are quite consistent (at least for molecules of the size of acetone and benzene). Whether the polymer is polar like cellulose nitrate or polyvinylacetate or non-polar like polystyrene and independent of the character of the diffusing molecule, diffusion is Fickian if the polymer is above its second-order transition and anomalous if the polymer–solvent mixture is below T_g. Furthermore for systems below T_g the diffusion process causes increased orientation in the direction of diffusion. This change in the character of the diffusion at T_g is undoubtedly a result of the marked change in the mobility of polymer segments which occurs at the second order transition. Presumably above T_g the polymer-penetrant system can adjust to changes in penetrant concentration with sufficient rapidity that the normal process of hole formation is the rate-determining step and hence the diffusion is Fickian. The anomalous diffusion which occurs below T_g can formally be explained by postulating that the diffusion coefficient is a function of variables other than concentration. A more specific suggestion is that, because of the low segment mobility below T_g, the diffusion coefficient does not immediately reach its equilibrium value as the penetrant concentration changes, leading to a D which depends on time as well as concentration. As Crank and Park[3] have pointed out such an added dependence of D on time can easily lead to the sort of anomalous diffusion that is observed.

ITHACA, N. Y.

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

The Conversion of Ortho–Parahydrogen by Cuprous Acetate in Quinoline[1]

BY W. K. WILMARTH AND MAX K. BARSH

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The conversion of ortho–parahydrogen by cuprous acetate in quinoline has been studied over the temperature range 60–100°. The rate of the conversion can be represented by the equation: $-d(p - \mathrm{H_2})/dt = 6.6 \times 10^{11} \exp.(-16{,}000/RT)(\mathrm{l.\ mole^{-1}\ min.^{-1}})^2(\mathrm{CuOAc})^2(\mathrm{H_2})$. It has been experimentally verified that the same activated intermediate is formed during the cuprous acetate-catalyzed hydrogenation of cupric acetate and the conversion process. This conclusion has been further substantiated by a calculation of the rate of hydrogenation from the rate constant for the parahydrogen conversion. The exchange of deuterium gas with a solution of cuprous acetate in quinoline has also been observed.

It was shown by Calvin[2] and subsequently by Wilmarth[3] that homogeneous catalytic hydrogenation of solutions of cupric acetate occurred at 100° and 38 cm. pressure, and that the autocatalytic reaction was catalyzed by one of the reduction products, the cuprous species. Other investigations by Tyson and Vivian[4a] and Fobes and Tyson[4b] on the magnetic properties of hydrogenated pyridine solutions of cupric and nickelous disalicylaldehyde, seemed to indicate that the hydrogenation of the cupric compound in pyridine solution did not involve reduction to a cuprous species, but instead involved the reduction of the salicylaldehyde to salicylyl alcohol. A comparison, however, of the similarities of the copper solution reactions in pyridine and quinoline, such as color change during hydrogenation and chemical nature of the solvent, led one to suspect that the reactions described by Calvin,[2] Wilmarth,[3] and Tyson and Vivian[4a] probably involved the same mechanism and reaction products. The possibilities that either the cuprous compounds were paramagnetic, or that the measurements of Tyson and Vivian[4a] were in error, were investigated by Wilmarth, Barsh and Dharmatti.[5]

Magnetic susceptibility measurements demonstrated that the cupric species was paramagnetic but that both the pure cuprous species and the direct hydrogenation products of the cupric species were diamagnetic. This was in contradiction to the results of Tyson and Vivian[4a] and of Fobes and Tyson,[4b] but was in substantial agreement with the conclusions of Calvin[2] and of Wilmarth.[3]

Calvin[2] also reported that ortho–parahydrogen conversion was not observed during hydrogenation with para-rich hydrogen, but that when the reduced solution was allowed to stand overnight, conversion did occur.

The main purpose of this investigation was to study the rates of conversion of ortho–parahydrogen by solutions of cuprous acetate in quinoline and, if possible, to relate the conversion process to the hydrogenation process. The latter was achieved through a study of the rate of ortho–parahydrogen conversion during and after hydrogenation, with para-rich hydrogen, of a solution of cuprous and cupric acetates in quinoline.

In addition, an exploratory study was made of the exchange of deuterium gas with a solution of cuprous acetate in quinoline.

Theoretical Considerations

In the presence of a suitable catalyst in a homogeneous system, ortho- and parahydrogen reach equilibrium as

$$(p\text{-H}_2) + \mathrm{C} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (o\text{-H}_2) + C \qquad (1)$$

where C is the concentration of the catalyst. At equilibrium the ratio of k_1 to k_2 at room temperatures is known to be 3. The rate at which the

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[1] A large portion of this investigation was carried out under Task Order IV, Contract No. N6onr-238, with the Office of Naval Research.

