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Medium Effects in the Homogeneous Catalytic Activation of Molecular Hydrogen by Metal Salts. I. Cupric and Cuprous Heptanoates in Heptanoic Acid[1]

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The kinetics of the hydrogen reduction of cupric heptanoate ($CuHp_2$) to the cuprous salt were examined in heptanoic acid solution over the temperature range 125 to 155°. The reaction is homogeneous, and proceeds autocatalytically, the rate law at low cuprous heptanoate concentrations being, $-d[H_2]/dt = k_1[H_2][CuHp_2] + k_2[H_2][CuHp]$, where $k_1 = 1.4 \times 10^{13} \exp[-30{,}200/RT]$ and $k_2 = 1.0 \times 10^{10} \exp[-21{,}000/RT]$ M^{-1} sec.$^{-1}$. The two rate constants were identified with separate reaction paths, in which the rate-determining steps involve the heterolytic splitting of H_2 by $CuHp_2$ and CuHp, respectively, giving rise to unstable hydride intermediates which react rapidly with $CuHp_2$ or other reducible substrates such as quinone With increasing cuprous heptanoate concentration, the kinetic dependence of the Cu(I)-catalyzed reaction on the total Cu(I) concentration, was found to shift from first toward one-half order. This was attributed to association of CuHp to form an inactive dimer. Sodium heptanoate was found to decrease the rate of reaction, apparently by forming inactive higher cupric and cuprous heptanoate complexes. The deuterium isotope effect and exchange reaction were also examined and found to be consistent with the proposed mechanism.

Introduction

The homogeneous reduction of cupric salts by molecular hydrogen previously has been examined in two solvent systems, (i) aqueous solutions[2,3] and (ii) organic amines especially quinoline.[4] Profound differences in the kinetics and mechanisms of the reaction in the two types of solvents were noted. Perhaps the most striking is the observation, as yet unexplained, that in aqueous solution hydrogen is activated by Cu(II) but not by Cu(I) while the reverse is the case for the amine solvents.

To obtain further insight into this phenomenon, the study of hydrogenation of cupric salts has been extended to other solvent systems notably carboxylic acids and hydrocarbons, the latter being considered as approaching most closely to a truly inert medium. The present paper describes a kinetic study of the hydrogenation of cupric heptanoate in heptanoic acid solution. Since heptanoic acid is one of the products of the reaction, its choice as solvent minimizes complications such as have been encountered in earlier related studies,[4c] due to medium changes as reaction proceeds. The results are reported in some detail since they differ significantly from those for both solvent systems examined earlier. Subsequent papers in this series describe studies involving other cupric and cuprous salts and other solvents, as well as some related studies on silver and mercuric salts. The heptanoate salts of these several metals did not react detectably with hydrogen in heptanoic acid solution at temperatures of up to 150°: Fe(III), Ce(IV), Co(II), Ni(II), Cd(II).

Experimental

Materials.—Heptanoic acid (HHP), an Eastman white label product, was purified by distillation, b.p. 220–221°. Sodium heptanoate (NaHp) was prepared by neutralizing a solution of reagent grade sodium hydroxide with heptanoic acid, washing with benzene and drying at 110°. Cupric heptanoate ($CuHp_2$) was prepared by mixing in stoichiometric proportions, concentrated aqueous solutions of cupric sulfate and sodium heptanoate; the precipitated product was recrystallized from 1,2-dichloroethane and dried at 100°. 2,2′-Biquinoline (cuproin), an Eastman white label product, was purified by vacuum sublimation. Hydrogen, obtained from Canadian Liquid Air Co., was passed through a "deoxo" catalytic purifier and dried over P_2O_5. Deuterium was obtained from the Stuart Oxygen Co. and similarly purified. Mass spectrometric analysis showed it to contain 0.7% HD.[5]

Kinetic Measurements.—The reaction kinetics were followed by measuring the volume of hydrogen gas taken up at constant pressure using conventional apparatus and techniques.[6] The reaction vessel and gas buret were separately thermostated, the former in a silicone bath maintained at the reaction temperature (±0.08°), the latter in a water-bath maintained at 30.0 ± 0.05°. Prior to commencing the reaction, the solution was dehydrated by heating at about 145° under reduced pressure and degassed by repeated freezing and melting under vacuum. The shaking rate of the reaction vessel generally exceeded 250 cycles per minute and this, combined with the use of small volumes of solution in a relatively large vessel (~2 ml. in 30–50 ml.) with an indented surface, ensured absence of physical control (*i.e.*, due to slow dissolution of hydrogen).

Deuterium Exchange.—Deuterium exchange measurements involved removing samples of the gas into evacuated bulbs, connected through stopcocks to the apparatus just above the reaction vessel. Following removal of each sample, the apparatus was refilled with D_2 to atmospheric pressure. The gas samples were analyzed mass-spectrometrically.[5] However, because the volume of gas replaced through the removal of each sample was not accurately known and because of the likelihood of non-uniform gas composition throughout the apparatus (the reaction vessel and gas buret being connected by a considerable length of capillary), the results are only of semi-quantitative significance.

