

# Studies of the thermal decomposition of copper hydride

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## Abstract

Decomposition of copper hydride has been investigated by differential scanning calorimetry (DSC) and the thermogravimetric analysis (TGA) methods. The samples were prepared from aqueous solution by reduction of copper sulfate with hypophosphorous acid. The crystal structure was determined by energy dispersive X-ray diffraction method. Mass spectrometric and volumetric methods were used for the determination of hydrogen concentration in solid CuH. A special procedure was employed to obtain sample free of water and other contaminations in order to avoid obstacles from the impurity-related processes, in our opinion, responsible for the discrepancies in the thermodynamic properties of copper hydride. The enthalpy of pure copper hydride was found to be  $27.5 \pm 0.4 \text{ kJ mol}^{-1}$ . The activation energy was calculated from DSC data as about  $73.7 \text{ kJ mol}^{-1}$ . The equilibrium pressure of hydrogen over copper hydride and the possibility of copper hydride formation at high pressure from the elements will be discussed. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Copper hydride; DSC; TGA; Enthalpy of decomposition; High pressure

## 1. Introduction

Copper hydride, CuH, occupies a specific place among the hydrides. It does not belong to any of the three main hydride types (covalent hydrides, ionic hydrides and metallic hydrides) and can be synthesized at room temperature in aqueous solution. Copper hydride was first prepared by Wurtz [1] in 1844 by reaction of aqueous copper sulfate with hypophosphorous acid. It forms a red-brownish crystalline powder of the wurtzite structure with  $a = 2.89 \text{ \AA}$  and  $c = 4.62 \text{ \AA}$  as determined by Goedkoop and Andresen [2].

Several other methods have been used to obtain copper hydride including precipitation of the hydride from pyridine solution of CuJ and  $\text{LiAlH}_4$  [3], by

reaction of copper sulfate with sodium borohydride in aqueous solution [4], and by electrolysis of alkaline solutions containing Cu (II) complexes [5]. The samples always contain impurities (water, alcohol, organic compounds) dependent on the method of preparation. The characteristic feature of this hydride is its relatively low stability. It slowly decomposes even at room temperature. Warf and Faitknecht [6] have shown that the kinetics of the decomposition of copper hydride can be expressed by a first-order kinetic equation. Under water, its half-life time is 30 min at  $70^\circ\text{C}$  and 70 h at  $30^\circ\text{C}$ . The stability of the hydride depends on the surrounding medium: organic solvent and aqueous solution of sodium chloride make it higher, but it is lower in base solution.

CuH decomposes exothermically, although different authors have reported contradicting data concerning the parameters of this process. For the copper hydride prepared according to Wurtz method,

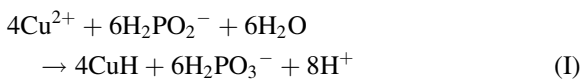
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Mikheeva and Mal'tseva [7] found a single exotherm between 97 and 137°C for the completely dry material. Fitzsimons et al. [8] obtained three distinct transitions at 90°C (endothermic), 105°C (endothermic) and at 142°C (exothermic). CuH precipitated from organic solution is stable up to 60°C as reported by Wiberg and Hoenle [3]. Up to now, only two studies on the enthalpy of decomposition of CuH have been published. The data obtained by Sieverts and Gotta [9] ( $-21.4 \text{ kJ mol}^{-1}$ ) and Warf [10] ( $-32.9 \text{ kJ mol}^{-1}$ ) are in poor agreement and outside experimental error. These discrepancies in the light of the present knowledge could be attributed to the samples purity and the method of preparation used for those studies.

The purpose of this paper is to determine the decomposition enthalpy of copper hydride carried out on well-defined sample of CuH (without contamination) and the temperature dependence of this process.

## 2. Experimental

Copper hydride was prepared by reaction of aqueous copper sulfate with hypophosphorous acid at 45°C [6] based on the following equation:



Small amount of sodium chloride was added to avoid decomposition of copper hydride during synthesis. The precipitate was cooled, filtered, and rinsed with ice water and cold absolute alcohol. The CuH was purified in vacuum at 0°C using liquid nitrogen trap. The powder was stored for further investigations in solid carbon dioxide at  $-50^\circ\text{C}$ .

