The Nature of Soluble Copper(I) Hydride

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Abstract: The synthesis of pure CuH by the reaction of $LiAlH_4$ with CuI, which was first reported by Wiberg and Henle, has been shown to be substantially correct. The final product contains pyridine, CuI, and LiI which were not reported in the initial account. In contrast to copper (I) hydride prepared from aqueous solution, this compound is nearly amorphous as indicated by X-ray powder patterns. This high degree of subdivision and/or the presence of pyridine may account for its solubility in pyridine, alkyl sulfides, alkylphosphines, and phosphites. Cryoscopic measurements show the CuH is a monomer in pyridine solution. Decomposition reactions and the reaction of DCl are described.

As first reported by Würtz in 1844, copper(I) hydride may be prepared by the reduction of Cu^{2+} with aqueous hypophosphorous acid.[2-4] It is a thermodynamically unstable compound and generally contains from 0.6 to 0.9 hydrogen atom per copper. Furthermore, variable amounts of water are retained which cannot be removed without decomposition of the sample. Despite this lack of stoichiometry, X-ray and neutron diffraction studies reveal that copper hydride is a crystalline substance with the wurtzite structure.[5] A thorough study of the CuH decomposition has revealed some unusual features, the most striking of which is the enhanced rate in the presence of base, and the observation that when CuD is decomposed in the presence of OH^- the gaseous product is exclusively D_2.[6] Warf postulates that OH^- attacks the surface of a copper hydride particle to produce a local defect which initiates the decomposition of the particle.[7] Another property of the Würtz copper hydride is its insolubility in nondestructive solvents.[6] This, along with its instability, has undoubtedly imposed a limit on chemical investigations of CuH.

A seemingly different copper(I) hydride (reported by Wiberg and Henle) is obtained when $LiAlH_4$ in ether solution is mixed with CuI in pyridine.[8] (Earlier, Warf and Feitknecht reported the synthesis of an impure CuH by the reaction of $LiAlH_4$ with CuI in ether.[6]) The copper-containing metathesis product was reported to form a blood-red solution in pyridine and was precipitated by excess ether. Repeated dissolution in pyridine and precipitation by ether was reported to yield pure CuH.

The present work was designed to more thoroughly characterize CuH prepared in organic media with the hope of clarifying the apparent differences between this material and the product of reductions in aqueous solution.

Experimental Section

Pyridine for preparative purposes was distilled from calcium hydride and stored under nitrogen. For molecular weight determinations it was first distilled from calcium hydride and then subjected to a careful fractionation from Linde molecular sieves (5A). The fractionated material was collected and stored under nitrogen in a grease-free needle-valve container which permitted withdrawal of solvent under a nitrogen flush.

The molecular weight apparatus was calibrated with sublimed zone-refined naphthalene. Copper(I) iodide, obtained from Alfa Inorganics, was purified by dissolving it in saturated potassium iodide solution followed by treatment with decolorizing charcoal. It was precipitated by dilution and dried at elevated temperatures and 10^{-5} mm. Lithium tetrahydroaluminate was used as obtained (Metal Hydrides, Inc.).

Wiberg and Henle give few details in their reported preparation of copper hydride so the method will be outlined here. An ethereal solution of $LiAlH_4$ (0.56 g in 25 cc) was slowly added to a pyridine solution of CuI (7.62 g in 200 cc). The reaction mixture was allowed to stir for 8 hr under nitrogen. The solution was then filtered to remove the insoluble AlI_3 and the filtrate collected in a large centrifuge bottle equipped with a septum stopper which permitted addition of solvents under a nitrogen flush. Copper hydride was precipitated by addition of an equal volume of ether. After three to four cycles of precipitation, removal of the supernatant, and solution in pyridine, the product was washed with several 50-cc portions of ether and dried under vacuum for 15–20 min. Yields for this process are typically *ca.* 60%. X-Ray (Cu Kα radiation) powder data were obtained on freshly prepared samples sealed in Lindemann glass capillaries. Uv spectra were determined on a Cary 14 spectrophotometer.

Pyrolysis was carried out on a standard vacuum line employing a Toepler pump to collect and measure noncondensable gases (at −196°). The condensable material was identified as pyridine by gas-phase infrared spectra, while the noncondensable was identified as hydrogen by its mass spectrum. In several cases the residue left on pyrolysis was extracted with boiling distilled water and the iodide content determined by the Volhard method. This iodide was assumed to be due to LiI in the copper hydride sample. The remaining solid was extracted with hot 10% NaOH and again the iodide content determined by titration. The origin of iodide in this sample was taken to be CuI. For all samples the total copper content was determined by an EDTA titration.