Solubility of Hydrogen.—The same apparatus was used to measure the solubility of hydrogen in heptanoic acid at various temperatures. After a known volume of heptanoic acid was equilibrated with H_2 at about 150 mm. pressure, shaking was stopped and the pressure of H_2 increased to some new value. Shaking then was resumed and the amount of gas taken up to saturation was determined. By this procedure it was also possible to measure the rate of solution of H_2 and thus establish directly that the reaction under any given set of conditions was free from physical control.

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[1] Support of this work through grants from the Research Corporation and the National Research Council of Canada is gratefully acknowledged.

[2] R. G. Dakers and J. Halpern, *Can. J. Chem.*, **32**, 969 (1954).

[3] E. R. Macgregor and J. Halpern, *Trans. Met. Soc. A.I.M.E.*, **212**, 244 (1958).

[4] (a) M. Calvin, *Trans. Faraday Soc.*, **34**, 1181 (1938); THIS JOURNAL, **61**, 2230 (1939); (b) S. Weller and G. A. Mills, *ibid.*, **75**, 769 (1953); L. Wright and S. Weller, *ibid.*, **76**, 3345 (1954); L. Wright, S. Weller and G. A. Mills, *J. Phys. Chem.*, **59**, 1060 (1955); (c) M. Calvin and W. K. Wilmarth, THIS JOURNAL, **78**, 1301 (1956); W. K. Wilmarth and M. Barsh, *ibid.*, **78**, 1305 (1956).

[5] We are grateful to Dr. E. W. C. Clarke for this and other mass spectrometric analyses reported in this paper.

[6] J. L. Bolland, *Proc. Roy. Soc. (London)*, **A186**, 218 (1946); A. J. Chalk and J. F. Smith, *Trans. Faraday Soc.*, **53**, 1214 (1957).

Spectra.—Spectra of cupric heptanoate solutions were recorded with a Cary Model 14 spectrophotometer.

All data were corrected for changes in density with temperature.

Results and Discussion

1. Stoichiometry and Kinetics.—Typical rate plots depicting the uptake of hydrogen by solutions containing various initial concentrations of $CuHp_2$ are shown in Fig. 1. The reaction occurring is

$$2CuHp_2 + H_2 \longrightarrow 2CuHp + 2HHp \qquad (1)$$

At the reaction temperatures, CuHp is soluble in HHp and stable with respect to disproportionation. Completion of reaction 1 (at which point the initially blue solutions are clear and colorless) is marked by a sharp break in the rate plot, followed by a much slower reduction of CuHp to Cu

$$2CuHp + H_2 \longrightarrow 2Cu + 2HHp \qquad (2)$$

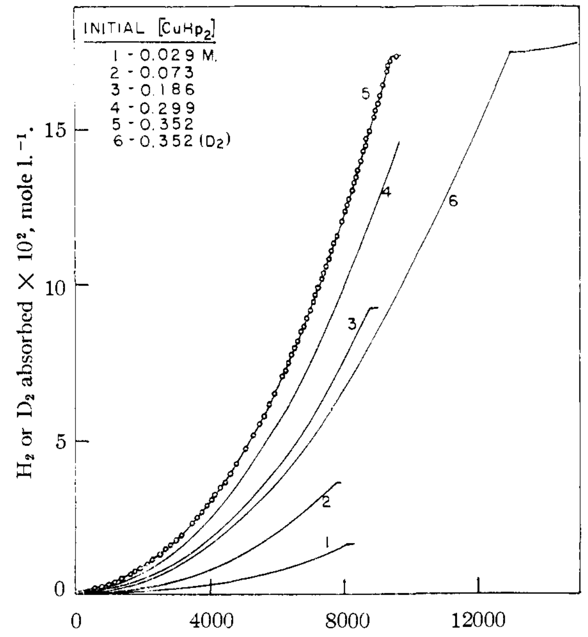

Fig. 1.—Absorption of hydrogen by solutions of cupric heptanoate in heptanoic acid at 145°, 700 mm. H_2. (Experimental points shown only for one plot.)

Reaction 1 was unaffected by the addition of glass wool, by varying the volume of solution or of the reaction vessel, and was clearly homogeneous in character.

The essential features of the kinetics are revealed by the rate-extent plots[7] shown in Figs. 2 and 3. These differ markedly from the kinetics in aqueous solutions[2,3] but bear some resemblance particularly in respect of the autocatalytic nature of the reaction and the sharp breaks in the rate plots, to the behavior observed in quinoline solutions.[4] As in the latter case the autocatalysis is attributed to activation of hydrogen by Cu(I). However, there are also important differences between the two systems including (i) the finite initial rates in heptanoic acid due to activation of hydrogen by Cu(II), and (ii) the kinetic dependence on Cu(I) which is second order in quinoline but (at least at low Cu(I) concentrations, see Fig. 2) close to first order in heptanoic acid; (the apparent departure from first-order dependence at higher Cu(I) concentrations, reflected in the curvature of the rate-extent plot in Fig. 3, will be discussed later).

