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.

VANCOUVER, B. C., CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA]

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

BY A. J. CHALK AND J. HALPERN

RECEIVED APRIL 22, 1959

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 non-polar 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]/[$CuHp_2$] ~ 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	ΔH_1,‡ kcal./mole	ΔS_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	≪1	24.0	− 5
Cu^{++} in water	2.0[c]	Not detected	≪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.

---

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

(2) A. J. Chalk and J. Halpern, THIS JOURNAL, **81**, 5846 (1959).

(3) E. Peters and J. Halpern, *J. Phys. Chem.*, **59**, 793 (1955).

(4) E. Peters and J. Halpern, *Can. J. Chem.*, **34**, 554 (1956).

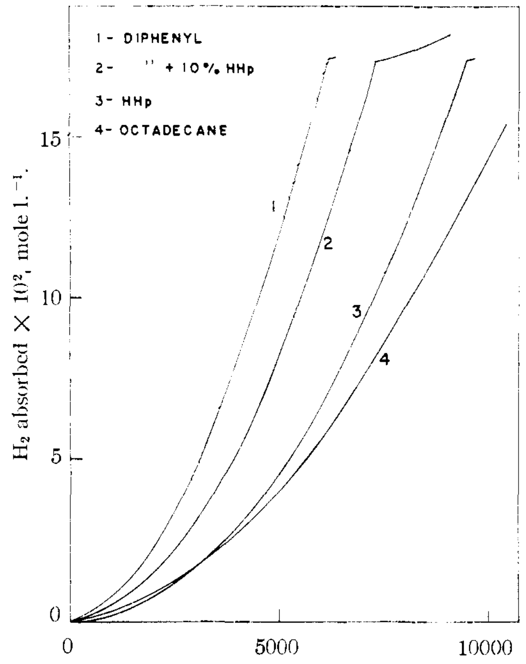


Fig. 1.—Reduction of 0.35 *M* $CuHp_2$ in various solvents at 145°, 700 mm. H_2.

2. **Anion Effects.**—It was considered that the effect of anion variation could best be studied by comparing the hydrogenation of a series of cupric salts of different acids in a given inert solvent such as biphenyl. Unfortunately, solubility and stability considerations referred to earlier imposed severe limitations on the scope of such a study and only a few salts proved suitable for this purpose. The kinetic results for these, as well as for two salts compared in heptanoic acid, are summarized in Table II. In general, the kinetics in each case were similar to those already described for cupric heptanoate, *i.e.*, the reduction of the cupric to the cuprous salt was autocatalytic giving rise to initially linear rate-extent plots from whose intercepts and slopes, rate constants k_1 and k_2, analogous to those defined by equation 1, could be evaluated.

TABLE II

COMPARISON OF REACTIVITIES OF COPPER SALTS OF VARIOUS ANIONS AT 145°

Solvent	Anion	pKa of acid[a]	$k_1 \times 10^3$, M^{-1} sec.$^{-1}$	$k_2 \times 10^2$, M^{-1} sec.$^{-1}$	k_2/k_1
Biphenyl	Heptanoate	4.9	6.2	16.0	26
Biphenyl	*o*-Toluate	3.9	8.0	13.8	17
Biphenyl	*m*-Chlorobenzoate	3.8	10.0	8.5	8.5
Heptanoic acid	Heptanoate	4.9	2.3	9.0	40
Heptanoic acid	Naphthalene-2-sulfonate	~1	4.8	2.1	4.4

[a] At 25° in aqueous solution.

To the extent that the limited data in Table II reveal any trend, it is that k_2 increases and k_1 decreases with the basicity of the anion (as measured by the pK_a of the corresponding acid in aqueous solution).