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

[3] W. K. Wilmarth, Ph.D. Dissertation, University of California, Berkeley, 1942.

[4] (a) G. N. Tyson, Jr., and R. E. Vivian, THIS JOURNAL, **63**, 1403 (1941); (b) M. A. Fobes and G. N. Tyson, Jr., *ibid.*, **63**, 3530 (1941).

[5] W. K. Wilmarth, M. K. Barsh and S. S. Dharmatti, *ibid.*, **74**, 5035 (1952).

p-H_2 is converted to o-H_2 can be expressed as

$$-\mathrm{d}(C_{p-\mathrm{H}_2})/\mathrm{d}t = k_1(C)(C_{p-\mathrm{H}_2}) - k_2(C)(C_{o-\mathrm{H}_2}) \quad (2)$$

Replacing hydrogen concentration by percentage of hydrogen and evaluating k_2 in terms of k_1 at room temperatures, the above equation becomes

$$-\mathrm{d}(P_{p-\mathrm{H}_2})/\mathrm{d}t = k_1C(P_{p-\mathrm{H}_2}) - \frac{1}{3}\,k_1C\,(100\text{-}P_{p-\mathrm{H}_2}) \quad (3)$$

Substituting

$$k^0 = k_1 + k_2 \quad (4)$$

into equation (3) gives

$$-\mathrm{d}(P_{p-\mathrm{H}_2})/\mathrm{d}t = k^0\,C(P_{p-\mathrm{H}_2} - 25) \quad (5)$$

Upon integration this becomes

$$\ln\,(P_t - 25)/(P_0 - 25) = \ln\,(P_t - P_\infty)/(P_0 - P_\infty) = -\,k^0Ct \quad (6)$$

where P_t, P_0 and P_∞ represent percentage p-H_2 at time t, 0 and infinity.

Farkas[6] has shown that the measured resistance of a Pirani gage containing para-rich hydrogen can be substituted directly for the percentage values in equation 6, giving

$$\ln\,(R_t - R_\infty)/(R_0 - R_\infty) = -k^0(C)t \quad (7)$$

where R_t, R_0 and R_∞ are the resistance values of the gage corresponding to the percentages of the parahydrogen at time t, 0 and infinity, and k^0 has the previously defined value. When the ortho–parahydrogen conversion occurs in a liquid phase, such as in a solution of cuprous acetate in quinoline, and the rate is followed by Pirani gage analysis of small samples extracted from the gaseous phase, a rate constant k can be determined according to the equation

$$\ln\,(R_t - R_\infty)/(R_0 - R_\infty) = -kt \quad (8)$$

It can be shown that the rate constant for conversion occurring in the solution, k^0, is related to the rate constant, k, as

$$k = [k^0(C) + k_s][aV_l/(V_g + aV_l)] \quad (9)$$

where k_s is the rate constant for the pure solvent, a is the solubility of the hydrogen in the solvent in ml./ml., V_l is the volume of the liquid phase, and V_g is the volume of the gas phase. Equations 8 and 9 are true only if the stirring is sufficiently violent that diffusion is not rate-determining.

The rate of exchange of deuterium with an exchangeable substrate in solution can also be followed by Pirani gage analysis of small samples extracted from the gaseous phase, if the experimental conditions are so chosen that the resistance reading for hydrogen deuteride is approximately the same as for normal hydrogen. Under these conditions equation 8 becomes

$$\ln\,(R_t - R_\mathrm{H})/(R_0 - R_\mathrm{H}) = -k_\mathrm{D}t \quad (10)$$

where R_0 and R_t are the Pirani gage resistance values at times 0 and t, R_H is the resistance value for normal hydrogen, and k_D is the rate constant for the exchange process corresponding to k, for the conversion process.

Experimental Procedures

A. **Materials Used.**—The quinoline for all the experiments was the end-product of several vacuum distillations of Eastman Kodak Co. synthetic quinoline, over KOH, BaO and anhydrous $Cu(OAc)_2$, respectively, through an all-glass 15-plate Oldershaw perforated plate fractionating column and multi-ratio take-off head. The resultant product boiled between 137.5 and 138.5° at 48 to 50 mm. pressure, and was collected at a ten-to-one reflux ratio after the first fraction had been discarded. The clear colorless liquid was stored in a brown, glass-stoppered bottle under nitrogen gas.

The anhydrous cupric acetate was prepared according to the directions of Spath.[7] The preparation consisted of gently heating appropriate quantities of $Cu(NO_3)_2{\cdot}3H_2O$ with acetic anhydride under a reflux condenser until the evolution of gases ceased. The crystals which precipitated on cooling were filtered and washed several times with acetic anhydride and finally with dry ether. The solid was dried in a vacuum desiccator over H_2SO_4 and NaOH. The solid was a light blue powder which did not change weight in air during an average weighing time.