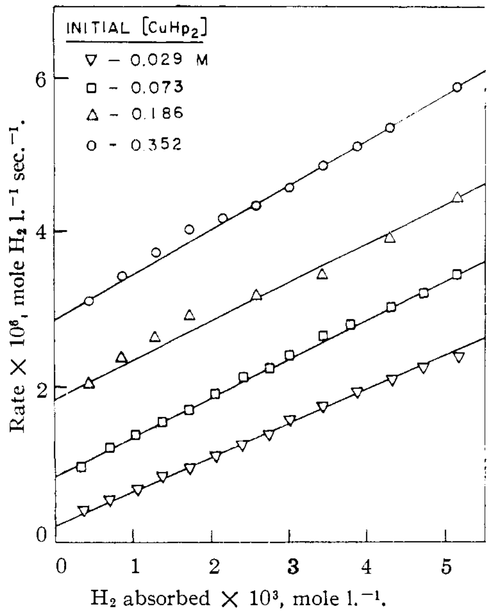

Fig. 2.—Initial variation of the rate with extent of reaction (145°, 700 mm. H_2).

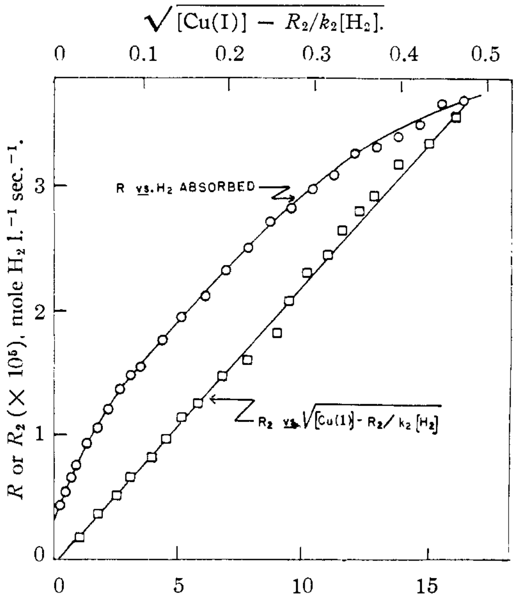

Fig. 3.—Variation of the rate with the extent of reduction of 0.352 *M* $CuHp_2$ at 145°, 700 mm. H_2.

The kinetic behavior in heptanoic acid is interpreted in terms of the rate law

$$-d[H_2]/dt = R_1 + R_2 = k_1[H_2][CuHp_2] + k_2[H_2][CuHp] \qquad (3)$$

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[7] The points in these plots represent instantaneous rates determined by drawing tangents to the rate plots at various times and are precise to within ±5%. In determining rates by this method it is essential that the individual points on the rate plots be very accurate and closely spaced. The present procedure which gives nearly continuous rate plots is very satisfactory from this standpoint.

where R_1 and R_2 are the rates due to the activation of H_2 by $CuHp_2$ and CuHp, respectively. Introducing the stoichiometry relation

$$[\mathrm{CuHp_2}] + [\mathrm{CuHp}] = [\mathrm{CuHp_2}]_0 \qquad (4)$$

the rate law becomes

$$-\mathrm{d}[\mathrm{H_2}]/\mathrm{d}t = k_1[\mathrm{H}]_2[\mathrm{CuHp_2}]_0 + (k_2 - k_1)[\mathrm{H_2}][\mathrm{CuHp}] \qquad (5)$$

The initial linear portions of the rate-extent plots in Fig. 2 are in accord with this, and their intercepts and slopes, in conjunction with values of $[H_2]$ computed from the solubility data in Table II, yield the values of k_1 and k_2 which are listed in Table I. Within the limits of experimental scatter, these show no systematic variation over a twenty-five-fold variation in $[CuHp_2]_0$ and a threefold variation in $[H_2]$.

Table I

Variation of the Initial $CuHp_2$ Concentration and the H_2 Partial Pressure at 145°

$[CuHp_2]_0$, M	P_{H_2}, atm.	Initial rate $\times 10^6$, M sec.$^{-1}$	Initial slope[a] $\times 10^4$, sec.$^{-1}$	$k_1 \times 10^3$, M^{-1} sec.$^{-1}$	$k_2 \times 10^2$, M^{-1} sec.$^{-1}$
0.014	0.92	0.15	6.4	2.9	8.9
.045	.92	.43	7.4	2.5	10.2
.073	.92	.69	7.4	2.5	10.2
.097	.92	1.0	7.4	2.9	10.2
.146	.92	1.3	6.2	2.3	8.6
.186	.92	1.8	5.6	2.7	7.8
.225	.92	2.1	5.0	2.4	7.0
.299	.92	2.3	6.0	2.1	8.4
.352	.92	2.8	6.2	2.2	8.6
.029	.25	0.08	1.3	2.7	7.0
.029	.56	.16	2.6	2.3	6.1
.029	.73	.17	4.5	2.1	7.9
.029	.92	.24	5.0	2.3	7.0

[a] Of plot of rate *vs.* H_2 absorbed.