The hydrogen content was determined by mass spectroscopic and volumetric methods and was equal to about 0.9 in atomic ratio. Energy dispersive X-ray diffraction analysis showed the characteristic h.c.p. copper hydride lines with no trace of metallic copper (Fig. 1). Lattice parameters  $a = 2.89 \text{ \AA}$  and  $c = 4.61 \text{ \AA}$  calculated from the diffraction lines were in good agreement with that obtained by Goedkoop and Andresen.

The thermal decomposition of CuH was investigated in the temperature range from 25 to 200°C. All experiments were carried out using a Du Pont Thermal Analyst 2100 Instrument: DSC 910 and TGA 951 under argon atmosphere ( $100 \text{ ml min}^{-1}$ ) and at a heat rate  $10^\circ\text{C min}^{-1}$ . The DSC instrument was calibrated for high purity indium. The average sample size was about 10–20 mg.

## 3. Results

TGA and DSC experiments were carried out on conventionally prepared sample as shown in Figs. 2

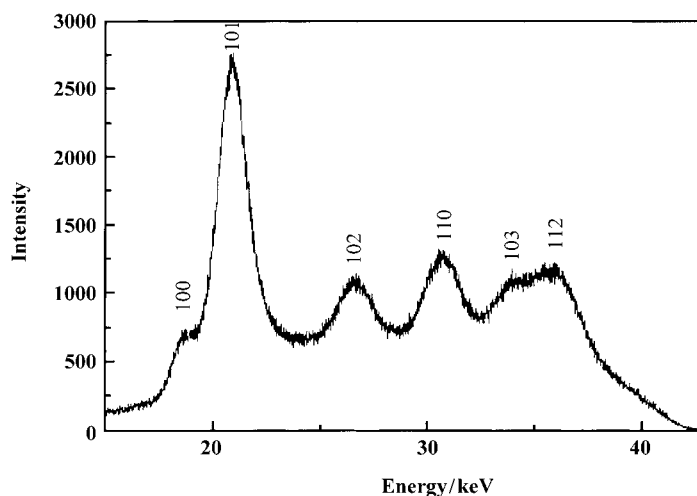


Fig. 1. Energy dispersive X-ray diffraction pattern of copper hydride.

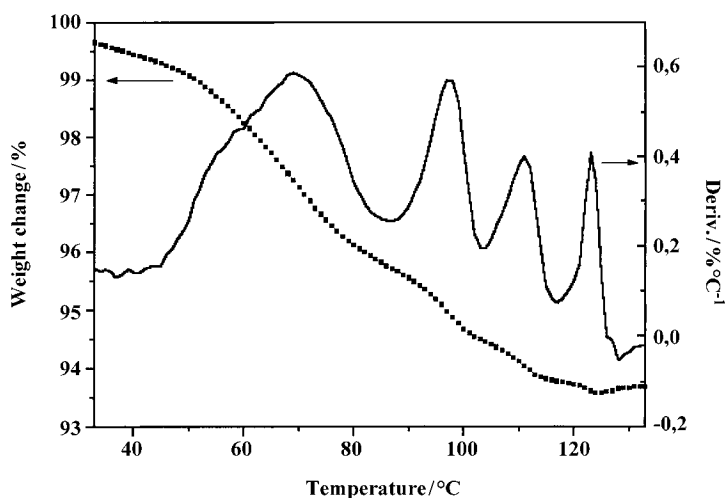


Fig. 2. TGA curve for the initial copper hydride sample.

and 3, respectively. The TGA curve shows several processes leading to a gradual weight loss which can hardly be connected with evolution of hydrogen from the sample. This coincides with the DSC data where the main hydride decomposition and small unexpected thermal effects overlap. We obtained a large number of almost identical results for both DSC and TGA measurements from different runs and samples. The total weight loss was about 6%. Assuming that the hydrogen concentration was 0.9 in atomic ratio, the weight loss due to the decom-

position process should be 1.4% at most. The weight loss observed is caused by the presence of the organic and inorganic impurities in the sample under investigation. It was clearly confirmed by the mass spectroscopic analysis. All processes that could contribute to the total heat effect, connected with the impurities of the sample, end at the temperature of about 120°C. The total exothermic effect was found to be about 20 kJ mol<sup>-1</sup>. From the above TGA and DSC data, one important conclusion can be drawn: impurities in the CuH sample make the determination of the

