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.

BERKELEY, CALIFORNIA
LOS ANGELES, CALIFORNIA

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

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]

RECEIVED JULY 5, 1955

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

---

[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).

solution, the corrections proved to be negligibly small. After the initial buret reading was obtained, saturation of the solution was rapidly achieved by starting the magnetic stirrer. The final buret reading was taken after repeated reading of the buret indicated that saturation had been reached.

The solubility data for both hydrogen isotopes are listed in Table II; because of the improved design of the measuring apparatus, the results are believed to be considerably more accurate than those previously reported.[5]

Results and Discussion

The data for the hydrogenation of cupric acetate are collected in Table I. In order to permit a ready comparison with the results in the literature, the rates are reported as the ml. of hydrogen (measured at 25°) which would be absorbed per minute in a reaction vessel containing 50 ml. of solution.

TABLE I

RATE OF HYDROGENATION OF CUPRIC ACETATE

	Deuterium		Hydrogen	
T, °C.	(CuAc)	Rate[a]	(CuAc)	Rate[b]
60	0.028	0.033	0.040	0.078
	.042	.064		
50	.029	.020	.040	.049
	.041	.037		
40	.030	.0098	.040	.025
	.041	.0161		
	.042	.0164		
25	.030	.0033	.040	.0080
	.042	.0047		
	.042	.0043		

[a] Rates reported as ml. of H_2 (measured at 25°) observed per minute in 50 ml. of quinoline solution at temperature T. [b] Rates for hydrogen are smoothed values calculated from the straight lines in Fig. 1.

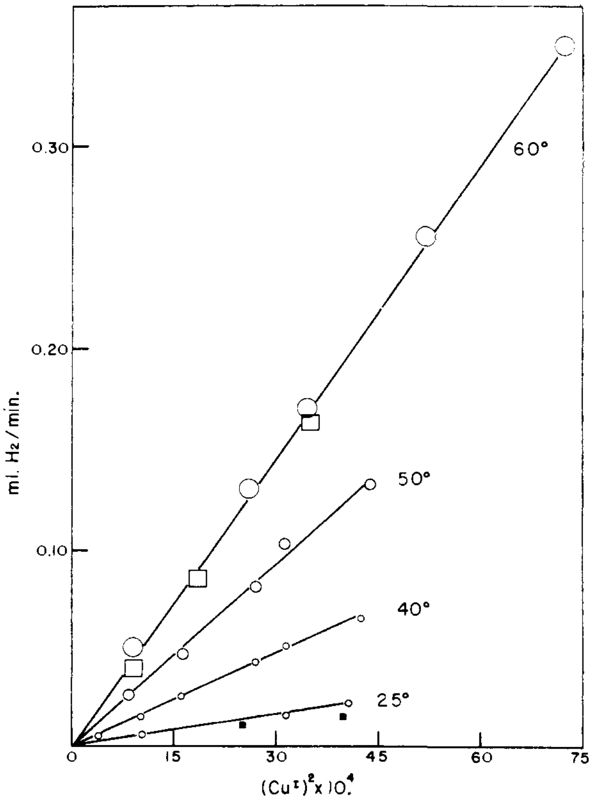

Fig. 1.—Rate of hydrogenation of cupric acetate: at 60° ○, direct measurement; □, calculated from parahydrogen conversion. Points at all other temperatures represent hydrogenation experiments. See text for the significance of the squares lying below the 25° line.

At 60, 50 and 40° the results were entirely reproducible and the general kinetic behavior resembled that observed at 100°. However, at 25° it was found that reproducibility could be obtained only if 0.10 g. or more of solid cupric acetate was present in the reaction vessel; in the presence of a suitable excess the rate was independent of the exact amount of the solid. Qualitative studies at 25° showed that the solubility of cupric acetate was very small and saturation only very slowly achieved. It would appear that the rate of solution of the solid can be partially rate determining at this temperature. The two points lying below the 25° curve in Fig. 1 illustrate the order of magnitude of this effect. At 0° the rate proved to be so dependent upon the amount of solid that meaningful results could not be obtained.

At each temperature the results obtained in this study are in agreement with the rate law adopted on the basis of the 100° data.[4] However, the rate law has been established with much greater certainty by the present experiments. In particular, the 60° data plotted in Fig. 1 constitute the strongest evidence in favor of the strict second-order dependence of rate upon cuprous acetate concentration. At present it is our feeling that there is no compelling evidence, either at 100° or at lower temperatures, which would justify the postulate that cuprous acetate exists in a dimeric form in kinetically detectable amounts.[4]

The hydrogen solubility data listed in Table II are required in the calculation of the rate constant, k_1, for the rate-determining step of the hydrogenation process.

$$2Cu^I + H_2 \xrightarrow{k_1} 2Cu^I \cdot H$$

Calculated values of k_1 for either hydrogen or deuterium can be obtained by substituting the appro-