2. Dimerization of Cuprous Heptanoate.—The curvature of the rate-extent plots, beyond the initial region (Fig. 3), corresponding to an apparent decrease in k_2 as the reaction proceeds and cuprous heptanoate accumulates, is attributed to association of cuprous heptanoate to form an inactive dimer

$$2\mathrm{CuHp} \rightleftharpoons (\mathrm{CuHp})_2 \qquad (6)$$

whence

$$[(\mathrm{CuHp})_2]/[\mathrm{CuHp}]^2 = K \qquad (7)$$

and

$$[\mathrm{Cu(I)}] = [\mathrm{CuHp}] + 2[(\mathrm{CuHp})_2] \qquad (8)$$

These expressions, in conjunction with the rate law

$$R_2 = k_2[\mathrm{H_2}][\mathrm{CuHp}] \qquad (9)$$

yield the relation

$$\sqrt{[\mathrm{Cu(I)}] - R_2/k_2[\mathrm{H_2}]} = (\sqrt{2K}/k_2[\mathrm{H_2}])R_2 \qquad (10)$$

In accord with this, the kinetic data for each experiment yielded a linear plot, such as that shown in Fig. 3, of $\sqrt{[\mathrm{Cu(I)}] - R_2/k_2[\mathrm{H_2}]}$ *vs.* R_2. The slopes of these plots showed a slight systematic dependence on the initial $CuHp_2$ concentration, reflected in values of the dimerization constant, K, ranging from 19.5 M^{-1} at $[CuHp_2]_0 = 0.045$ M to 11.0 M^{-1} at $[CuHp_2]_0 = 0.35$ M. This is attributed to a medium effect and is in the expected direction.

3. Effect of Temperature.—Kinetic measurements and hydrogen solubility data over the temperature range 125 to 155° are summarized in Table II. The values of k_1 and k_2 gave good Arrhenius plots fitted by

$$k_1 = 1.4 \times 10^{13} \exp[-30{,}200/RT]\ M^{-1}\,\mathrm{sec.}^{-1} \qquad (11)$$

and

$$k_2 = 1.0 \times 10^{10} \exp[-21{,}000/RT]\ M^{-1}\,\mathrm{sec.}^{-1} \qquad (12)$$

respectively. The corresponding heats and entropies of activation are listed in Table II. $\Delta S_1^{\ddagger}$ appears to lie just above and $\Delta S_2^{\ddagger}$ just below the normal range of entropy values (approximately −5 to −10 e.u.) for simple bimolecular reactions in solution.

Table II

Summary of Kinetic and Related Data

Temp., °C.	H_2 solubility $\times 10^3$, M atm.$^{-1}$	$k_1 \times 10^3$, M^{-1} sec.$^{-1}$	$k_2 \times 10^2$, M^{-1} sec.$^{-1}$	K, M^{-1}
125	3.8	0.36	2.7	15.3
135	3.9	0.92	5.3	12.6
145	4.0	2.3	9.0	11.0
155	4.1	5.3	17.6	9.3
ΔH^0 or $\Delta H^{\ddagger}$ (kcal./mole)	1.0	29.4	20.2	−5.6
ΔS^0 or $\Delta S^{\ddagger}$ (e.u.)		−1	−15	−8.9

Values of the dimerization constant K, listed in Table II, show an inverse temperature dependence. The corresponding thermodynamic parameters are of the order expected for an association reaction in solution and lend support to the interpretation given.

4. Catalytic Hydrogenation of Substrates.—Further evidence that cupric heptanoate activates hydrogen was provided by its ability to catalyze the hydrogenation of substrates such as benzoquinone or ferric heptanoate when these were present in the solution. In each case the normal autocatalytic reaction was preceded by an initial stage during which hydrogen was taken up at a constant rate approximating to the initial rate in the absence of substrate. During this stage, hydrogen was being activated by cupric heptanoate but consumed in the reduction of substrate. Since there was no change in the cupric heptanoate concentration and no cuprous heptanoate was formed, the rate remained constant. At low quinone concentrations (<0.003 M) the amount of hydrogen taken up prior to onset of autocatalysis was approximately equivalent to the quinone (Table III); at higher concentrations, however, reduction of the cupric heptanoate itself commenced prior to complete reduction of the quinone. This discrepancy was even more marked with ferric heptanoate and implies that the reduction potentials of the substrate and of cupric heptanoate do not differ greatly.

Similar catalysis of the reduction of substrates by hydrogen has been demonstrated for cupric salts in aqueous solution[8] and for cuprous salts in quinoline solution.[4]

5. Effect of Cuproin.—It was considered of interest to examine the effect of cuproin (2,2′-

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(8) E. Peters and J. Halpern, *Can. J. Chem.*, **33**, 356 (1955); **34**, 551 (1956); *J. Phys. Chem.*, **59**, 793 (1955).

biquinoline) on the course of the reaction in view of the very stable chelate complexes which this reagent is known to form with cuprous ions. In this connection, it has been reported[9] that cuproin inhibits cupric-catalyzed autoxidation reactions by forming an inactive complex with the cuprous intermediate. Similarly, inhibition of autocatalysis might be anticipated in the present case.

An experiment was made in which 0.10 *M* cuproin was added to a solution containing initially 0.144 *M* $CuHp_2$ and the resulting rate-extent plot is shown in Fig. 4. Quantitative interpretation of the results is complicated by the fact that the reduction potential of Cu(II) is lowered by cuproin (due to stabilization of Cu(I) by complexing) to the point where there is some accompanying autoreduction of $CuHp_2$ by heptanoic acid and the reaction with hydrogen is therefore not stoichiometric. However the qualitative significance of the results is fairly clear. The higher initial rate reflects enhanced reactivity of $CuHp_2$ due to complexing with cuproin. In the first stages of the reaction, all the Cu(I) formed combines with cuproin to form an inactive complex, probably $Cu^I(cuproin)_2$; hence the rate decreases as reaction proceeds and attains a minimum value at the point (↑) when all the cuproin is consumed in this way. The subsequent increase in rate is attributable to accumulation of a reactive lower Cu^I-cuproin complex.