Protium-deuterium ratios of hydrogen samples were determined with a CEC 21-104 mass spectrometer.

DCl was prepared by the interaction of D_2O with excess freshly distilled benzoyl chloride. Purification was accomplished by trap-to-trap distillation on a vacuum line that had been conditioned previously with D_2O. Before initiating an experiment, the vacuum system was conditioned with several hundred millimeters of DCl for several hours. Isotopic purity of the DCl was estimated as better than 95% by the infrared spectrum. The vapor pressure of the purified product was found to be 119.9 mm at −111.95° in agreement with the literature value of 120 mm.[9]

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[1] Alfred P. Sloan Fellow.

[2] A. Würtz, *Ann. Chim. Phys.*, [3] **11**, 250 (1844). Subsequently, this synthesis has been improved and other reducing agents have been employed in aqueous solution (see ref 3 and 4).

[3] V. I. Mikheeva and N. N. Mal'tseva, *Russ. J. Inorg. Chem.*, **6**, 1 (1961); **9**, 1071 (1966).

[4] V. I. Mikheeva, "Hydrides of the Transition Metals," AEC-tr-5224, 1962, p 128 ff.

[5] J. A. Goedkoop and A. F. Andersen, *Acta Cryst.*, **8**, 118 (1955).

[6] J. C. Warf and W. Feitknecht, *Helv. Chim. Acta*, 33, 613 (1950).

[7] J. C. Warf, *J. Inorg. Nucl. Chem.*, **19**, 304 (1961).

[8] E. Wiberg and W. Henle, *Z. Naturforsch.*, **7b**, 250 (1952).

[9] "Selected Values of Properties of Chemical Compounds," Manufacturing Chemists' Association Research Project, Chemical

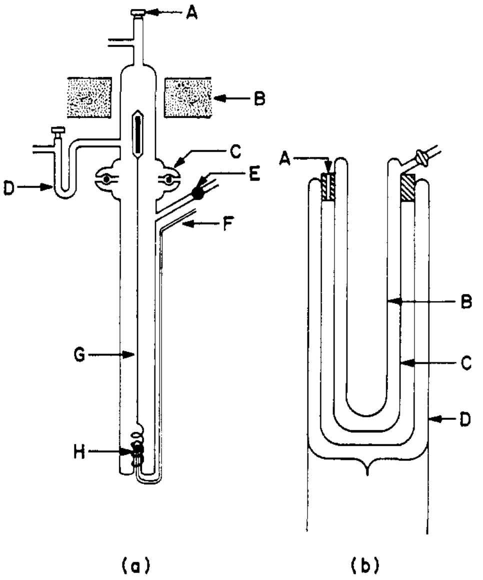

Figure 1. (a) Cryoscopy cell: (A) needle-valve stopcock for venting purge gas after cap has been removed from cell, (B) solenoid, (C) O-ring joint, (D) side arm with micro stirring bar which is used to minimize supercooling (a needle-valve stopcock is included to allow venting), (E) needle-valve stopcock used to evacuate cell and introduce nitrogen, (F) leads to bridge and recorder, (G) stirrer with glass-encased steel slug at upper end and glass helix at the bottom, (H) thermistor. (b) Cell jacket: (A) stopper with vent hole, (B) well to receive cryoscopy cell, (C) evacuable chamber used to moderate cooling rate, (D) dewar of liquid nitrogen.

The cryoscopy apparatus (Figure 1) used in this work incorporates a number of features which make it particularly useful with dilute solutions of air-sensitive compounds in organic solvents. O-Ring joints and needle-valve stopcocks are used to provide flexibility and good exclusion of air without the potential of contamination which exists with greased joints and stopcocks. The cell is equipped with a side arm (E) through which it may be evacuated and filled with inert gas, and later flushed with inert gas, while solutions or solids are being added. To minimize interference with the solenoid actuated stirrer, the thermistor sensing element is placed in a well which extends up from the bottom of the cell (H). Supercooling is minimized by cooling side arm D with liquid nitrogen and flicking a micro stirring bar from this side arm into the cell by means of a hand magnet. A bridge circuit employing an operational amplifier was used to minimize the current through the thermistor and provide a linear relationship between resistance and temperature.

Results and Discussion

Characterization of Soluble CuH. Seventeen separate analyses on ten different preparations were performed with a resulting range in the ratio of H to total Cu of 0.58 and 0.96 and an average of 0.81. When four "complete" analyses were carried out on two separate samples, pyridine was found to vary from 4 to 20%, LiI from 1 to 2%, and CuI from 10 to 20%. On a molar basis the CuH to pyridine ratios vary from 13:1 to 2.7:1. Since LiI and CuI are soluble under the conditions used to precipitate CuH, these impurities must arise from coprecipitation or adsorption. On the last cycle of purification, it was occasionally noted that considerable amounts of hydride formed a suspension which did not settle upon centrifugation. This suggests colloid formation which was destabilized during the earlier precipitations by the presence of LiI and CuI.