Anal. Calcd.: C, 26.48; H, 3.31; Cu, 35.00. Found: C, 26.24; H, 3.25; Cu (residue), 34.18.

The anhydrous cuprous acetate had been prepared by Wilmarth[3] by the reduction in inert atmosphere of an ammoniacal solution of cupric acetate monohydrate with the acetate salt of hydroxylamine. The products of the reduction were precipitated out of glacial acetic acid, washed repeatedly with dry acetic acid and dry ether until only the pure cuprous salt remained. The product was dried under vacuum and was sealed into evacuated tubes which were to be opened just before use.

Anal. Calcd.: C, 19.57; H, 2.54; Cu, 51.9. Found: C, 19.78; H, 2.45; Cu (residue), 50.03, 49.74.

All other chemicals used were of the usual C.P. quality.

B. **Preparation of Cuprous Acetate Solutions.**—The first attempts at preparing solutions of CuOAc in quinoline by dissolving weighed amounts of anhydrous CuOAc in quinoline were abandoned; first, because of the difficulty in making the anhydrous solid salt and, second, because of the difficulty in preparing and transferring the air-sensitive solution to the reaction vessel. An alternative method was developed which avoided the necessity of preparing the cuprous salt directly. This involved the reaction of the anhydrous $Cu(OAc)_2$ with Cu metal as follows.

A weighed sample of anhydrous $Cu(OAc)_2$, a thoroughly cleaned coil of no. 24 copper wire, and the necessary amount of quinoline were added to a small narrow-neck flask having a ground joint at the neck. This flask was then attached by the joint to a side arm of an all-glass jacketed reaction vessel equipped with magnetic stirrer (see Wilmarth[5]) in such a manner that the contents of the flask would be delivered to the vessel by rotation of the flask through 180°. The contents of the flask were then degassed thoroughly under vacuum, and were heated under vacuum to about 130° by immersing and occasionally shaking the flask and contents alone in a hot oil-bath for several hours or until the reduction, as evidenced by striking color change from green to clear ruby red, had occurred. In order to prevent distillation of the quinoline into the reaction vessel during heating, a stream of cold air was directed at the neck of the flask. After the flask and contents had cooled somewhat, the flask was rotated through 180° and the solution was delivered into the reaction vessel, the copper coil being held back by the narrow neck of the flask. The flask was then sealed off from the reaction vessel. The copper coil was removed, washed several times in methanol, and weighed. From the difference in weight of the copper, the weight of the cupric salt, and the volume of quinoline added, the concentration of the solution in the reaction vessel was calculated. The concentrations were checked against analysis by electrodeposition.

C. **Preparation and Analysis of Para-rich Hydrogen.**—The preparation and analysis of para-rich hydrogen was done according to the methods of Wilmarth and Baes.[8]

D. **Ortho–Parahydrogen Conversion.**—The solution in the jacketed vessel (see section B) was first agitated with normal hydrogen at 100° (hot circulating oil in outer jacket) for several minutes to ensure the presence of only the cuprous species. The vessel and contents were cooled and

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[6] A. Farkas, *Z. physik. Chem.*, **B10**, 419 (1930).

[7] H. Spath, *Monatsh.*, **33**, 237 (1912).

[8] W. K. Wilmarth and C. F. Baes, Jr., *J. Chem. Phys.*, **20**, 116 (1952).

evacuated. Para-rich hydrogen was then introduced at 50 cm. pressure above the solution. The vessel was heated at 100.0 ± 0.04° for about 20 minutes, at which time temperature equilibrium was established. The stirrer was then started and brought immediately to 1000 r.p.m. Small samples of gas were removed periodically. The time of removal was noted. This same procedure was followed for conversion runs at 80 and 60°. Zero time is thus the time of removal of the first sample.

E. Minimum Stirring Speed Determination.—The conversion of the ortho–parahydrogen occurs in the liquid phase but the conversion rate is followed by extraction of samples of the gas phase. Therefore it is necessary that the stirring be rapid enough so that it is not the rate determining factor in the conversion process. The minimum stirring speed was determined by measuring the rate of conversion of a solution of cuprous acetate at various stirring speeds. The results indicated that for an observed half-life of 20 minutes a stirring speed of 800 r.p.m. was adequate. Accordingly all the conversion runs were stirred at 1000 r.p.m.