TABLE III

CATALYTIC HYDROGENATION OF SUBSTRATES

Initial $[CuHp_2]$, *M*	Substrate	Initial rate $\times 10^7$, *M* sec.$^{-1}$	H_2 absorbed by substrate,[a] *M*
0.073	Nil	6.9	....
.073	0.0010 *M* quinone	9.5	0.0009
.073	.0025 *M* quinone	10.8	.0022
.073	.0051 *M* quinone	8.3	.0028
.073	.015 *M* quinone	6.5	.005
.073	.032 *M* quinone	5.0	.008
.058	Nil	5.0	....
.058	0.009 *M* $FeHp_3$	6.0	0.001
.058	.016 *M* $FeHp_3$	4.3	.001
.058	.048 *M* $FeHp_3$	6.2	.004

[a] Prior to onset of autocatalysis.

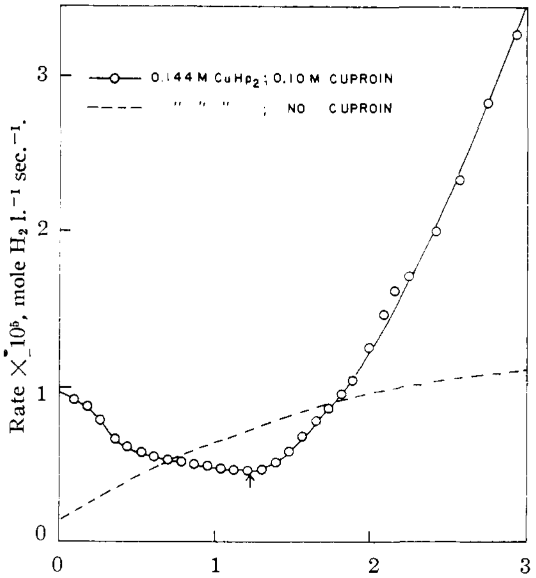

Fig. 4.—Effect of cuproin on reduction of cupric heptanoate (145°, 700 mm. H_2).

6. Effect of Sodium Heptanoate.—Addition of sodium heptanoate was found to lower both the initial rate and that due to Cu(I)-autocatalysis, as shown in Fig. 5. These effects are attributable to the formation of higher cupric and cuprous heptanoate complexes which are inactive in the reaction.

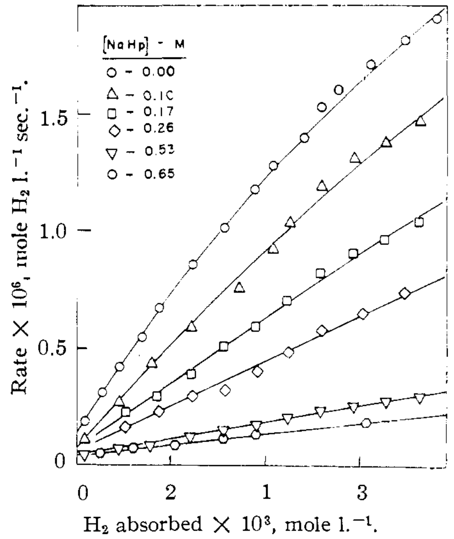

Fig. 5.—Effect of sodium heptanoate on the hydrogenation of 0.014 *M* $CuHp_2$ (145°, 700 mm. H_2).

The dependence of the rate on the sodium heptanoate concentration reduces to a simple form if it is assumed that in each case only a single complex is formed. In the case of cuprous heptanoate, if the composition of the complex is Na_nCuHp_{n+1}, its concentration is governed by the equilibrium relation

$$[NaCuHp_{n+1}]/[NaHp]^n[CuHp] = K' \quad (13)$$

which in combination with equation 9 leads to a dependence of R_2 on [NaHp], of the form

$$[Cu(I)]/R_2 = 1/k_2[H_2] + K'[NaHp]^n/k_2[H_2] \quad (14)$$

Values of $[Cu(I)]/R_2$ were obtained from the initial slopes of the rate-extent plots and plotted against $[NaHp]^n$ for various values of *n*. A good linear plot was obtained for $n = 2$, implying that the inactive complex is Na_2CuHp_3. The slope and intercept of this plot (8.1×10^4 M^{-2} sec. and 4.6×10^3 sec., respectively) through equation 14 yield a value of 17.6 M^{-2} for K'. However this behavior is not very sensitive to the exact nature of the complexing equilibrium, and the possibility cannot be excluded that instead of a single inactive complex, a mixture of complexes of average complexity number $n + 1$ is involved.

