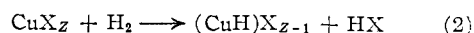
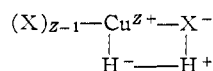


splitting of H₂ as the rate-determining process, *i.e.*



where X⁻ represents the anion and Z = 2 for Cu(II) and 1 for Cu(I). It has been suggested⁶ 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



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 solution⁸ 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 reported⁹ to be first order in cuprous acetate suggesting, as in the systems described here, heterolytic splitting. These differences remain to be explained.

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(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 Salts¹

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 $k_{\text{AgHep}} = 1.1 \times 10^{11} \exp[-18,700/RT]$ and $k_{\text{HgHep}_2} = 2.0 \times 10^8 \exp[-21,700/RT]$ 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 solution³ and by silver salts in aqueous solution⁴ and in pyridine.⁵

(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).

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 P₂O₅ *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 earlier² 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.

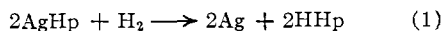
(5) (a) L. Wright, S. Weller and G. A. Mills, *ibid.*, **59**, 1060 (1955);

(b) W. K. Wilmarth and A. F. Kapauan, *THIS JOURNAL*, **78**, 1308 (1956).

TABLE I
SOLUBILITY OF H₂

Solvent	Temp., °C.	H ₂ solubility × 10 ⁴ , M atm. ⁻¹
Heptanoic acid	86	3.3
Heptanoic acid	93	3.4
Heptanoic acid	100	3.5
Heptanoic acid	108	3.6
Heptanoic acid	120	3.7
Biphenyl	160	2.1
Biphenyl	170	2.2
Biphenyl	180	2.3
Biphenyl	190	2.3

Reaction with hydrogen was measurable above 80° and conformed to reduction of silver heptanoate to metallic silver



Typical rate plots depicting the uptake of hydrogen and the corresponding decrease of the silver heptanoate concentration are shown in Fig. 1. The reaction is seen to be first order in silver heptanoate and there is no evidence of appreciable autocatalysis due to the precipitated silver metal even after 95% reaction. The complete rate law was found to be

$$-d[\text{H}_2]/dt = k[\text{H}_2][\text{AgHp}] \quad (2)$$

Values of k , listed in Table I, are seen to be substantially independent of the AgHp concentration and the H₂ partial pressure over a considerable range of each and unaffected by addition of 0.5 M NaHp. Furthermore there is no kinetic evidence of a dimerization equilibrium such as was observed for CuHp.²

TABLE II

REDUCTION OF SILVER HEPTANOATE IN HEPTANOIC ACID			
Temp., °C.	P _{H₂} , atm.	Initial [AgHp], M	k , M ⁻¹ sec. ⁻¹
108	0.98	0.044	2.12
108	.98	.030	2.13
108	.98	.027	2.17 ^a
108	.98	.018	2.08
108	.98	.009	1.70
108	.36	.018	1.97
100	.98	.033	1.15
93	.98	.023	0.72
93	.98	.008	0.75
86	.98	.009	0.43

^a 0.5 M sodium heptanoate added.

Kinetic measurements over the temperature range 86 to 108° (Table I) yielded a good Arrhenius plot fitted by

$$k = 1.1 \times 10^{11} \exp [-18,700/RT] M^{-1} \text{sec.}^{-1} \quad (3)$$

The kinetic parameters for this system together with corresponding kinetic data for silver salts in other solvents are listed, for purposes of comparison, in Table III.

Solubility considerations preclude comparison of the reactivities of the same silver salt in different solvents of widely varying polarity. However, where different carboxylate salts of the same metal ion (Cu⁺⁺ or Hg⁺⁺) have been compared in aqueous solution, the reactivity generally has been little affected by the chain length of the

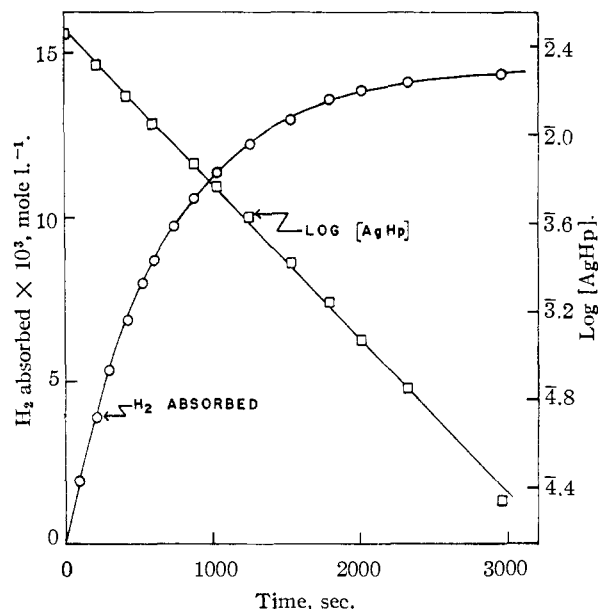


Fig. 1.—Reduction of 0.03 M silver heptanoate in heptanoic acid at 108°, 750 mm. H₂.