F. Ortho–Parahydrogen Conversion by a Solution of Cuprous and Cupric Acetates in Quinoline.—A 0.0997-g. sample of cupric acetate and 15.0 ml. of quinoline were added to the reaction vessel. A small copper coil, 5.0 ml. of quinoline and 0.0118 g. of cupric acetate were added to the small narrow-necked flask attached to the reaction vessel (see above for description of preparation of cuprous acetate). The reduction in the flask proceeded as previously described. The contents of the flask were added to the main reaction vessel and the flask was then sealed off from the system under vacuum. The vessel and contents were heated with stirring until the cupric acetate had dissolved. The resulting solution containing known amounts of cupric and cuprous acetate was cooled to 22° and para-rich hydrogen was introduced at 60 cm. pressure. The system was preheated at 100° (without stirring) for 15 minutes and then the solution was stirred at 1000 r.p.m. Small gas samples were removed periodically and the time of removal and color of the solution was noted. The samples were analyzed for their parahydrogen content and the data tabulated.

G. Deuterium Exchange with Cuprous Acetate in Quinoline.—A 6.06×10^{-2} *M* solution of cuprous acetate in quinoline was treated as described in section D above, except that deuterium was used instead of parahydrogen.

H. Solubility of Hydrogen in Quinoline.—A 35.0-g. quantity of pure quinoline was weighed into a jacketed all-glass reaction vessel attached to a 10-ml. buret and leveling bulb. The quinoline was degassed by boiling under vacuum and was then heated with stirring, until temperature equilibrium was established. Then the stirring was stopped and the hydrogen was quickly introduced at one atmosphere pressure above the solution and into the buret. Volume readings were taken as soon as possible and an initial value was obtained by extrapolation to zero time. The system was then stirred until solubility equilibrium was achieved. The stirring was stopped and final volume readings were taken. Thus the solubility was determined at 23.3, 60.0, 80.0 and 100.0°.

Results and Conclusions

The rates of conversion of ortho–parahydrogen by solutions of cuprous acetate in quinoline were measured at 60, 80 and 100° and are summarized in Table I. The values of k^0C in column 7 were calculated according to equation 9 from the rate constants, k, the values of V_1/V_g, the measured rate constant for pure quinoline,[9] k_s (equal to 0.0028), and the hydrogen solubility data[10] in Table II. The values of k^0C were plotted against the square of the corresponding cuprous acetate concentrations in column 4 of Table I, as shown in Figs. 1, 2 and 3.

TABLE I

ORTHO–PARAHYDROGEN CONVERSION BY CUPROUS ACETATE IN QUINOLINE

Run no.	Temp., °C.	Cu(OAc) Concn.[a] $\times 10^2$ *M*	(Concn.)^2 $\times 10^4$ M^2	k, min.$^{-1}$	V_1/V_g	k^0C, min.$^{-1}$
1	100.0	1.02	1.06	0.00263	0.826	0.0543
2	100.0	2.03	4.13	.00516	.826	.111
3	100.0	2.99	8.96	.0100	.826	.218
4[b]	100.0	3.24	10.5	.00663	.423	.285
5	100.0	3.87	15.0	.0176	.826	.386
6	100.0	4.24	17.9	.0219	.826	.481
7	100.0	4.77	22.8	.028	.826	.621
8	80.0	2.99	8.96	.00335	.808	.0742
9	80.0	4.27	18.3	.00604	.808	.136
10	80.0	5.25	27.6	.00877	.808	.199
11	80.0	5.81	33.8	.0110	.808	.249
12	60.0	3.03	9.19	.000745	.786	.0170
13	60.0	4.34	18.8	.01154	.786	.0381
14	60.0	5.91	35.1	.00290	.786	.0733

[a] Corrected for volume expansion of solvent. [b] From final slope of Fig. 5. See following discussion.

TABLE II

SOLUBILITY OF HYDROGEN IN QUINOLINE

Conditions: 1 amt. at 23.3°

T, °C.	Solubility, ml./ml.
100.0	0.0574
80.0	.0564
60.0	.0496
23.3	.0263

The above results indicate a second-order dependence of the conversion rate on the total concentration of the cuprous acetate. While several possible mechanisms are consistent with this concentration dependence, probably the most reasonable involves the assumptions that (1) the cuprous acetate is involved in a rapid monomer, dimer equilibrium, (2) the dimer is the active species for conversion, and (3) the concentration

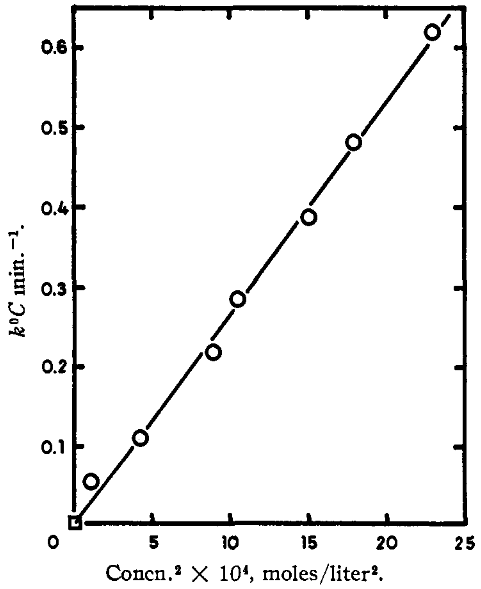

Fig. 1.—Effect of concentration on the conversion rate constants at 100.0°.