Unfortunately, in the presence of sodium heptanoate, the initial rates are too low for accurate estimation and therefore the above treatment could not be applied to R_1. However some indi-

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[9] R. Flitman and E. Frieden, THIS JOURNAL, **79**, 5198 (1957).

cation of the complexes formed by Cu(II) can be obtained from a spectral examination of the solutions. The absorption spectrum of $CuHp_2$ in heptanoic acid (curve 1 in Fig. 6) has a main peak at 6800 Å., as well as a smaller peak at 3800 Å., close to the long wave length limit of the charge transfer band. Both peaks were found to obey Beer's law, indicating that they are due to the principal species in the solution rather than to a minor dissociation or association product in equilibrium with it. Furthermore, the intensities of both peaks are reduced by sodium heptanoate to limiting values (at [NaHp] > 0.2 M) corresponding to curve 2 in Fig. 6. The dependence of the height of the 6800 Å. peak on the sodium heptanoate concentration is depicted in Fig. 9. It seems reasonable to interpret this change in terms of a complexing equilibrium similar to that suggested for CuHp, *i.e.*

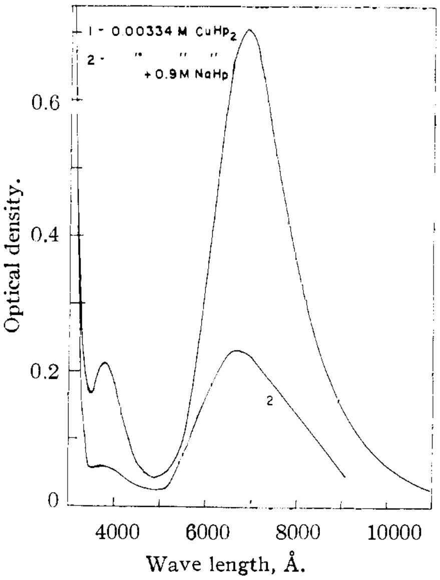

Fig. 6.—Absorption spectra of cupric heptanoate in heptanoic acid.

$$CuHp_2 + n\ NaHp \rightleftharpoons Na_nCuHp_{n+2} \quad (15)$$

and to identify the initial and limiting optical densities D_0 and D_∞ with $CuHp_2$ and Na_nCuHp_{n+2}, respectively. On this assumption, the dependence of the optical density (D) on the sodium heptanoate concentration can be shown to be of the form

$$(D_0 - D)^{-1} = \{K''(D_0 - D_\infty)\}^{-1}[NaHp]^{-n} + (D_0 - D_\infty)^{-1} \quad (16)$$

where K'' is the equilibrium constant for reaction 15. The best linear plot of $(D_0 - D)^{-1}$ *vs.* $[NaHp]^{-n}$, shown in Fig. 7, was again obtained for $n = 2$, suggesting that the limiting complex is Na_2CuHp_4. The slope and intercept of this plot yield a value of $4 \times 10^2\ M^{-2}$ for K''.

It should be emphasized that the spectral measurements and conclusions based on them refer to room temperature. However, it is reasonable to expect qualitatively similar behavior under reaction conditions.

7. Deuterium Isotope Effect and Exchange.—Both k_1 and k_2 were reduced when D_2 was used instead of H_2 (Fig. 1), the kinetic isotope effect (k_H/k_D) at 145° being in each case 1.4. This is of the same order as the isotope effect for the activation of hydrogen by cuprous acetate in quinoline[4] and is consistent with a mechanism involving splitting of the hydrogen molecule in the rate-determining step, although it does suggest, as might be expected in view of the relatively low activation energies, that hydrogen is still bound strongly in the transition state.

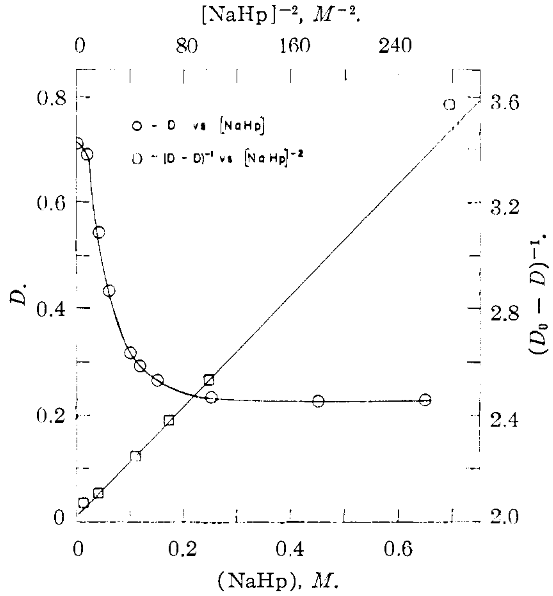

Fig. 7.—Effect of sodium heptanoate on the optical density (D) at 6800 Å. of 0.00334 M $CuHp_2$ in heptanoic acid.

The data in Table IV show that there was very little formation of HD by exchange of D_2 with HHp in these experiments until the reduction of $CuHp_2$ to CuHp had proceeded to completion. Beyond this point, exchange occurred with a rate comparable to that of the preceding reduction reaction (because of the experimental limitations noted earlier only a rough comparison is possible). These results are analogous to those reported for cuprous acetate in quinoline solution[4] and demonstrate (i) that no back reaction leading to the regeneration of hydrogen occurs in the presence of the $CuHp_2$ and (ii) that following reduction of the $CuHp_2$ activation of hydrogen by CuHp continues but that the hydride intermediate formed, instead of

Table IV

HD Formation during Reduction of 0.35 M $CuHp_2$ at 145°

Expt.	Time × 10^{-3}, sec.	Extent of reduction of $CuHp_2$,[a] %	HD in gas sample, %[b]
1	12.3	90	0.7
	16.1	100+	17
2	10.5	62	1.8
	12.5	88	1.5
	12.9	93	1.6
	13.3	100	1.3
	14.0	100+	3.8
	17.2	100+	9.7

[a] Reduction to CuHp complete in each experiment at about 13000 sec. [b] Corrected for HD(0.7%) originally present in deuterium gas.

being oxidized, undergoes back-reaction to regenerate hydrogen. The fact that the initial exchange product is HD rather than H_2 suggests that D_2 is split heterolytically in the activation process.