carboxylic acid.^{3,6} Hence it seems reasonable to assume (as has been done previously for cupric salts²) that the comparison involving AgHp and AgAc in Table III reflects principally the effect

TABLE III

KINETIC DATA FOR THE ACTIVATION OF HYDROGEN BY SILVER AND MERCURIC SALTS^a

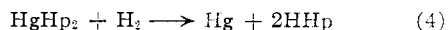
System	k , ^b M ⁻¹ sec. ⁻¹	ΔH^\ddagger , kcal./mole	ΔS^\ddagger , e.u.
Ag ⁺ in water ⁵	6.3×10^{-4}	23.3	-5.5
AgAc in water ⁵	9.0×10^{-2}
AgHp in HHp	1.2×10^{-1}	18.0	-10.4
AgAc in pyridine ⁶	4.9×10^{-1}	12.0	-25.4
Hg ⁺⁺ in water ⁴	3.3	17.4	-12.5
HgAc ₂ in water ⁴	1.4×10^{-1}	18.7	-14.8
HgHp ₂ in HHp	3.0×10^{-3}
HgHp ₂ in biphenyl	1.9×10^{-4}	20.8	-22.9

^a Anion designations: Ac⁻, acetate; Hp⁻, heptanoate. ^b Data for silver salts are at 70° and for mercuric salts at 120°, the only temperatures common to all the systems in each group.

of solvent variation. In this case it is of interest to note that the reactivities of the carboxylate salts show relatively little solvent dependence, k being of the same order in heptanoic acid, pyridine and aqueous solution. These values of k are however greater, by a factor of more than a hundred, than for the corresponding path (*i.e.*, that first order in Ag⁺) involving the uncomplexed Ag⁺ ion in aqueous solution. This difference appears to be reflected chiefly in the activation energy (the similar reactivities of AgHp in HHp and AgAc in pyridine however are due apparently to compensating variations in ΔH^\ddagger and ΔS^\ddagger) and is attributed to the higher basicity of the carboxylate ion relative to water and consequent stabilization of the proton released when hydrogen undergoes heterolytic splitting.

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

3. **Mercuric Heptanoate.**—The reaction of mercuric heptanoate with hydrogen was examined both in biphenyl and in heptanoic acid solution. In each case the reduction product was metallic mercury according to



The reaction was found to be slow, and temperatures in excess of 120° were required for kinetic measurements. At these temperatures there was some auto-reduction of the mercuric salt (possibly due to heptanoate ion or the solvent itself) and this interfered with the study of the hydrogenation reaction to completion. For example in a typical experiment in biphenyl, carried to completion, although the mercury metal recovered was equivalent to the initial mercuric heptanoate, the total hydrogen uptake was only about half the stoichiometric equivalent. Under these circumstances the relation between the HgHp_2 concentration and the H_2 uptake as reaction proceeds was uncertain and kinetic interpretation beyond the early stages of reaction, difficult. Kinetic measurements therefore were confined to initial rates of H_2 uptake (generally extending over about 5% reaction) and identified with the known initial HgHp_2 concentration. This procedure appeared to be reliable.

Most of the measurements were made in biphenyl since, despite the higher temperatures required, the complications described above were less severe in this solvent than in heptanoic acid. The linearity of the H_2 uptake rate plots, shown in Fig. 2,