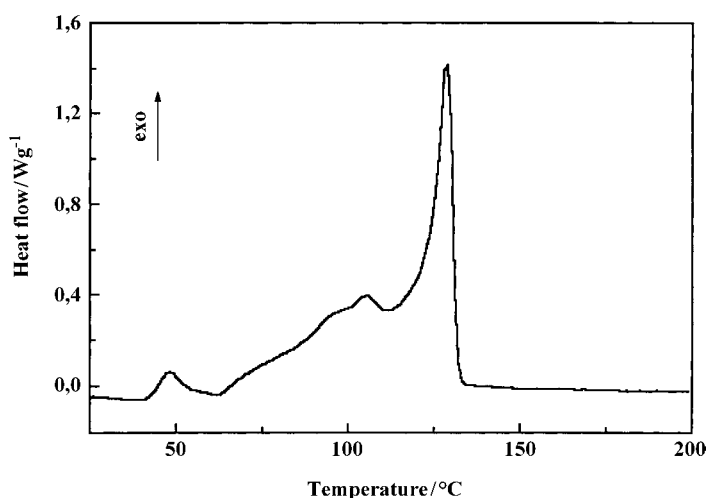


Fig. 3. DSC curve for the initial copper hydride sample.

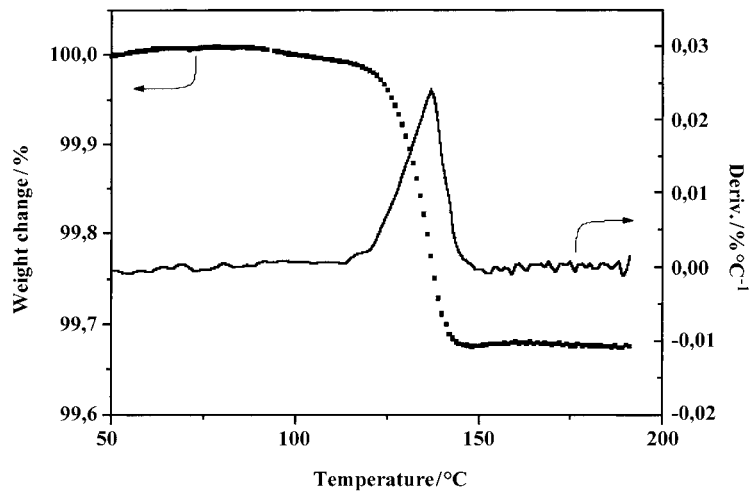


Fig. 4. TGA curve for purified CuH sample.

hydrogen weight loss or the heat effects of decomposition impossible. In order to make use of the TGA and DSC results it was decided to heat the sample to just below 120°C, where most of weight loss is observed and so remove all impurities. This procedure, of course, also leads to the partial decomposition of the hydride sample. The heating rate of the sample in inert atmosphere was similar to that in DSC or TGA measurements and after reaching 120°C, the sample was rapidly quenched. The hydrogen content in the CuH samples after treatment

described above varied within the range 0.15–0.25 in atomic ratio as determined by the volumetric method.

As it can be seen from the TGA and DSC curves (Figs. 4 and 5) performed on the purified sample, only one process in the whole temperature range of investigation is manifested. The weight loss of about 0.3% observed in TGA measurements clearly corresponds to the hydrogen concentration in the sample. For the sample without impurities, the TGA measurements on hydride which decomposes in the temperature range

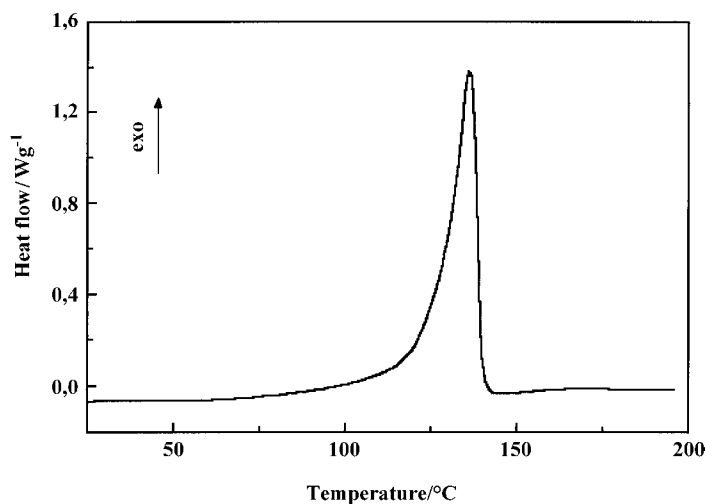


Fig. 5. DSC curve for purified CuH sample.