TABLE II

T, °C.	Hydrogen[a] solubility	$10^2 k_1$ (mole/l.)$^{-2}$ sec.$^{-1}$
	Hydrogen	
24.6	0.0300	5.6
40.1	.0333	15.4
50.0	.0355	28.8
60.8	.0376	43.3
80.8	.0422	138
100.8	.0467	510
100	.0467	438[b]
	Deuterium	
24.6	.0314	3.0
40.1	.0345	9.7
50	.0366[c]	20.6
60.8	.0386	33.3

[a] Tabulated as ml. of H_2 (measured at 25°) per ml. of quinoline. [b] Calculated from parahydrogen conversion measurements. Aside from the difference in the unit of time, the symbol $k°$ of reference 5 is to be identified with k_1. [c] Obtained by interpolation.

priate values in the equation

$$k_1 = \frac{\text{rate}}{60\,V_sS(\text{Cu}^{\text{I}})^2}\ (\text{mole/l.})^{-2}\ \text{sec.}^{-1}$$

Here V_s is the volume of the solution, S is the solubility of hydrogen in the units of ml. of H_2 (measured at 25°) per ml. of solution, and the rate is expressed, as described above, in ml. of H_2 absorbed per minute in 50 ml. of solution. The factor 60 in the denominator is required to convert the units of time from min.$^{-1}$ to sec.$^{-1}$.

The rates for hydrogen were evaluated from the straight lines in expanded second-order plots similar to those of Fig. 1. Similar graphs (not included here) with about the same scatter of points were used to evaluate the rate constants for the deuterium data of Table I. The calculated values of k_1 for both hydrogen isotopes are collected in Table II.

The Arrhenius plots of the rate constants of Table II are presented in Fig. 2. A straight line has been drawn through the points for the hydrogen isotope H_2, but a slight concave curvature in the line would provide a better representation of the data. Rate constants consistent with the straight line can be calculated from the equation $k_1 = 1.62 \times 10^8\, e^{\frac{-13{,}000}{RT}}$ (mole/l.)$^{-2}$ sec.$^{-1}$.[6] The corresponding equation for the straight line through the deuterium points is $k = 3.31 \times 10^8\, e^{\frac{-13{,}700}{RT}}$ (mole/l.)$^{-2}$ sec.$^{-1}$.

The activation energy for the hydrogenation process using normal hydrogen is in good agreement with the value of 13,000 cal./mole reported by Calvin for the cuprous acetate-catalyzed hydrogenation of benzoquinone.[7] Since his experiments were less extensive than the present ones the agreement may be said to add support to his early measurements. Our present value for the activation energy may also be compared with the value "in the neighborhood of 14–15 kcal./mole" reported by Weller and Mills, but any agreement here would seem to be somewhat fortuitous since their rate constants are much smaller than the ones reported in this paper.[8]

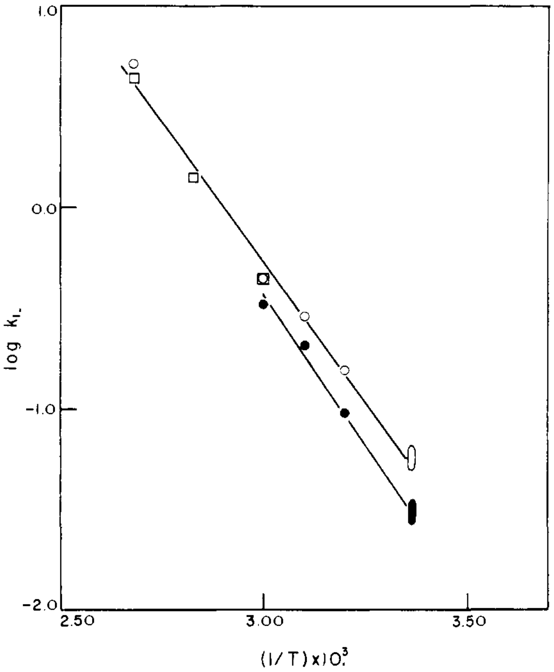

Fig. 2.—The temperature dependence of k_1: ○, direct measurement using H_2; □, calculated from parahydrogen conversion; ■, direct measurement using D_2.

When the reaction is carried out with deuterium replacing normal hydrogen a marked decrease in rate is observed. The rate data are accurate enough to establish an approximate difference in the activation energy for the two hydrogen isotopes, but no significance can be attached to the relative values of the pre-experimental frequency factors. However, there is no doubt that a frequency factor of the order of magnitude of 10^8 (mole/l.)$^{-2}$ sec.$^{-1}$ is required for both isotopes. So few third-order reactions have been studied in a condensed phase that a "normal" value for such a frequency factor cannot be given, but our observed value seems to be of a plausible order of magnitude.

LOS ANGELES, CALIFORNIA

---

(6) Calculation of an activation energy from the parahydrogen data would lead to a somewhat larger value, since both the 60 and 80° points lie below the line.[5] The value of 14,500 cal./mole obtained by using only these data would be lower than that previously reported because of the correction imposed through use of the improved hydrogen solubility data.

(7) M. Calvin, THIS JOURNAL, **61**, 2230 (1939).

(8) S. Weller and G. A. Mills, *ibid.*, **75**, 769 (1953).