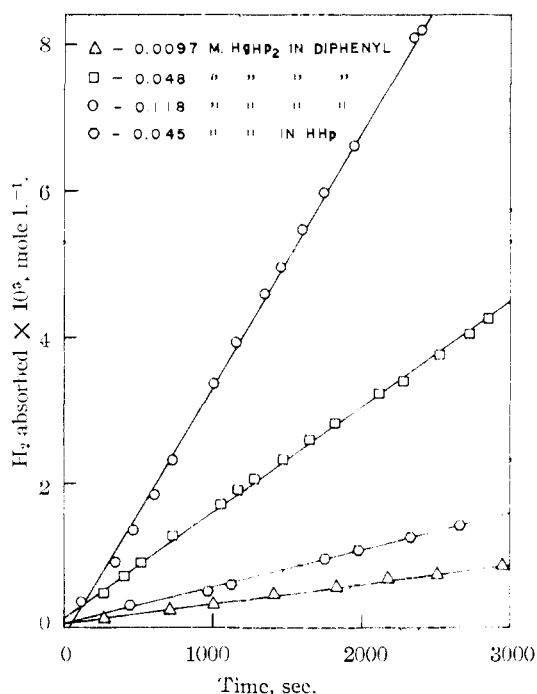


Fig. 2.—Reduction of mercuric heptanoate in biphenyl (190° 610 mm. H_2) and in heptanoic acid (120°, 750 mm. H_2).

is consistent with the assumption that the HgHp_2 concentration does not change appreciably over the extent of reaction depicted. The complete rate law was found to be

$$-d[\text{H}_2]/dt = k[\text{H}_2][\text{HgHp}_2] \quad (5)$$

and values of k at 190°, listed in Table IV, show no trend with variation of the initial HgHp_2 concentration between 0.01 and 0.1 M and of the H_2 partial pressure between 0.34 and 0.81 atm. Addition of 0.067 M NaHp was also without effect on k . Rate measurements over the temperature range 160 to 190° (Table IV) yielded a good Arrhenius plot for k , fitted by

$$k = 2.0 \times 10^8 \exp[-21,700/RT] M^{-1} \text{sec.}^{-1} \quad (6)$$

A few values of k , determined in heptanoic acid at 120°, also are listed in Table IV. The kinetics in this solvent were similar to those in biphenyl but because of greater interference from side reactions are considered of lesser accuracy, and no attempt was made to extend these measurements to other temperatures.

TABLE IV
REDUCTION OF MERCURIC HEPTANOATE

Solvent	Temp., °C.	P_{H_2} , atm.	Initial $[\text{HgHp}_2]$, M	$k \times 10^2$, $M^{-1} \text{sec.}^{-1}$
Biphenyl	190	0.81	0.118	11.8
Biphenyl	190	.81	.048	12.7
Biphenyl	190	.81	.052	10.7 ^a
Biphenyl	190	.81	.0097	11.9
Biphenyl	190	.61	.108	13.1
Biphenyl	190	.40	.097	10.8
Biphenyl	190	.34	.096	11.0
Biphenyl	180	.87	.115	7.4
Biphenyl	170	.90	.122	4.3
Biphenyl	160	.93	.130	2.4
Heptanoic acid	120	.98	.107	2.9
Heptanoic acid	120	.98	.058	3.0
Heptanoic acid	120	.98	.045	3.0

^a 0.067 M sodium heptanoate added.

The kinetic data for these system and for Hg^{++} and HgAc_2 in aqueous solution, are summarized in Table III. These differ in two important respects from the pattern for silver salts. (a) In aqueous solution the reactivity of HgAc_2 is considerably lower than that of the Hg^{++} ion and (b) the reactivity of the carboxylate salts appears to fall off markedly with solvent polarity ($\text{H}_2\text{O} > \text{HHp} > \text{biphenyl}$). Differences in both ΔH^\ddagger and ΔS^\ddagger contribute to these trends, which in both cases are opposite to those for silver. The cupric ion, discussed earlier,² appears to occupy an intermediate position. Thus, its reactivity in aqueous solution, like that of Ag^+ , is enhanced by carboxylate complexing. On the other hand it differs from silver and resembles mercury in respect of the inverse dependence of the reactivity of its carboxylate salts on solvent polarity.

Discussion

Mechanisms involving the heterolytic splitting of hydrogen, in which the activated complexes resemble that suggested earlier² for cupric and cuprous salts, also appear applicable to silver and mercuric salts and can accommodate most of the above observations.

Thus, the low reactivity of mercuric acetate in aqueous solution, relative to that of the uncomplexed ion, is attributable to the much greater

strength of the metal-ligand bond (reflected in the high stability constant of this complex) which must be stretched or broken in the activation process. Furthermore because of the large charge separation involved, the energy required to stretch this bond will increase, and the reactivity correspondingly decrease, with decreasing solvent polarity. Silver forms a much weaker acetate complex and its high reactivity relative to the aqua-ion suggests that the increase, if any, in the metal-ligand bond strength is more than compensated for by the higher ligand

basicity. Further, because of the smaller charge separation involved in stretching the metal-ligand bond, the reactivity of silver carboxylates should be much less dependent on solvent polarity. This should be the case also for cuprous salts while cupric salts, in view of the fact that Cu^{++} resembles Hg^{++} in its charge but forms much weaker carboxylate complexes, should exhibit behavior intermediate between that of mercuric and silver salts. As noted earlier, this is the case.