Table 1  
Experimental data of the enthalpy of decomposition of CuH

No.	H/Cu (atomic ratio)	Heat, $Q$ (J g <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )
1	0.19	83.22	-27.3
2	0.23	96.99	-27.0
3	0.15	63.35	-28.2

of investigations could be used as independent probe of the hydrogen concentration.

The enthalpy of decomposition for different contents of hydrogen, determined from DSC measurements curve, are shown in Table 1. The enthalpy is related to the temperature at 125°C.

The kinetic parameters were calculated from DSC curve predicting first-order reaction in temperature range to be most linear according to the equation

$$\ln\left(\frac{d\alpha/dt}{1-\alpha}\right) = \ln\left(\frac{Z - E_a}{RT}\right) \quad (1)$$

where  $\alpha$  is the rate of process,  $t$  the time,  $Z$  the pre-exponential factor,  $E_a$  the activation energy,  $R$  the gas constant, and  $T$  the temperature.  $\alpha$  was calculated from the equation

$$\alpha = \frac{\Delta H}{\Delta H_0} \quad (2)$$

where  $\Delta H$  the time-dependent heat effect, and  $\Delta H_0$  the total heat effect.

$$\frac{d\alpha}{dt} = \frac{d}{dt} \left( \frac{\Delta H}{\Delta H_0} \right) \quad (3)$$

The kinetic parameters were obtained from DSC curve in the temperature range from 70 to 115°C. The activation energy is  $73.7 \pm 0.5$  kJ mol<sup>-1</sup> and pre-exponential factor is  $(1.15 \pm 0.01) \times 10^7$  s<sup>-1</sup>. The main part of the sample decomposes in the temperature range from 110 to 145°C, but the maximum of peak was found to be located in between 135 and 140°C. The substance begins to decompose notably above 50°C.

#### 4. Discussion

The determination of the thermodynamic properties of copper hydride is difficult due to the following

reasons. Firstly, the problem of the thermal stability of CuH. Most authors agree that even at the temperature of 0°C it decomposes slightly. As a result, to avoid sample decomposition, CuH should be investigated at hydrogen pressure equal to or higher than the equilibrium pressure, which so far has not been experimentally determined. Furthermore, samples prepared in the proposed ways so far always retain some amounts of solvents and other substances used in process of preparation. They cannot be removed without partial decomposition of CuH. Therefore, the properties of the sample investigated can differ and they depend on the quantities and nature of the impurities. This situation leads very often to contradictory results and feeble interpretations as one can find in the literature. The only solution, the synthesis of copper hydride from elements at high pressure, has not been achieved yet.

Regarding the DSC and TGA studies reported so far, one can find inconsistencies which concern not only value or peak numbers but also sign of the heat effects observed in these studies [7,8]. It is not surprising that the authors did not calculate the enthalpy of decomposition since the exact value cannot be calculated for the reason of overlapping of peaks corresponding to the unspecified processes taking part in these studies.

The only two papers attempting to determine the enthalpy of decomposition of copper hydride presented different values. That could be justified by the different methods of preparation and purification of the samples. The authors have admitted that large amounts of other compounds retain in the sample even after purification in vacuum. Thus, they may react with main reagent or evaporate to induce additional heat effects. Thus, our value of 27.5 kJ mol<sup>-1</sup>, placed between values obtained before, could be regarded as not affected in respect to any processes accompanying the decomposition of CuH.

In the case of copper hydride, it is very important to be sure that all processes observed are related to pure hydride. In our paper, data carried out on the samples after partial desorption, correspond to the pure copper hydride decomposition, that is supported by DSC and TGA curves. The data obtained in the case of contaminated CuH are close or even less than that for the pure sample. This effect could be explained by the fact that, although the additional peaks are seen as an

exothermic, they could be suppressed by the endothermic effects related to endothermic evaporation processes. It also could be affected by reaction of hydrogen with admixtures. For instance, we found ethane during mass spectrometric analysis in the initial sample, which could be considered as a product of reaction of hydrogen with ethyl alcohol used in preparation and adsorbed on CuH surface. So the total heat effect of these reactions can be, and usually is, combination of different and hardly specified effects coming out from different processes when CuH is not pure. We believe that our results are correct in respect to the process under investigation, i.e. decomposition of CuH.

The kinetics of the decomposition of copper hydride cannot be described in terms of any particular stage of reaction. Generally, three steps are indicated: firstly with slow rate of decomposition, in temperature range from 25 to 70°C, secondly first-order process with parameters given above, and lastly very fast, in some cases almost explosive, caused by local overheating quickly decomposed sample.

