coal in water; for an equilibrium concentration of 10 millimoles per liter we have (Freundlich and Schikorr): a (maleic acid) = 0.992; a (fumaric acid) = 1.56.

The more hydrophilic nature of *cis*-azobenzene compared with the *trans* compound also is indicated in the differences of solubilities. According to Hartley the solubility (at 25°) of the *cis* isomer in water is 0.65 millimole per liter, that of the *trans* isomer 0.02 millimole per liter in petroleum ether (b. p. 40 to 60°); on the other hand, the *cis* isomer is less soluble (at 0°), 49.4 millimoles per liter, compared to a value of 192 for the *trans* isomer. We determined colorimetrically the solubilities in methyl alcohol at 0° and found a succession as in water: 410 millimoles per liter for *cis*-azobenzene, 164 for the *trans* isomer.

It is quite probable that the *cis* isomers are generally more hydrophilic than the *trans* isomers. Perhaps it is due to a *cis–trans* difference in structure that maltose is more hydrophilic than cellobiose—as it appears to be—and accordingly starch so much more hydrophilic than cellulose.

Summary

The adsorptions of pure *cis*- and *trans*-azobenzene by aluminum oxide and by charcoal in solutions of petroleum ether and of methyl alcohol were measured and compared. The *cis* isomer is adsorbed more strongly by aluminum oxide, particularly in petroleum ether, less in methyl alcohol; the *trans* isomer is adsorbed more strongly by charcoal, particularly in methyl alcohol, less in petroleum ether. This is in agreement with other experimental results, according to which the more hydrophilic solute, here the *cis* isomer, is adsorbed more strongly by a hydrophilic adsorbent, here aluminum oxide, in a more hydrophobic medium, here petroleum ether, than by a more hydrophobic adsorbent, here charcoal, in a more hydrophilic medium, here methyl alcohol.

That *cis*-azobenzene is more hydrophilic than *trans*-azobenzene is also shown by the *cis* isomer being more strongly soluble in water and methyl alcohol and less soluble in petroleum ether than the *trans* isomer.

MINNEAPOLIS, MINNESOTA RECEIVED MAY 23, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Homogeneous Catalytic Hydrogenation

BY M. CALVIN

Last year it was announced[1] that quinone in quinoline solution could be hydrogenated using dissolved cuprous acetate as homogeneous catalyst. This is a report of further study of the kinetics of this reaction in the attempt to discover precisely what structure has this important property of bringing the highly inert hydrogen molecule into reaction.

Experimental

The apparatus was essentially the same as already has been mentioned,[1] and the experiments consisted of following the rate at which hydrogen was absorbed by a given solution varying the conditions of concentration, solvent, temperature, and reactants. The detail of the reaction vessel is shown in Fig. 1. The internal condenser was removed and weighed amounts of the catalyst and substrate introduced. The vessel was then mounted in the shaker and connected to the vacuum system through the ground joint J. The solvent was run in from a pipet and the condenser quickly replaced and the tap to the vacuum system opened. But before the air could be removed some oxidation had taken place, so that blank runs without substrate were made on a given catalyst to determine the correction to be applied to the amount of hydrogen absorbed. The heating was then commenced and pumping was continued until the McLeod gage at the other end of the system showed a pressure of 10^{-4} mm. or less. This degassing sometimes took as long as thirty minutes after the thermostating liquid had reached its boiling point. For runs at 100° water was used and for 117.7° *n*-butyl alcohol was used as thermostating liquid. In all the runs the shaker speed was about 325 vibrations per minute. In the course of one run the shaker speed was increased to 530 vibrations per minute for a time and then decreased to 325 again and no appreciable break in the rate curve was observed, showing that the rate of solution of the gas was sufficiently fast not to be a disturbing factor.

Materials

Quinoline.—Eastman Kodak Co. synthetic quinoline was purified by (1) initial fractionation at atmospheric pressure to within 1°, (2) treatment with benzoyl chloride for several days and then washed with sodium hydroxide solutions followed by distilled water, (3) fractionation at atmospheric pressure to remove water, (4) final fractionation in a 1-foot (30-cm.) Widmer column at 50–60 mm. pressure. The quinoline so obtained remains water white for months when kept in a glass-stoppered uncolored glass bottle.