Samples of copper hydride may be stored under an inert atmosphere at −196° for months without apparent decomposition, but decomposition occurs slowly at room temperature. Unlike the Würtz copper hydride, pyrolysis occurs smoothly under vacuum and proceeds to completion below 100°.

In the cryoscopic investigation of copper hydride in pyridine, measurement of the freezing point depression was followed by copper determination on an aliquot from the cell contents and the molecular weight was calculated assuming all copper was present as CuH. The average of eight determinations on five separate CuH samples gave an apparent molecular weight of 60 ± 6,[10] and no concentration dependence was evident over the range studied, 0.03–0.18 *m*. (The CuI contaminant does influence this result because separate experiments show that CuI is monomeric in pyridine.) Thus, CuH forms a true solution containing one formula unit of expected molecular weight 65. Presumably, the species present in solution is coordinated to one or more pyridine molecules; however, pyridine is too weakly held to allow isolation of a stoichiometric solid complex.

The origin of the solubility difference between CuH prepared from aqueous solution and that obtained from an organic medium may originate from differences in subdivision. Whereas the former material yields a sharp X-ray powder photograph, the latter gives two broad halos indicative of a particle size less than 0.01 μ. The estimated particle size for copper hydride prepared in aqueous media is in the range of 0.1–0.2 μ depending on the temperature of preparation.[6] The presence of pyridine might also be a deciding factor, for substantial amounts of residual pyridine might be more effective than the water found in the insoluble hydride in producing a soluble species. The presence of CuI impurity does not seem to be responsible for the solubility, since treatment of the insoluble Würtz copper hydride with copper iodide in pyridine does not yield a CuH solution. Furthermore, lithium iodide in pyridine causes decomposition of Würtz copper hydride.

Blood-red to brown solutions of Wiberg and Henle's copper hydride may be obtained in a number of "soft" donor solvents, including alkylphosphines, phosphites, alkyl sulfides, and pyridines. However, "hard" donors such as ethers and alkylamines are not solvents. It is noteworthy that copper hydride solutions are about as unstable as the solid. Thus, unlike many main group and transition metal hydrides, coordination does not appreciably enhance the thermal stability of the parent hydride.

Unsuccessful attempts were made to obtain evidence for copper–hydrogen bonds by solution infrared and ^{1}H nmr spectroscopy. The lack of success may be attributed to low solubility of CuH (*ca.* 0.2 *M*) and, in the case of nmr, to high nuclear spin and quadrupole moment of copper. Other investigators have been unable to detect a copper–hydrogen stretch in the infrared

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[10] This standard deviation is about five times that of determinations made under similar conditions on more tractable and easily purified substances.

spectrum of insoluble copper hydride.[11] Similarly, we did not find a Cu–H stretch for mulls of soluble copper hydride. However, there is strong chemical evidence for the existence of Cu–H bonds in solution. Copper hydride may be repeatedly dissolved and precipitated, from the above-mentioned solvents, without change in composition. While this observation might be explained for some of the aromatic ligands by a facile metal–ligand hydrogen shift, this is less reasonable for the alkyl-substituted ligands. Furthermore, it is unlikely that metal–ligand hydrogen interchange occurs in pyridine, since isotopically pure CuD may be prepared in normal pyridine.

The origin of the intense color of copper hydride solutions presents an interesting problem. Therefore, spectra were obtained on capillary films of solution and on samples in 1-mm cells. These show no absorption maxima or distinct shoulders at wavelengths longer than 360 mμ. The color results solely from the broad tail of strong absorption(s) in the ultraviolet. The absorption maxima in pyridine solution are obscured by the solvent; however, a shoulder at 346 mμ may be due to CuH. For copper hydride in other solvents new bands are observed at 254 mμ (max) in tri-*n*-butylphosphine and <250 mμ in 2,4-dithiahexane. By contrast, the lowest energy transition, $^1\Sigma^+ \leftarrow {}^1\Sigma^+$, of gaseous CuH occurs at 4290 Å (0–0) with a pronounced band head at 4280 Å.[12,13] Higher energy transitions occur around 3805 ($^1\Sigma^+ \leftarrow {}^1\Sigma^+$), 3689 ($^1\pi \leftarrow {}^1\Sigma^+$), and 2240 Å ($^1\pi \leftarrow {}^1\Sigma^+$).[8,9] Thus, the net effect of solvation is to obscure the visible and near-uv bands.