8. **Mechanism of the Reaction.**—All these observations can be accommodated by the mechanisms shown, in which it is required that $k_3 > k_1$ and $k_4, k_3 > k_{-2} > k_2, k_5$.

Path I (uncatalyzed reduction of $CuHp_2$)

$$CuHp_2 + H_2 \xrightarrow{k_1} (CuH)Hp + HHp \quad (17)$$

$$(CuH)Hp + CuHp_2 \xrightarrow{k_3} 2CuHp + HHp \quad (18)$$

Path II (CuHp-catalyzed reaction)

$$CuHp + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CuH + HHp \quad (19)$$

$$CuH + CuHp_2 \xrightarrow{k_4} (CuH)Hp + CuHp \quad (20)$$

$$(CuH)Hp + CuHp_2 \xrightarrow{k_3} 2CuHp + HHp \quad (18)$$

$$CuH + CuHp \xrightarrow{k_5} 2Cu + HHp \quad (21)$$

Exchange proceeds through the reversal of reaction 19 and is thus inhibited by $CuHp_2$ which oxidizes CuH rapidly and irreversibly (reactions 20 and 18). Reaction of CuH with HHp leading to regeneration of H_2 (or HD) is faster than the reaction with CuHp in which metallic copper is formed. The latter is, however, thermodynamically favored and does proceed slowly with some autocatalytic tendency, presumably due to heterogeneous catalysis of step 21 by metallic copper. In contrast to this behavior, metallic copper forms readily when cupric salts are reduced in aqueous solution.[3] This is attributable in part at least to the higher equilibrium constant for the cuprous disproportionation reaction, as a result of which copper deposition occurs while the cupric concentration in the solution remains fairly high.

The above mechanism for the uncatalyzed reaction (Path I) is analogous to that demonstrated for the hydrogen reduction of cupric salts in aqueous solution.[3] On the other hand, the mechanism of the CuHp-catalyzed reaction differs from that found earlier[4] for cuprous acetate in quinoline, particularly in respect of the homolytic splitting of hydrogen in the latter case. A special feature of the present system, in relation to those examined earlier, is the demonstration of the simultaneous activation of hydrogen by both the cupric and cuprous salts. The significance of this and other aspects of solvent comparison are considered further in a subsequent paper.[10]

9. **Nature of the Species in Solution.**—Probably the chief uncertainty arising in the interpretation of these kinetics is that relating to the nature of the species present in the solution. Far less is known about the nature of metal salts in non-polar solvents than in aqueous solution and in view of this, the assumptions that have been made that cupric and cuprous heptanoate are present in these solutions predominantly as the undissociated mononuclear molecules $CuHp_2$ and CuHp, and that these are the active species, require some further comment.

Dissociation of either salt into ions is very unlikely in view of the low dielectric constant of heptanoic acid; the fact that essentially similar behavior has been observed[10] in completely nonpolar solvents such as octadecane and biphenyl further reinforces the view that it is also unimportant in this solvent. (Even in aqueous solution the tendency of cupric acetate to dissociate is known to be small.[11]) Similarly it seems reasonable to represent the higher complexes which are formed in the presence of sodium heptanoate, as the undissociated sodium salts.

The possibility of dimerization or association is, however, more difficult to discount since the general tendency of metal alkanoate salts, including those of copper(II), to associate in non-polar solvents is well known. It should, however, be pointed out that many cases of such association have been demonstrated at low temperatures[12] and would be less favored in the temperature range (125–155°) of the present investigation.

In the case of cuprous heptanoate, the kinetics provide indirect information about the dimerization equilibrium which proceeds to a moderate degree ($K \sim 15$) under the conditions of the reaction, and it is fairly clear that the active species is the monomer which predominates at concentrations below about 0.05 *M*. The fact that a dimer is formed in this system but is inactive is of interest in view of evidence[4] favoring a dimer of cuprous acetate rather than the monomer as the catalytically active species in quinoline solution.

The evidence concerning the nature of the reactive species in the case of cupric heptanoate is less conclusive. The first-order kinetic dependence on cupric heptanoate over a wide concentration range (0.014 to 0.35 *M*) implies that a single species predominates over this whole range and that this is the reactive species (or alternatively that reactivity is unaffected by association). In view of the high temperatures involved and because cupric heptanoate is not likely to be associated to a greater degree than the more polar cuprous salt, it is considered probable that this species is the monomer rather than dimer. This would also bring the mechanism of the reaction of cupric heptanoate into line with those of the kinetically analogous reactions of cupric acetate and other cupric alkanoates in aqueous solution.