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[9] The constant was determined at 100.0°; its temperature coefficient was assumed to be negligibly small.

[10] The solubility of hydrogen in cuprous acetate solutions and in pure quinoline was assumed to be the same.

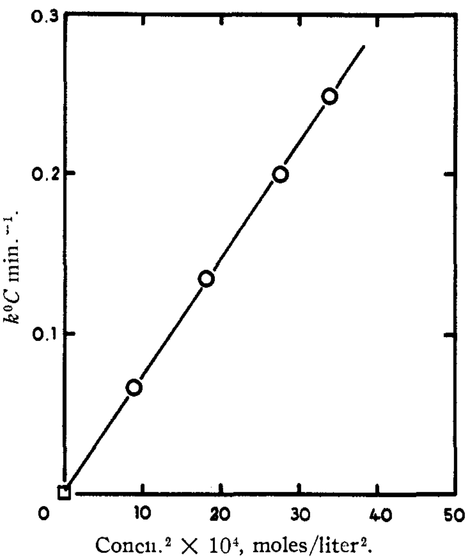

Fig. 2.—Effect of concentration on the conversion rate constants at 80.0°.

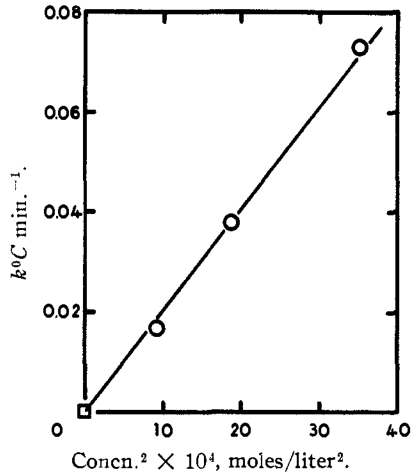

Fig. 3.—Effect of concentration on the conversion rate constants at 60.0°.

of the dimer is always small with respect to that of the monomer

$$2\text{Cu}^{\text{I}} = (\text{Cu}^{\text{I}})_2,\ (\text{Cu}^{\text{I}})_2/(\text{Cu}^{\text{I}})^2 = K \ll 1 \quad (11)$$

$$k^0C = k^0(\text{Cu}^{\text{I}})_2 = k^0K(\text{Cu}^{\text{I}})^2 \quad (12)$$

Thus the values of k^0K in Table III were obtained from the slopes of the curves in Figs. 1, 2 and 3.

Table III

Temperature Coefficients of the Rate Constants

T, °C.	k^0K	ln k^0K	$1/T°A \times 10^3$
100	267	5.589	2.68
80	72.9	4.290	2.83
60	20.5	3.021	3.00

The values of ln k^0K from Table III were plotted against $1/T$ as shown in Fig. 4. The measured slope of the curve, -8.0×10^3, yields a value of E of 16 kcal./mole, where E is the sum of E^*, the activation energy of the conversion process, and ΔH, the heat of association of the cuprous acetate monomer. However, since ΔH is probably small, $E \cong E^*$.

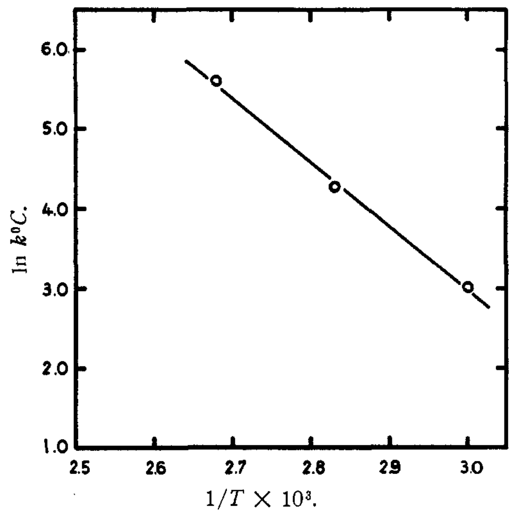

Fig. 4.—Temperature coefficient of conversion rate constants. Slope equals -8.0×10^{-3}.