As we mentioned above, the synthesis of CuH from elements could prevent any trouble with thermodynamic characterization of this hydride. Quite large number of hydrides have been synthesized under high pressure of gaseous hydrogen so far [11,12] and it seems that the high enough hydrogen activity or chemical potential is only requirement to create new hydrides [13].

Let us discuss the conditions required to create copper hydride under high hydrogen pressure. So far, well-proven route is to determine experimentally the minimum hydrogen pressure which is necessary to maintain the equilibrium between hydrogen gas and the solid hydride as it was done for NiH and CrH [11]. Unfortunately, up to now this value has not been obtained for the CuH, although Sieverts and Gotta [9] have made estimation of the equilibrium pressure calculated from their enthalpy measurements indicating value of  $10^{13}$  atm. In these estimations, the deviation from ideality of hydrogen gas at high pressure was neglected due to the lack of knowledge of equation of state. For the estimation of equilibrium pressure for CuH, we have applied following procedure for the reaction:



neglecting volume changes of copper and copper hydride under pressure. Gibbs free energy can be written in terms of chemical potential of hydrogen as

$$\Delta G = RT \ln f^{1/2} \quad (4)$$

where  $\Delta G$  is the Gibbs free energy,  $R$  the gas constant,  $T$  the temperature, and  $f$  the fugacity of hydrogen.

From another side, Gibbs free energy can be calculated according to the equation

$$\Delta G = \Delta H_{\text{form}} - T \Delta S_{\text{form}} \quad (5)$$

where  $\Delta H_{\text{form}}$  is the enthalpy of formation, and  $\Delta S_{\text{form}}$  the entropy of formation. Accepting that  $\Delta H_{\text{form}} = -\Delta H_{\text{decomp}}$  and assuming that  $\Delta S_{\text{form}}$  for many metal-hydrogen systems is equal to about  $52.25 \text{ J mol}^{-1}$  and we have calculated Gibbs energy and fugacity of hydrogen to be in equilibrium with copper hydride at the temperature of 125°C (398 K) as equal to  $48.3 \text{ kJ mol}^{-1}$ . According to the well-known relation between pressure and fugacity for hydrogen, the value of equilibrium pressure was found to be 60 kbar. To obtain the equilibrium pressure at ambient temperature, we have used the fact that for many metal-hydrogen system the value  $d(\ln f^{1/2})/d(1/T)$  is approximately constant over wide temperature range and is equal to about  $\Delta H/R$ . Thus,

$$\frac{\ln(f_1)^{1/2} - \ln(f_2)^{1/2}}{(1/T_1) - (1/T_2)} = \frac{\Delta H}{R} \quad (6)$$

Expressing  $f_2$  from this equation, we have obtained fugacity and then the equilibrium pressure for ambient temperature. It was found to be 59 kbar.

These values should be quite easily accessible by modern diamond anvil technique as proven recently for some metal-hydrogen systems [14,15]. Our preliminary studies have indicated pressure as high as 4.2 GPa for the decomposition process of CuH at ambient temperature [16] but more work has to be done since the rate of decomposition is strongly accelerated by the hydrogen pressure.

## 5. Conclusions

The enthalpy of decomposition of copper hydride has been determined as equal to  $25.5 \pm 0.4 \text{ kJ mol}^{-1}$ . Different methods of preparation resulting in different

levels of contamination of CuH sample could be blamed for the discrepancies observed in previously published data. Our results obtained on the sample free of contamination reflect true value of enthalpy of decomposition of CuH. Excellent reproducibility of measured value of CuH observed for both different samples and different experiments supports this conclusion. Kinetic data suggest three steps in decomposition process. First is the incubation period at lowest temperature followed by main process of the first-order with activation energy of about  $73.7 \text{ kJ mol}^{-1}$ . At the highest temperature, self-acceleration of decomposition is observed due to the local overheating of the sample. The measurements done on the well heat conducting substrate or mixture with the inert metal should minimize this phenomenon. We believe that suspension of the hydride in copper metal in our experiment is the reason for the lack of the small explosions or “puffs” reported earlier and also observed in our initial sample without heat treatment described above. The possibility of determination of equilibrium pressure over solid copper hydride as well as formation of CuH from elements under high hydrogen pressure using diamond anvil cell technique was discussed.

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