-all activity of the carboxylic acid salts as compared with the salicylaldehyde derivatives. Here, if our explanation is applicable, the more favorable basicity of the salicylaldehyde derivative is almost completely compensated for by the steric hindrance imposed by the extensive chelation of the cuprous atom and the carbonyl oxygen. The inactivity of the *o*-nitro derivatives may also be of steric origin but an explanation based upon acidity considerations would be equally applicable.

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# Homogeneous Catalytic Hydrogenation. VI. The Rate Law and Temperature Coefficient for the Hydrogenation of Cupric Acetate[1]

BY W. K. WILMARTH AND MAX K. BARSH[2]

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The homogeneous hydrogenation of cupric acetate has been studied in quinoline over the temperature range 25–100°. At all temperatures the rate of hydrogenation was proportional to the concentration of hydrogen and the square of the cuprous acetate concentration. The third-order rate constant has the value $3.31 \times 10^3 e^{\frac{-13{,}700}{RT}}$ (mole/l.)$^{-2}$ sec.$^{-1}$. When the hydrogenation was carried out using deuterium gas the rate was somewhat slower; over the temperature range 25–60° the decrease in rate was accompanied by an increase in the activation energy of approximately 700 cal./mole.

## Introduction

It has been shown previously that in quinoline solution cuprous salts catalyze the homogeneous hydrogenation of the cupric salts of various organic acids.[3,4] A recent paper has dealt with the catalytic properties of cuprous acetate at 100°.[4] The present work extends this kinetic study to lower temperatures in order to confirm the general validity of the rate law and to obtain an activation energy for the hydrogenation process.

## Experimental

**Materials.**—Quinoline solutions of cuprous and cupric acetate were prepared in the manner previously described.[5] Commercial electrolytic hydrogen was purified by passing it slowly through a deoxo unit to remove oxygen and dried by passage through two phosphorus pentoxide drying towers and a liquid nitrogen trap. Deuterium gas of 99.9% purity was obtained from the Stuart Oxygen company of San Francisco by arrangement with the Atomic Energy Commission.

**Hydrogenation Apparatus.**—A magnetic stirrer was used in a reaction vessel similar to that described previously.[5] It was attached to a vacuum line which was constructed of capillary tubing in order to minimize the volume of the system. The vacuum line also had a mercury manometer designed to maintain automatically a constant hydrogen pressure in the reaction vessel by changing the mercury level in the gas buret. The volume of hydrogen absorbed at any time could be determined with an accuracy of ±0.02 ml. by direct reading of the gas buret.

The gas buret was maintained at 25° and the reaction vessel at any desired temperature by pumping liquid from a constant temperature bath through the glass outer jackets surrounding these portions of the apparatus.

**Hydrogenation Procedure.**—At 60° the hydrogenation was rapid enough so that the reaction could be followed to completion. A plot was made of the volume of hydrogen absorbed *vs.* the time, and the slope of the curve, taken at selected cuprous acetate concentrations, provided a measure of the rate of hydrogenation. This rate was corrected for the inhibitory effect of acetic acid by extrapolating all rates to zero acetic acid concentration.[4] The magnitude of the correction was small and about the same as that made at 100°; the average correction at the two temperatures averaged only about 5–10%.

At temperatures below 60° the time required to perform a complete hydrogenation was inconveniently long and an alternate procedure for measuring rates was devised. At a given temperature and at known concentration of all reagents, this was achieved by following the rate of hydrogenation for a period just sufficient to ensure that the volume of hydrogen absorbed could be measured with the required accuracy; a volume of 1–3 ml. usually sufficed. The slope of a plot of volume of hydrogen absorbed *vs.* time over this segment of the hydrogenation curve provided a measure of the rate of hydrogenation. After such a rate measurement had been completed, the concentration of cuprous acetate was increased to some new desired value by rapidly absorbing the required amount of hydrogen at some higher temperature. The reaction vessel was then returned to the original temperature and a value of the reaction rate at the new concentration of reagents obtained by repeating the procedure outlined above. In view of the fact that the acetic acid correction did not change appreciably from 60 to 100°, and in the absence of data that would provide a direct correction, the 60° correction curves were used to extrapolate the rate data to zero acetic acid concentration. Since the corrections were all small, no significant error could be introduced by this procedure.

The solubilities of hydrogen and deuterium were determined at various temperatures between 0 and 100°. The results were obtained by direct measurement of the amount of hydrogen absorbed from a gas buret by a degassed quinoline solution. For high accuracy by this method, the gas volume in the system must be as small as possible. This was achieved in our system by almost completely filling the thermostated measuring vessel with quinoline and using a small gas buret attached to the manometer and measuring vessel with a minimum length of capillary tubing. The initial reading of the buret was somewhat uncertain since a small amount of hydrogen was absorbed by the solution during the 10–20 seconds required to balance the buret. However, a correction for this unknown volume of hydrogen was obtained by following the very slow absorption of hydrogen by the unstirred solution for a few minutes and extrapolating the volume readings back to zero time. Under the conditions of the experiment, where care was taken to avoid all possible convection and vibrational stirring of the

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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] Taken in part from the Dissertation submitted by Max K. Barsh in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Chemistry, University of Southern California, June, 1955.

(3) M. Calvin, *Trans. Faraday Soc.*, **34**, 1181 (1938).

(4) M. Calvin and W. K. Wilmarth, THIS JOURNAL, **78**, 1301 (1956).

(5) W. K. Wilmarth and Max K. Barsh, *ibid.*, **75**, 2237 (1953).