Calvin[2] has postulated the following mechanism to explain the homogeneous autocatalytic hydrogenation of cupric acetate in quinoline: a slow rate-determining activation of the hydrogen molecules by some form of the cuprous species followed by a rapid reaction between the activated hydrogen and the cupric acetate. The above is most simply expressed by the equations[11]

$$n\text{Cu}^{\text{I}} + \text{H}_2 \underset{k_2'}{\overset{k_1'}{\rightleftarrows}} (\text{Cu}^{\text{I}})_n\cdot\text{H}_2 \quad (13)$$

$$(\text{Cu}^{\text{I}})_n\cdot\text{H}_2 + 2\text{Cu}^{\text{II}} \xrightarrow{k_3'} (n+2)\text{Cu}^{\text{I}} + 2\text{H}^+ \quad (14)$$

where $k_3' \gg k_2' \gg k_1'$.

The above implies that the rate-determining step in the hydrogenation of cupric acetate in the presence of the cuprous acetate is the same as that in the ortho–parahydrogen conversion. If this is true then cuprous acetate should cause no conversion during the hydrogenation of cupric acetate with para-rich hydrogen. However, a slow rate of conversion[12] would be produced by the paramagnetic cupric acetate (all paramagnetic substances catalyze the conversion).

An experiment to verify the above predictions (see experimental section F) was performed and the

Table IV

Ortho–Parahydrogen Conversion during and after Hydrogenation of Cupric Acetate in Quinoline, T = 100°

Time, min.	$\dfrac{R_t - R_\infty}{R_0 - R_\infty}$	$\log_{10} \dfrac{R_t - R_\infty}{R_0 - R_\infty}$	Color of soln.
0.0	1.00	2.30	Green
24.5	0.968	2.27	Yellow-green
45.6	.939	2.24	Muddy green
61.7	.923	2.22	Orange-red
74.8	.904	2.20	Red
104.7	.735	1.99	Red
150.0	.536	1.68	Red

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[11] Since cuprous and cupric acetates are probably negligibly ionized but appreciably solvated in quinoline, any reference to either only indicates its existing valence state in solution.

[12] Exploratory experiments indicated that the rate of conversion by cupric acetate would be approximately 1/10 the rate of that by the cuprous acetate under comparable conditions.

results are shown in Table IV. The data plotted in Fig. 5 are shown in columns one and three. The rate constants *k*, as defined in equation 8, which were determined from the initial and final slopes of the curve, are 0.0014 and 0.00663, respectively. It should be pointed out that a new zero time should have been chosen for the evaluation of the final slope. However, when this was done it gave a slope not significantly different from the one plotted. The results clearly establish the identity of the rate-determining steps of the conversion and the hydrogenation processes.

Since the hydrogenation and the conversion processes occur through a common mechanism one should also be able to calculate the rate of hydrogenation from the known conversion rate at the same concentration and temperature. The rate of absorption of hydrogen in terms of the rate constant, *k*, can be shown to be

$$\text{ml./min.} = V_l'k(1 + V_g/aV_l)a \qquad (15)$$

where V_l' is the volume of the solution phase in the hydrogenation reaction and the other terms have their previously designated meanings. Since, under the experimental conditions used, the following was true

$$V_g/aV_l > 1 \qquad (16)$$

equation 15 simplifies to

$$\text{ml./min.} = V_l'k(V_g/V_l) \qquad (17)$$

The above equation was evaluated at a cuprous concentration of 3.8×10^{-2} *M* at V_l/V_g equal to 0.826 with the aid of the data of Table I, columns 5 and 6, and was compared with observed hydrogenation data. The results are: calcd. rate of absorption of H_2, 1.11 ml./min.; obsd. rate of absorption of H_2, 1.05 ml./min. While the agreement is well within the experimental error of the data at this concentration range (0 to 0.04 *M* in CuOAc), comparisons at higher concentrations are not as satisfactory. This will be discussed in more detail in a later publication.

In his discussion of the hydrogen activation, Calvin[2] has suggested that the cuprous acetate dimer has a ring structure similar to that formed by the acid in non-polar solvents and in the gas phase. Here the bridging would have to be through the cuprous atoms instead of through the hydrogen atoms. The activation can then be visualized as an interaction of each copper atom with an atom of the hydrogen molecule. Complete cleavage of the hydrogen molecule would formally require copper–hydrogen bonds of 44 cal./mole.[13] Actually this calculation is somewhat uncertain since electron promotion would presumably be required to open the full d shell of electrons in the cuprous ion, but some energy might be regained through metal–metal interaction across the ring. In support of this mechanism it should be noted that the nickel atom, which is isoelectronic with the cuprous ion, forms a gaseous hydride NiH, with a dissociation energy of approximately 60 kcal./mole.[14] Furthermore there is some experimental evidence that the copper atoms in the cuprous acetate dimer can form additional bonds since a compound whose empirical formula,[15] $(CuOAc)_2 \cdot CO \cdot (quinoline)_x$, is precipitated if a quinoline solution of cuprous acetate is saturated with carbon monoxide. If one accepts the copper–hydrogen bond mechanism involving the cleavage of the hydrogen molecule, it is evident that a reversal of this process would result in ortho–parahydrogen conversion. In addition, the copper–hydrogen bonds might be chemically reactive enough to account for reduction of cupric acetate.