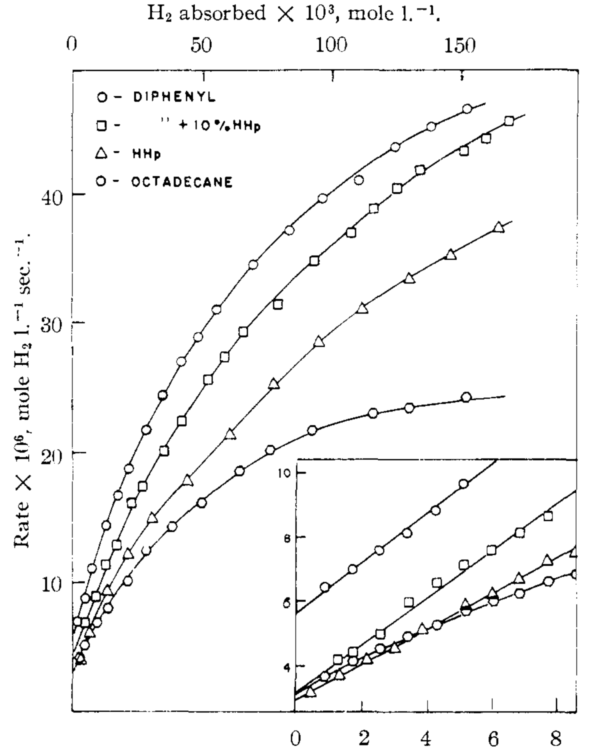


Fig. 2.—Reduction of 0.35 *M* $CuHp_2$ in various solvents at 145°, 700 mm. H_2. Insert shows initial portions of plots on enlarged scale.

The hydrogenation of several other cupric salts (cinnamate, benzoate, *o*-toluate) was examined using in each case the corresponding acid as solvent. Because the solubilities of hydrogen were not known, only pseudo-rate constants $k_1[H_2]$ and $k_2[H_2]$ could be evaluated for these systems. For cupric cinnamate at 155° these are 3.6×10^{-6} and 3.4×10^{-4} sec.$^{-1}$ ($k_2/k_1 = 94$) and for cupric *o*-toluate at 135°, 2.3×10^{-6} and 1.2×10^{-4} sec.$^{-1}$ ($k_2/k_1 = 52$). For cupric benzoate in benzoic acid, only $k_2[H_2]$ could be evaluated (7.1×10^{-4} sec.$^{-1}$ at 155°). These values are all close to those for cupric heptanoate in heptanoic acid and the minor variations among them do not show any significant trend.

Discussion

Unfortunately, because of the experimental limitations noted earlier, the range of systems for which quantitative kinetic data could be obtained is not as extensive as was hoped for and therefore, for some of the results at least, only a tentative interpretation can be given.

Significance is attached to two observations arising from this work, (i) the large decrease in the reactivity of the cupric salt (k_1) and corresponding increase in k_2/k_1, in going from water to non-polar solvents, and (ii) the inverse dependence of k_1 and direct dependence of k_2, in non-polar solvents, on the basicity of the anion. In the case of k_1 this trend is the reverse of that observed in aqueous solution.[5]

This pattern can be interpreted in terms of the proposed mechanism[2] involving the heterolytic

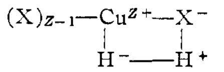
---

[5] J. Halpern, *J. Phys. Chem.*, **63**, 398 (1959).

splitting of H_2 as the rate-determining process, *i.e.*

$$CuX_Z + H_2 \longrightarrow (CuH)X_{Z-1} + HX \qquad (2)$$

where X^- represents the anion and $Z = 2$ for Cu(II) and 1 for Cu(I). It has been suggested[5] that the activation process in reactions of this type involves heterolytic stretching of the Cu–X and H–H bonds and incipient formation of covalent Cu–H and H–X bonds, the configuration of the activated complex resembling



$$\begin{array}{ccc}(X)_{Z-1}\text{—}Cu^{Z+} & \text{—} & X^- \\ | & & | \\ H^- & \text{——} & H^+\end{array}$$

This implies an inverse dependence of the rate on the Cu–X bond strength and direct dependence on the H–X bond strength. It is to be expected that both of these will increase with the basicity of X^- and, depending on which predominates, the effect of the latter on the rate may therefore be in either direction.