Reactions of Soluble CuH. Several qualitative experiments have been performed to investigate the base-catalyzed decomposition of soluble copper hydride. Warf observed that the decomposition of Würtz copper hydride is strongly base catalyzed with a half-life of decomposition less than 0.1 min in 0.045 *M* NaOH at 40°.[7] In contrast, aqueous base does not have a dramatic effect on the decomposition of solid copper hydride which was prepared in organic solvents. Decomposition was very slow at room temperature, and it was necessary to warm the mixture to achieve appreciable hydrogen evolution. In the presence of base the reaction was brought to 73% completion overnight by warming the reaction tube to 60°. When CuD is used, the primary product is D_2 (Table I).

In the case of soluble copper hydride, the lack of catalysis by hydroxide may be due to the residual pyridine which is coordinated to the surface and thus blocks active sites from attack by hydroxide. However, an attempt to check this hypothesis by washing Würtz copper hydride with pyridine resulted in a material which quickly decomposed in the presence of hydroxide ion. Therefore, we conclude that either the pyridine wash failed to displace all of the water from the surface or else some unknown difference exists between the two preparations of copper hydride.

Homogeneous decomposition of copper deuteride in pyridine was carried out in the presence of methanol saturated with KOH. This reaction was somewhat more rapid than the heterogeneous decomposition and was 60% complete in 1.5 hr. The noncondensable gas removed within the first hour of the reaction contained mainly D_2, with significant amounts of HD and only a trace amount of H_2 (Table I). The most significant conclusion from this experiment is that copper hydride in solution does not have appreciable acidity toward OH^-, since this would lead to proton exchange and considerable H_2 formation.

Table I. Base Decomposition of CuD

Reaction	% DD	% HD	% HH
Heterogeneous			
CuD(s) + NaOH (aq soln)	90	8	2
Homogeneous			
CuD (pyridine soln) + KOH (methanol soln)	73	24	3
Pyrolysis	95	3	2

On the contrary, the hydrogen bound to copper seems to be weakly hydridic. The reaction of CuH with DCl gas leads to the evolution of hydrogen; isotopic analysis of this material showed considerable amounts of HD as well as H_2 with virtually no D_2 (Table II). Solid copper hydride treated with a 2 *M* DCl–D_2O solution also yields considerable amounts of HD. However, unlike the more ionic hydrides such as NaH, HD is not the sole product.[14]

Table II. Acid Decomposition of CuH

Reaction	% HD	% HH	Ratio DCl:CuH
CuH(s) + DCl[a]	69	31	2.2:1
CuH(s) + DCl[b]	34	66	3.3:1
CuH (pyridine soln) + DCl[c]	49	51	1.06
CuH(s) + DCl (2 *M* in D_2O)[d]	20	80	1.67:1

[a] Total molecular hydrogen: Cu = 0.85:1, ^{1}H:Cu = 1.0:1; conditions: −78° for 15 hr, −45° for 1.5 hr, and overnight at room temperature. [b] Conditions: −78° for 0.5 hr, and room temperature for 9 hr. [c] Conditions: −30° for 4 hr, and room temperature for 4 hr. [d] Conditions: 0° for 0.5 hr, and room temperature for 0.5 hr.

While copper metal has some catalytic activity in the hydrogenation of olefins at elevated temperatures,[15] the solid CuH does not appear to be reactive at room temperature or below. In one experiment at −45.2°, incremental addition of 1,3-butadiene led to a reversible

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(11) K. I. Mikheeva and N. N. Mal'tseva, *J. Struct. Chem.*, **4**, 643 (1963).

(12) R. W. B. Pearse and A. G. Gaydon, "Identification of Molecular Spectra," John Wiley and Sons, Inc., New York, N. Y., 1941, p 154.

(13) G. Herzberg, "Molecular Spectra and Molecular Structure." Vol. I. "Spectra of Diatomic Molecules," 2nd ed, D. Van Nostrand Co., Princeton, N. J., 1950.

(14) It is to be emphasized that the reaction in the presence of acid is quite different from the base-catalyzed decomposition. Hydrochloric acid reacts with CuH to produce CuCl (identified by its X-ray powder pattern) plus 1 mol of H_2 per mole of CuH. On the other hand, OH^- catalyzes the decomposition of CuH to give copper metal and 0.5 mol of H_2 per mole of CuH.

(15) G. C. Bond, "Catalysis by Metals," Academic Press, New York, N. Y., 1962, Chapter 11.

adsorption isotherm. Infrared and vpc analysis of the recovered butadiene showed no hydrogenation products. Tetrafluoroethylene also failed to react under analogous conditions.

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