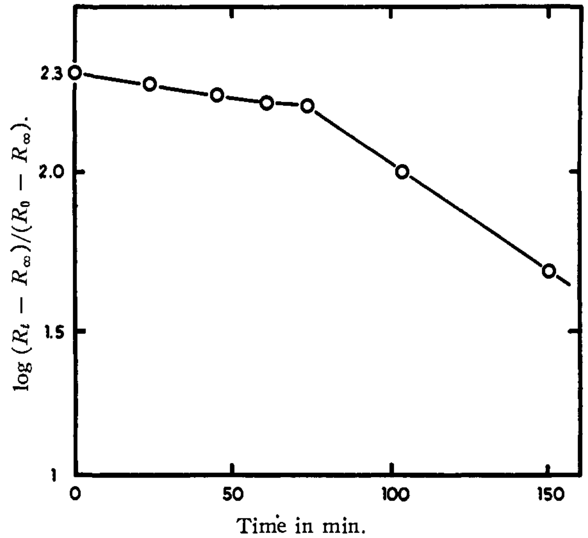

Fig. 5.—Ortho–parahydrogen conversion during and after hydrogenation of cupric acetate at 100.0°.

In a recent publication, Wender[16] has reported another example of a homogeneous catalytic hydrogenation. He concluded that $[Co(CO)_4]_2$ acted as such a catalyst in the hydrogenation of butyraldehyde. A chain mechanism involving $Co(CO)_4H$ and hydrogen atom was postulated[17] although no evidence was presented. Such a mechanism would not be entirely ruled out in our case although, in the hydrogenation experiments, the usual tests for a chain reaction were negative. In addition, such a mechanism requires a metal–hydrogen bond twice as strong as the one we have postulated in the rate-determining step.

Copper–hydrogen bonds such as we have postulated might be expected to be quite reactive chemically and perhaps it is not too surprising to find that when deuterium was substituted for hydrogen, exchange was found to occur with either the acetate groups or the quinoline solvent. The rate of exchange appears to be of the same order of magnitude as the parahydrogen conversion and hence the possibility exists that it is an integral part of the conversion mechanism.[18] As an alternate to the

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[13] This value is 1/2 the difference between the dissociation energy of the hydrogen molecule and the measured activation energy for the conversion process.

[14] A. G. Gaydon, "Dissociation Energies," Dover Publishing, Inc., New York, N. Y., 1945, p. 212.

[15] Calculated from the stoichiometry of the reversible absorption of CO by a solution of cuprous acetate in quinoline at 100.0° and 1 atm. pressure (unpublished work).

[16] I. Wender, THIS JOURNAL, **72**, 4842 (1950).

[17] I. Wender, R. Levine and M. Orchin, *ibid.*, **72**, 4375 (1950).

[18] Dr. Sol Weller of the Houdry Process Corporation has indicated, in a private communication, that the deuterium exchange occurs only in the presence of trace impurities in the solvent.

previous mechanism one might assume that the hydrogen molecule adds to the double bond in the quinoline ring. Since the cuprous atoms are probably solvated by the basic nitrogen atoms of the quinoline, a catalytic addition might occur although the exact mechanism is somewhat difficult to visualize. Such a partially hydrogenated quinoline would be expected to be thermodynamically unstable and a reversal of the formation would account for both the parahydrogen conversion and the deuterium exchange.

LOS ANGELES, CALIF.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Stabilities of +4 and +5 Oxidation States of the Actinide Elements—the Np(IV)-Np(V) Couple[1] in Perchloric Acid Solution

BY L. B. MAGNUSSON AND J. R. HUIZENGA

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Equilibria in the reaction Np(IV) + Fe(III) = Np(V) + Fe(II) in perchlorate solutions were measured with hydrogen reference electrodes. The apparent equilibrium constant is inversely dependent on the fourth power of the hydrogen ion concentration. The formal potential of the reaction $Fe^{+3} + {}^1/_2H_2 = Fe^{+2} + H^+$ is 0.738 v. in 1 molar perchloric acid at 25°. The heat of reaction is −9.7 kcal. The formal potential of the reaction $NpO_2^+ + {}^1/_2H_2 + 3H^+ = Np^{+4} + 2H_2O$ in 1 molal perchloric acid is 0.7423 v. at 25°. The heat of reaction is −35.3 kcal. Consideration of disproportionation reactions for the +4 and +5 oxidation states of uranium, neptunium and plutonium leads to the prediction that the stability of the X^{+4} ion will decrease and the stability of the XO_2^+ ion will increase with increasing temperature. The extinction coefficient of the 723 mμ absorption band of Np(IV) decreases with increasing temperature.