At variance with this conclusion is the small absorption band exhibited by cupric heptanoate in the region of 3800 Å. (Fig. 6). This band is not exhibited by cupric salts in aqueous solution but has been observed for a number of cupric salts in nonpolar solvents and attributed[12,13] to a dimeric species. However, because of some uncertainty concerning this assignment and because the spectral measurements refer to room temperature, this evidence is also inconclusive. Unfortunately attempts to determine the apparent molecular

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weight of cupric heptanoate ebulliometrically under conditions approaching more closely to those of the reaction and thus gain direct information on this point failed to yield results of meaningful accuracy.

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Medium Effects in the Homogeneous Catalytic Activation of Molecular Hydrogen by Metal Salts. II. Anion and Solvent Effects for Cupric and Cuprous Salts[1]

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The kinetics of the hydrogen reduction of a number of cupric carboxylate salts were examined using various hydrocarbons and carboxylic acids as solvents. In each case the reaction was found to be autocatalytic, reflecting activation of hydrogen by the cuprous as well as the cupric salt. Correlations of reactivity with solvent polarity and anion basicity are examined and interpreted.

Introduction

This paper describes further measurements on the hydrogen reduction of cupric salts in nonpolar media. Earlier studies[2] on cupric heptanoate in heptanoic acid have been extended to other solvents and to cupric salts of other organic acids.

Experimental

Cupric heptanoate was prepared as described earlier.[2] The other cupric salts were prepared by the same method except for cupric naphthalene-2-sulfonate which was prepared by treating cupric carbonate with an aqueous solution of 2-naphthalenesulfonic acid, filtering, recrystallizing from water and drying at 110°. All other reagents and solvents were Eastman white label products and were used without further purification except for heptanoic acid which was redistilled, and biphenyl, which was dissolved in benzene passed through an alumina column to remove polar impurities, followed by removal of the benzene by evaporation.

Kinetic measurements and determinations of hydrogen solubility were made using the apparatus and procedure described earlier.[2] At 145° the solubilities of hydrogen in heptanoic acid and biphenyl were found to be 0.0040 and 0.0026 M atm.$^{-1}$, respectively.

Results

The copper salts of a number of aliphatic and aromatic acids were examined particularly with a view to correlating the rates with solvent polarity and with the basicity of the anion. Unfortunately many of the systems tried proved unworkable either because the solubility of the salt was too low or because it was unstable in the temperature range (135 to 155°) required for reaction. The following results reflect these limitations.

1. **Effect of Solvent.**—The reduction of cupric heptanoate was examined in octadecane and in biphenyl. The rate plots shown in Fig. 1 and the rate-extent plots in Fig. 2 are very similar to those for heptanoic acid and, in the initial stages of the reaction, conform to the rate law

$$-d[H_2]/dt = k_1[H_2][CuHp_2] + k_2[H_2][CuHp] \quad (1)$$

Values of k_1 and k_2 obtained from the slopes and intercepts of the rate-extent plots are listed in Table I. Data for Cu^{++} and for cupric propionate in aqueous solution[3,4] are listed for comparison. Since similar results were obtained[4] for several cupric alkanoate salts in aqueous solution, the comparison between cupric propionate and heptanoate here should reflect principally a medium, rather than an anion, effect.

The similarity of the kinetic behavior in biphenyl, octadecane and heptanoic acid reinforces the view that the latter also acts essentially as an inert solvent for this reaction. The rate-extent plots in octadecane (Fig. 2) show markedly greater curvature than in heptanoic acid, probably due to enhanced dimerization of cuprous heptanoate. An experiment in biphenyl containing 10% heptanoic acid ($[HHp]/[CuHp_2] \sim 2$) gave results intermediate between those for the two solvents. Preferential solvation of cupric heptanoate is indicated by the observation that the initial rate is closer to that in heptanoic acid, than in biphenyl, despite the predominance of the latter.

TABLE I

COMPARISON OF THE REACTIVITIES OF CUPRIC AND CUPROUS SALTS IN VARIOUS SOLVENTS AT 145°

System[a]	$k_1 \times 10^3$, M^{-1} sec.$^{-1}$	$k_2 \times 10^2$, M^{-1} sec.$^{-1}$	k_2/k_1	$\Delta H_1^‡$, kcal./mole	$\Delta S_1^‡$, e.u.
$CuHp_2$ in HHp	2.3	9.0	40	29.4	− 1
$CuHp_2$ in biphenyl	6.2	16.0	26	..	..
$CuHp_2$ in 90% biphenyl + 10% HHp	3.1	13.6	44	..	..
$CuHp_2$ in octadecane[b]	2.4	7.5	31	..	..
$CuPr_2$ in water	200[c]	Not detected	$\ll 1$	24.0	− 5
Cu^{++} in water	2.0[c]	Not detected	$\ll 1$	25.8	−10

[a] Anion designations: Hp^--heptanoate; Pr^--propionate. [b] Solubility of H_2 assumed to be equal to that in heptanoic acid. [c] Extrapolated from data[4,5] over the temperature range 80 to 120°.

Perhaps the most significant trend indicated by the results in Table I, to which further reference will be made, is the marked decrease in k_1 and correspondingly large increase in the ratio k_2/k_1, in going from water to the less polar solvents. The one hundred-fold difference between k_1 for $CuPr_2$ in aqueous solution and that for $CuHp_2$ in heptanoic acid is accounted for by an increase of some 5 kcal./mole in the activation energy.

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