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

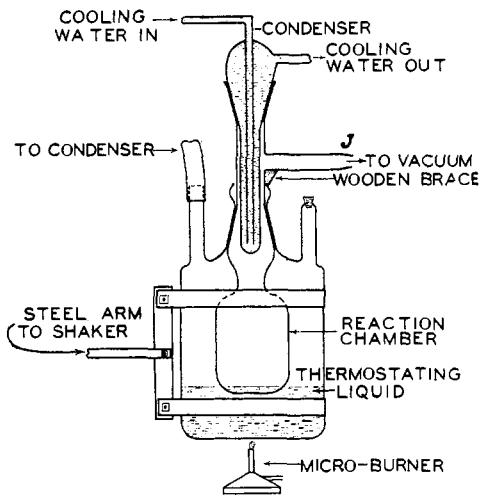


Fig. 1.

Quinone.—Eastman Kodak Co. quinone was purified by high vacuum sublimation and alternatively by recrystallization from alcohol. The two products gave the same results.

Cuprous Acetate.—Cuprous oxide (Baker) was extracted with glacial acetic acid containing 2–5% acetic anhydride, in a stream of hydrogen. The white cuprous acetate crystallized out and was filtered rapidly and washed with dry ether. The white cuprous acetate must be kept in a vacuum desiccator since moisture will hydrolyze it and oxygen oxidize it appreciably in as short a time as twenty-four hours. It was very difficult to prepare large quantities (10 g.) of absolutely pure cuprous acetate. It always contained some cupric salt. But since the method of starting the hydrogenation reaction involved some oxidation a large sample containing traces of cupric salt (pale greenish color) was standardized with respect to its catalytic power and this remained constant throughout a comparable series of experiments. The differences in individual samples were small in any case. The different samples of cuprous acetate are indicated by different letters in the tables.

α-Chloronaphthalene was fractionated in the Widmer column at 50–60 mm. pressure. The identified impurity was only naphthalene.

Hydrogen.—Normal hydrogen was prepared by collecting the gas as it evaporated from liquid hydrogen. Para-hydrogen was prepared by passing *n*-hydrogen through charcoal immersed in liquid hydrogen. Deuterium was obtained from the Stuart Oxygen Company. The thermal conductivity measurements indicated that all three hydrogens were sufficiently pure.

Results

A typical run is shown in Fig. 2. All the others are identical in form and differ only in the slope of the straight line, *i. e.*, the rate of the hydrogenation. The effect in pure quinoline solution, of variation of concentration of catalyst, substrate, and hydrogen are shown in Table I. This is for one catalyst preparation. Identical results have been obtained on other preparations.

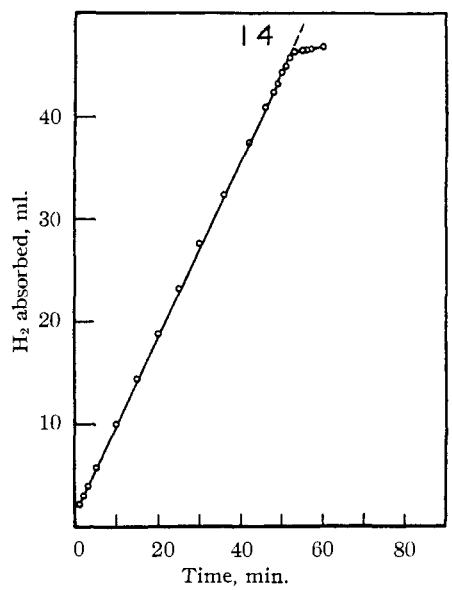


Fig. 2.—Expt. 2 in Table I.

TABLE I

Temperature, 100°; 50 cc. quinoline; catalyst preparation G.

Expt.	Catalyst, mmol.	Substrate, mmol.	Press. H_2, mm.	Rate, cc./min.	Rate per mmol. Cu^I	H_2 abs. mmol.
1	1.02	0.51	395	0.325	0.32	0.28
2	2.04	1.02	395	0.775	.39	0.57
3	4.08	2.04	395	1.81	.45	1.02
4	2.04	2.04	395	0.718	.36	1.05
5	2.04	1.02	595	.776	.39	0.60

The four points which emerge from this tabulation are: (1) the rate is strictly proportional to the concentration of hydrogen in solution (compare expts. 2 and 5; in expt. 5 the concentration of hydrogen in the gas phase and in solution has been increased by the ratio 595/395, so that when the rate in cc./min. remains the same, the rate in moles/min. has increased in precisely the same ratio); (2) the rate is somewhat more than proportional to the amount of cuprous acetate in solution, *i. e.*, when the concentration of cuprous acetate is doubled the rate is somewhat more than doubled; (3) the quinone has a small depressing effect on the rate (expts. 2 and 4); (4) the amount of hydrogen absorbed corresponds rather closely to half reduction of the quinone, *i. e.*, reduction to quinhydrone.