The inverse dependence of k_1 and direct dependence of k_2 on the basicity of X^- can be accounted for in these terms, as the strength of the Cu–X bond and its variation with X will clearly be greater for Cu(II) than for Cu(I). Furthermore the electrostatic charge separation associated with the stretching of the Cu–X bond will also be greater for Cu(II) than Cu(I), suggesting that k_1 should decrease more than k_2 in going from a polar solvent such as water to a non-polar one. This is in accord with the results in Table I and with related observations on silver and mercuric salts.[6]

Finally attention should be directed to the marked contrast between the behavior of the cuprous salts in these systems and that observed by Calvin and other workers for cuprous acetate in quinoline.[7] Activation of hydrogen in the latter system is of second order in the cuprous salt and presumably involves homolytic splitting. In the case of silver salts both types of mechanisms have been observed in aqueous solution[8] but, not surprisingly, homolytic splitting is favored only in the absence of a basic ligand (or solvent molecule) needed to stabilize the proton released by heterolytic splitting; this would hardly explain the behavior of cuprous acetate in quinoline. Furthermore the behavior found in quinoline does not appear to extend to the closely related solvents pyridine and dodecylamine where the activation of hydrogen was reported[9] to be first order in cuprous acetate suggesting, as in the systems described here, heterolytic splitting. These differences remain to be explained.

---

(6) A. J. Chalk, J. Halpern and A. C. Harkness, THIS JOURNAL, **81**, 5854 (1959).

(7) M. Calvin, *Trans. Faraday Soc.*, **34**, 1181 (1938); THIS JOURNAL, **61**, 2230 (1939); S. Weller and G. A. Mills, *ibid.*, **75**, 769 (1953); W. K. Wilmarth and M. Barsh, *ibid.*, **78**, 1305 (1956).

(8) A. H. Webster and J. Halpern, *J. Phys. Chem.*, **61**, 1239, 1245 (1957).

(9) L. Wright, S. Weller and G. A. Mills, *ibid.*, **59**, 1060 (1955).

VANCOUVER, B. C., CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA]

Medium Effects in the Homogeneous Catalytic Activation of Molecular Hydrogen by Metal Salts. III. Silver and Mercuric Salts[1]

BY A. J. CHALK, J. HALPERN AND A. C. HARKNESS

RECEIVED APRIL 22, 1959

The kinetics of the hydrogen reduction of silver and mercuric heptanoates have been examined using heptanoic acid and biphenyl, respectively, as solvents. In each case the reaction is homogeneous and of first order each in hydrogen and in the metal salt. The second-order rate constants for the two reactions, determined over the temperature ranges 86–108° and 160–190°, respectively, are given by $k_{AgHp} = 1.1 \times 10^{11} \exp[-18.700/RT]$ and $k_{HgHp_2} = 2.0 \times 10^8 \exp[-21,700/RT]$ M^{-1} sec.$^{-1}$. The results are compared with those obtained earlier for the reduction of silver and mercuric salts in aqueous solution.

Introduction

This paper describes kinetic studies of the homogeneous reduction, by molecular hydrogen, of silver and mercuric heptanoates in heptanoic acid and biphenyl solution. Of related interest are earlier studies on the homogeneous activation of hydrogen by cupric and cuprous salts in these solvents,[2] by mercuric salts in aqueous solution[3] and by silver salts in aqueous solution[4] and in pyridine.[5]

Experimental

Silver heptanoate was precipitated by mixing aqueous solutions of silver nitrate and sodium heptanoate. Mercuric heptanoate was prepared similarly from mercuric chloride and sodium heptanoate. Both precipitates were washed thoroughly with water and dried over P_2O_5 *in vacuo*. The source and purification of the other reagents and the apparatus and procedure used in the kinetic measurements were described previously.[3]

Results

1. Hydrogen Solubility.—The hydrogen solubility data, determined as described earlier[2] and used in the subsequent kinetic calculations, are listed in Table I.

2. Silver Heptanoate.—This salt was found to be substantially insoluble in biphenyl and kinetic measurements were confined to heptanoic acid solutions.

---

(1) Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research. Support in part through grants from the Research Corporation and the National Research Council of Canada is also gratefully acknowledged.

(2) A. J. Chalk and J. Halpern, THIS JOURNAL, **81**, 5846, 5852 (1959).

(3) G. J. Korinek and J. Halpern, *J. Phys. Chem.*, **60**, 285 (1956); *Can. J. Chem.*, **34**, 1372 (1956).

(4) A. H. Webster and J. Halpern, *J. Phys. Chem.*, **61**, 1239 1245 (1957).

(5) (a) L. Wright, S. Weller and G. A. Mills, *ibid.*, **59**, 1060 (1955); (b) W. K. Wilmarth and A. F. Kapauan, THIS JOURNAL, **78**, 1308 (1956).