As in the rare earths the properties of the +3 aqueous ions of the heaviest elements appear to differ only slightly and in a regular manner along the series.[2,3] The common occurrence of three higher oxidation states in the heavy element series poses the problem of the degree of similarity to be expected for these higher states. Heats and free energies of reactions relating +3, +4 and +6 states are known but no information was available at the time of this work on the thermal stability of a +5 state. From the practical point of view the disproportionation stabilities of the +4 and +5 states as functions of temperature were unknown.

To obtain a value for the relative entropy of a +5 state which would be useful with other data for predictions of approximate thermal stabilities, ΔH and ΔF for the reaction

$$Np(V) + {}^1/_2H_2 = Np(IV) + H^+ \qquad (1)$$

were determined in an e.m.f. cell. The stable ion of the +4 state is probably Np^{+4} in perchloric acid solution. If the +5 state is NpO_2^+, the complete form of reaction (1) should be

$$NpO_2^+ + {}^1/_2H_2 + 3H^+ = Np^{+4} + 2H_2O \qquad (2)$$

Preliminary to the heat of reaction determination, the predicted third power hydrogen ion dependence for reaction (2) was tested experimentally. Early work indicated that the Np(IV)–Np(V) couple does not establish an accurately measurable equilibrium at an inert metal electrode.[4] Reversible potential measurements with a hydrogen reference electrode were obtained in the present work in solutions containing Np(IV), Np(V), Fe(II) and Fe(III) ions in oxidation–reduction equilibrium. Equilibration times were known from previous kinetic data.[5] The concentration ratios at equilibrium were calculated from e.m.f. and spectrophotometric data. As a check on the e.m.f. apparatus the ΔH for the reaction

$$Fe^{+3} + {}^1/_2H_2 = Fe^{+2} + H^+ \qquad (3)$$

was obtained from potentiometric titrations at 15, 25 and 35°.

Experimental

E.m.f. Cell.—Ground glass stopcocks were sealed to the bottoms of two 15-ml. centrifuge tubes. The tubes were connected through the stopcocks by a short section of Tygon tubing for equalizing the liquid levels in the tubes.

The hydrogen electrode was fabricated from glass tubing, a one-hole rubber stopper and a strip of 1 mil platinum foil platinized at one end. The platinum strip was rolled along its length forming a semi-cylinder on a short piece of glass tubing with the platinized end projecting beyond the end of the tubing. The strip and tubing were held securely in the stopper. The stopper served as a closure for the hydrogen compartment of the cell as well as a support for the platinum electrode and hydrogen inlet. A glass sleeve surrounding the platinum and tubing was sealed to the assembly just below the stopper with Apiezon W. In operation the lower, open end of the sleeve was submerged in the electrolyte so that a portion of the platinized foil was exposed alternately to hydrogen and electrolyte as the gas bubbled from the end of the sleeve. The rubber stopper was slotted to vent the hydrogen. Tank electrolytic hydrogen was passed through a Deoxo purifier and presaturated with water vapor from a perchlorate solution of the same composition as that in the cell before the hydrogen entered the cell.

The two compartments of the cell with connecting tube were partially immersed in a water thermostat to a depth such that the water level was several centimeters above the level of electrolyte in the cell. The e.m.f. measurements were found to be independent of the depth of immersion with this arrangement. Bath temperatures were determined with a thermometer calibrated by the National Bureau of Standards.

The solution to be measured was placed in the open compartment of the cell. The stopcock below this compartment was greased only at the ends of the plug permitting electrical contact in the closed position through the thin film of electrolyte surrounding the plug. A platinum wire, wrapped on a glass stirring rod held in the chuck of a stir-

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[1] Presented in part before the Division of Nuclear Chemistry, XII International Congress of Pure and Applied Chemistry, New York, N. Y., September, 1951.

[2] K. Street, Jr., and G. T. Seaborg, THIS JOURNAL, **72**, 2790 (1950).

[3] S. G. Thompson, B. B. Cunningham and G. T. Seaborg, *ibid.*, **72**, 2798 (1950).

[4] J. C. Hindman, L. B. Magnusson and T. J. LaChapelle, *ibid.*, **71**, 687 (1949).

[5] J. R. Huizenga and L. B. Magnusson, *ibid.*, **73**, 3203 (1951).