In Table II are shown the rates for the different kinds of hydrogen and the temperature coefficient for normal hydrogen all in quinoline solution.

It should be noted in connection with the at-

TABLE II

Expt.	Temp., °C.	Catalyst, mmol.	Substrate, mmol.	Press. H_2, mm.	Rate, ml./min.
6	100	2.04(C)	1.0 chloranil	387 *n*-H_2	0.0
8	100	2.04(C)	1.02 quinone	387 *n*-H_2	.86
9	100	2.04(C)	1.02 quinone	387 *p*-H_2(95%*p*)	.86
10	100	2.04(C)	1.02 quinone	387 D_2(100%D)	.80
14	100	2.04(F)	1.02 quinone	387 *n*-H_2	.87
15	117.7	2.04(F)	1.02 quinone	387 *n*-H_2	2.07

50 ml. quinoline

tempted reduction of chloranil that not only was the hydrogenation completely stopped but the subsequent oxidation of the cuprous complex by oxygen was very markedly slower in the presence of the chloranil than in its absence or with quinone present. The difference between hydrogen and deuterium is surprisingly small though quite real, and whether this difference is a variation in activation energy or temperature independent factor still remains to be seen. Para hydrogen reacts at the same rate as *n*-hydrogen (expts. 8, 9 and 10). The apparent activation energy for the normal hydrogen reaction is 14,300 cal. and if the temperature coefficient of the solubility of hydrogen (given in Table III) is taken into account this activation energy is reduced to 13,000 cal.

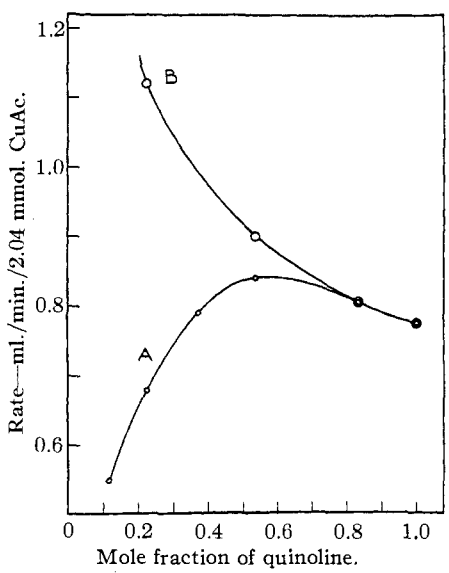


Fig. 3.—2.04 millimoles CuAc; 1.02 millimoles quinone; run at 100°; 50 ml. solvent measured at 20°; press. H_2, 395 mm. at 20°. Curve A, experimentally observed rate; Curve B, rate corrected for the solubility of CuAc.

The accuracy of these solubility measurements did not disclose any difference in the solubilities of deuterium and para hydrogen from that of normal hydrogen.

TABLE III

SOLUBILITY OF HYDROGEN

Temp., °C.	Solvent	Ml. H_2 (press. 380 mm.; temp. 20°)
100	54.5 g. quinoline,	2.1
20	(50 cc. at 20°)	1.35
117.7		2.30
100	54.5 g. quinoline + 1	2.05
20	mmol. quinone	1.4
100	54.5 g. quinoline + 2	2.2
20	mmols. CuAc	1.4
100	59.5 g. α-chloronaphthalene	
	(50 ml. at 20°)	2.15

A series of runs in quinoline–α-chloronaphthalene mixtures was made and the results are given in curve A, Fig. 3. Since the solubility of the cuprous acetate decreased as the mole fraction of the quinoline decreased, all the cuprous acetate which was added to the reaction mixture did not dissolve when the mole fraction of the quinoline dropped below about 0.55. Curve B, Fig. 3, gives the rate, calculated from the observed rate (curve A) and an independently measured solubility (Table IV), corresponding to the condition that all of the cuprous acetate added was completely dissolved.

TABLE IV

SOLUBILITY OF CUPROUS ACETATE IN QUINOLINE–α-CHLORONAPHTHALENE MIXTURES AT 100°[a]

N_Q (mole fraction quinoline)	Soly. (g. CuAc in 50 ml. solvent measured at 20°)
1	0.53
0.537	.23
.223	.14

[a] Since the solid phase was apparently different in the different solvents and in the absence of quinone, these solubilities can only be taken as an indication of what the concentration of cuprous acetate in the solution is.