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[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, CLARK UNIVERSITY]

Pyridoxine and Pyridoxal Analogs. III. Ultraviolet Absorption Studies and Solution Equilibria of 2- and 4-Hydroxymethyl-3-hydroxypyridines and Pyridine-2, 3- and 4-Aldehydes¹

BY KAZUO NAKAMOTO AND A. E. MARTELL

RECEIVED NOVEMBER 7, 1958

The ultraviolet spectra of compounds related to vitamin B₆, such as 2- and 4-hydroxymethyl-3-hydroxypyridines and pyridine-2, 3- and 4-aldehydes have been measured at various pH values in buffer solutions and in dioxane-water mixtures. Assignments of the observed bands are made, and a general rule for the band shifts of the dipolar and the uncharged species has been found from measurements in dioxane-water mixtures. The over-all ionization constants are determined from plots of pH versus the absorbancy. On the basis of empirical assignments of the absorption bands, and reasonable assumptions of the influence of solvent on absorption intensities, individual ionization constants and the percentage of each species are calculated. The values obtained for each compound are compared and discussed from the viewpoint of electronic structures of the molecules involved.

It has been suggested² that the hydroxyl and the aldehyde groups are the ones mainly involved in the biological functions of pyridoxal. For this reason, Heinert and Martell³ recently have synthesized 3-hydroxypyridine-2- and 4-aldehydes and their methoxy derivatives as simple models of vitamin B₆. The purpose of the present work is to study the reaction mechanism between these compounds and amino acids in the presence of metallic ions by spectroscopic measurements.

In order to apply the spectroscopic method to such a system, it is first necessary to study the spectra of the hydroxypyridinealdehydes as a function of pH. It was found, however, that even hydroxypyridinealdehydes and their methoxy compounds are in complicated equilibria in aqueous media. Therefore, in this paper, detailed studies of the spectra of 2- and 4-hydroxymethyl-3-hydroxypyridines and pyridine-2, 3- and 4-aldehydes are described. Investigation of the ultraviolet spectra and solution equilibria of 3-hydroxypyridine-2 and 4-aldehydes and their methoxy compounds is now in progress and will be described in a subsequent communication.

Similar work already has been reported by Metzler and Snell⁴ on 3-hydroxypyridine, pyridoxine, 5-desoxypyridoxal, pyridoxal and related compounds. More extensive measurements of the equilibria between the two neutral species of a number of N-heteroaromatic hydroxy compounds

were made recently by Mason⁵ with ultraviolet and infrared spectra. However, the present study differs from those of previous workers in the following respects: (1) All the observed bands are empirically classified either as $n-\pi^*$, $\pi-\pi_1^*$, or $\pi-\pi_2^*$ transitions. (2) The pH of the dioxane-water mixtures was calibrated with acetate buffer to take into account any solvent effects on the measurement of pH. (3) A new general rule was found for the band shifts in dioxane-water mixtures. (4) The over-all ionization constants obtained from a plot of pH versus absorbancy were broken down into the individual ionization constants for each equilibrium, and these values are discussed in detail from the viewpoint of electronic theory. The percentages of the various species as a function of pH are estimated from the spectral data.

Experimental

Measurements.—The ultraviolet spectra were obtained with a Cary model 14 spectrophotometer at 20°. A pair of 1 cm. quartz cells with stoppers was used. In all measurements, the concentration of the solution was 10^{-4} M. The pH of the solution was measured after the spectral measurement with a Beckman model G pH meter fitted with extension glass and calomel electrodes. The pH meter was calibrated with Beckman standard buffer solutions.

Materials.—2- and 4-hydroxymethyl-3-hydroxypyridines were prepared by Heinert and Martell.³ Pyridine-2-, 3- and 4-aldehydes were purchased from Fluka A. G., Switzerland. All the compounds were freshly recrystallized or distilled immediately before the preparation of solutions.

Buffer Solutions.—For each pH range, the following buffer solutions were employed: pH 0, 1 N HCl; 1 ~ 2.2, HCl + KCl; 3.6 ~ 5.4, $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$; 6.0 ~ 8.0, NaOH + KH_2PO_4 ; 8.9 ~ 11.4, $\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$; 12.0 ~ 14.0, NaOH. For most of the solutions, the ionic strength was 0.2.

(1) This work was supported by a research grant, H-3246, from the National Heart Institute, Public Health Service.

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