Discussion

The mechanism that has been proposed previously,[1] namely, that the rate-determining step in the reduction of cupric copper or quinone is an activation of molecular hydrogen by a cuprous quinoline complex followed by a rapid reduction of the substrate, still holds. The succeeding slow absorption of hydrogen after the reduction of substrate is complete is the reduction of cuprous to free copper. There is at least one important addition to be made to this mechanism, which is that the catalytically active species is a dimer of cuprous acetate. This is based primarily on the fact that the rate increases more than linearly with the concentration of cuprous acetate, taken

together with the following line of argument. There exist no data on the molecular weight of cuprous acetate in quinoline solution but the work of Beckmann[2] on other cuprous salts, especially the chloride, indicate just such a polymerization. From the data of Beckmann one can calculate an association constant for the reaction

$$2CuCl(solution) \rightleftarrows Cu_2Cl_2(solution)$$

in quinoline solution in the neighborhood of 238° to be about 5 to 10, expressing the concentrations in moles per liter. If it is assumed that the rate of hydrogenation is proportional to the concentration of dimeric cuprous acetate one can calculate a similar constant of about 700 to 800 for the cuprous acetate in quinoline at 100°. This is entirely reasonable considering the lower temperature and the more favorable conditions afforded by the carboxyl group for polymerization. The heat of dissociation of these dimers in solution can be estimated by assuming an entropy decrease on association of about 15 cal./deg. and using the above equilibrium constants. The dissociation heat for the acetate is then about 10 kcal. and that of the chloride about 8 kcal., both not unreasonable values. Although the molecular structure of a solute as derived from its crystal structure is no proof of the state of the solute in solution, it is a good indication of the tendency of the solute as the solution approaches saturation. Just such binuclear bridged structures as the one here proposed for cuprous acetate–quinoline have been found in crystals of other cuprous and palladous compounds.[3] The function of the quinoline is first of all to bring the cuprous salt into solution by virtue of its coördinating property and second to furnish in this coördinated compound the electrons which seem to be necessary for the catalytic activity. A correlation with the basic strength or aromatic character of the coördinated molecule awaits further investigation. Whether one or two quinoline molecules per copper atom are required is still not known and in the structures written here Q will be used to represent the quinoline in the complex without implying any number. An analysis of the corresponding chloride gave (CuCl–quinoline) although from the work of Mann[3a] it would seem that two quinolines per copper atom would be more likely. In any case the considerations as far as they go at present are unaffected by whether there are one or two quinolines per copper atom or whether, if the cuprous center is four-covalent, these four covalences are planar or tetrahedral. The fact that the rate increases as the mole fraction of the quinoline decreases in the quinoline–chloronaphthalene mixtures can be attributed to the shifting of the polymerization equilibrium toward the side of the dimer and thus increasing the amount of the catalyst, specified for the same concentration of cuprous acetate. However, it seems that the actual increase in going only to solutions which are 10 mole per cent. quinoline is too large to be accounted for on this basis alone since the association constant in pure quinoline is already 700. Any attempt at a quantitative correlation between the solubility (activity) and the rates has so far been futile and should so be, since the solid phase (standard state) does not remain constant (see footnote to Table IV).

The precise path by which the quinone is reduced is still very much in the dark. In any given run the rate is independent of the state of reduction of the quinone but the total amount of quinone present does have an effect on the rate (Table I). The only plausible explanation at the moment is that the quinone forms a complex with the cuprous acetate in competition with the hydrogen and that the reduction product (quinhydrone) is about equally effective in occupying the cuprous acetate and diminishing its availability in the hydrogen activating process. That such a complex is possible is evidenced by the fact that when quinone and white cuprous acetate are kept in the same vacuum desiccator the quinone sublimes over onto the cuprous acetate and forms a very dark blue-black compound. The case of the tetrachloroquinone also is illuminating. Here it seems that the complex formation with the cuprous acetate is so strong and so complete that not only is the hydrogenation prevented but the oxidation by oxygen of the cuprous acetate is inhibited very markedly. In writing out the following mechanism the condition of the quinone is left unspecified. All that can be said is that it is not involved in the rate determining step.

The previously proposed mechanism is essentially correct and is here rewritten with the aforementioned revisions. The notation is identical with that previously used.

(2) Beckmann, *Z. anorg. Chem.*, **51**, 240 (1906).

(3) (a) Mann, *et al.*, *J. Chem. Soc.*, 873, 1503 (1936). (b) Burawoy, *et al.*, *ibid.*, 1690 (1937). (c) A. F. Wells, *Proc. Roy. Soc.* (London), **167**, 169 (1938).

$$Cu^{I} + Q \rightleftharpoons Cu^{I}Q \quad (a)$$

$$2Cu^{I}Q \rightleftharpoons (Cu^{I}Q)_2 \quad (a_2)$$

$$(Cu^{I}Q)_2 + H_2 \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} (Cu^{I}Q)_2H_2 \quad (b)$$

$$(Cu^{I}Q)_2H_2 + 2Su \xrightarrow{k_2} (Cu^{I}Q)_2 + 2HSu \quad (c)$$

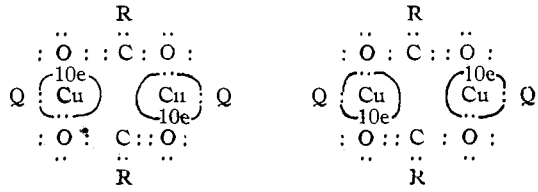
$$(Cu^{I}Q)_2H_2 \xrightarrow{k_3} 2Cu^{\circ} + 2Q + 2HAc \quad (d)$$

with $k_2 > k_1' > k_1 > k_3$

k_1' is set larger than k_1 since the equilibrium of (b) must be far to the left as evidenced by the only very small effect of cuprous acetate on the solubility of hydrogen in quinoline.

The temperature coefficient of the hydrogenation includes the shift of the equilibrium (a_2) as well as the change of the rate k_1. This shift of equilibrium affects the rate in the opposite direction from the change in k_1. If one makes a correction for this shift in equilibrium using the heat of dissociation of 10 kcal. previously calculated, one finds that the activation energy of k_1 is increased only slightly and probably is very close to 14,000 cal.

Thus it seems quite reasonable that the cuprous acetate is at least partially dimeric in solution, although the possibility of a higher polymer is not eliminated. The structure of this dimer analogous to that of other carboxylate dimers can be represented by a number of valence formulas containing chelated copper.



Any further speculation concerning the properties of such a dimer awaits an independent demonstration of its existence.

Summary

It has been shown that probably a dimer of a cuprous acetate–quinoline complex is responsible for the activation of molecular hydrogen in the homogeneous catalytic hydrogenation of quinone in solution.

BERKELEY, CALIF. RECEIVED FEBRUARY 6, 1939

[CONTRIBUTION FROM THE JOHNSON CHEMICAL LABORATORIES, UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA]

The Composition of the Colloidal Platinum Micelle

BY S. W. PENNYCUICK

Evidence brought forward by the author[1,2] has shown that the particles of colloidal platinum are composite in nature, containing platinum, platinic oxide and hexahydroxyplatinic acid.

This has now been confirmed by the microchemical analysis of the coagulated particles; and the relative amounts of the three constituents have been determined. The composition of the micelle in an average Bredig preparation is given by the formula $[3.9\ Pt, 1.16\ PtO_2, 1.0\ H_2Pt(OH)_6]_n$.

Isolation of the Micelle.—The sols were prepared from conductivity water by the Bredig method,[3] and the particles were isolated by coagulating the sol by freezing and then thawing the mixture.[4] In the preparation of the sol and in the isolation of the micelle no foreign electrolyte was added, nor was any foreign matter allowed to enter. The micelle was thus obtained in as pure a form as possible.

The particles in the frozen coagulum were sufficiently compact to settle readily; they were therefore washed free from the mother liquor by decantation, and allowed to drain and dry. Filtering was avoided.

Preliminary Observations.—In the previous work[1,2] it was not possible to decide whether the self-formed acid which acted as stabilizing electrolyte was hexahydroxyplatinic acid or one of its dehydration products. Now, however, the indications are fairly clear that the acid in the micelle is in its most highly hydrated form, namely, $PtO_2 \cdot 4H_2O$ or $H_2Pt(OH)_6$. This is based on the following observations.

First, the weight of any one sample of the air-dried micelle varies slightly from day to day. The changes are not in one direction, but appear to follow variations in the atmospheric vapor pres-

(1) Pennycuick, THIS JOURNAL, **52**, 4621 (1930).
(2) Pennycuick, *J. Chem. Soc.*, 1447 (1930), and previous papers.
(3) Pennycuick, *Aus. J. Expll. Biol.*, **4**, 99 (1927).
(4) Pennycuick, *J. Chem. Soc.*, 2108 (1928).