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Preparation and Characterization of Complex Metal Hydrides of Copper, $Li_mCu_nH_{m+n}$

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A series of complex metal hydrides of copper of composition $LiCu_2H_3$, $Li_2Cu_3H_5$, $LiCuH_2$, Li_2CuH_3, Li_3CuH_4, Li_4CuH_5, and Li_5CuH_6 have been prepared by the reaction of $LiAlH_4$ with the corresponding organocuprates in diethyl ether. Elemental analysis, x-ray powder-diffraction analysis, and DTA–TGA studies have been carried out to establish the integrity of these compounds. The thermal stability of this series of hydrides increases with increasing lithium content (20–145 °C). A most unusual observation is the THF solubility of $LiCuH_2$ and Li_4CuH_5 and the stability of Li_4CuH_5 in THF solution over a long period of time.

Introduction

Organocuprates have been the subject of considerable recent interest particularly because of their applications in synthetic organic chemistry. In this connection numerous reports and several reviews concerning reactions of lithium alkylcuprates[1] with organic substrates have appeared. Recently we have found low-temperature NMR evidence for the existence of some new organocuprates, namely $LiCu_2(CH_3)_3$ and $Li_2Cu(CH_3)_3$,[2] and have shown that these new cuprates behave differently from $LiCu(CH_3)_2$ toward enones[3] and organohalides (alkyl, cycloalkyl, and aryl halides).[4]

There has also been considerable interest in copper hydride (CuH) as a potential reagent in organic synthesis.[5,6] Dilts and Shriver[5] have prepared a stable solution of CuH in pyridine and suggested that the solubility of CuH is due to its complexation with pyridine. Stable complexes of CuH with PPh_3 have also been prepared by Churchill and co-workers.[6] Uncomplexed CuH is known to be quite unstable even at temperatures as low as −80 °C. Monnier has claimed the preparation of $CuAlH_4$; however, it is reported to be unstable above −80 °C and decomposes to Cu, CuH, Al, and H_2.[7] We have recently reported the formation of $CuAlH_4$ and Cu_3AlH_6 as intermediates in the reaction of $LiAlH_4$ and CuI at low temperature.[8] Also recently we have prepared the first stable complex metal hydride of copper, $LiCuH_2$, by the reaction of $LiAlH_4$ with $LiCu(CH_3)_2$ and found the product to be stable to 70 °C.[9]

In view of the unusual chemistry of the lithium alkylcuprates and the interest in preparing stable copper hydride derivatives as reducing agents, we have prepared the corresponding hydrides of several new lithium alkylcuprates. The method of preparation is similar to the method (eq I–III) that we

$$CH_3Li + CuI \rightarrow CH_3Cu + LiI \qquad (I)$$

$$CH_3Cu + CH_3Li \rightarrow LiCu(CH_3)_2 \qquad (II)$$

$$LiCu(CH_3)_2 + LiAlH_4 \rightarrow LiCuH_2 + LiAl(CH_3)_2H_2 \qquad (III)$$

reported earlier for $LiCuH_2$. In this connection, $LiCu_2H_3$, $Li_2Cu_3H_5$, $LiCuH_2$, Li_2CuH_3, Li_3CuH_4, Li_4CuH_5, and Li_5CuH_6 have been prepared and characterized.

Experimental Section

All operations were carried out either in a nitrogen filled glovebox equipped with a recirculating system[10] to remove oxygen and moisture or at the bench using typical Schlenk-tube techniques.[11] All glassware was heated and flushed with nitrogen prior to use.

Instrumentation. Infrared spectra were recorded in KBr cells using a Perkin-Elmer 621 high-resolution infrared spectrophotometer. X-ray powder diffraction of the products was obtained on a Philips-Norelco x-ray unit using a 114.6-mm diameter camera with Ni-filtered Cu Kα (1.540 Å) radiation. Single-walled capillaries of 0.5-mm diameter were used. The *d* spacings were evaluated using a precalibrated scale equipped with viewing apparatus. Line intensities were estimated visually. DTA–TGA data were obtained under vacuum using a modified Mettler Thermoanalyzer II.

Analyses. Hydrogen analysis was carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line and collecting the evolved hydrogen with a Toepler pump.[12] Lithium was determined by flame photometry. Iodide was determined by the Volhard procedure (analysis of all hydrides showed iodide in zero or trace quantities). Copper was determined by electrolytic deposition of a Pt electrode.

Materials. Tetrahydrofuran (Fisher Certified Reagent Grade) was distilled under nitrogen over $NaAlH_4$ and diethyl ether (Fisher Reagent) over $LiAlH_4$ prior to use. Methyllithium in THF and Et_2O was prepared by the reaction of $(CH_3)_2Hg$ with excess lithium metal. Both solutions were stored at −78 °C until employed. Cuprous iodide was purified by precipitation from an aqueous solution of KI–CuI.[13] The precipitated solid was washed with water, ethanol, and diethyl ether and then dried at room temperature under reduced pressure.

A solution of lithium aluminum hydride (Ventron, Metal Hydride Division) was prepared by stirring a diethyl ether slurry overnight followed by filtration of the slurry through dried Celite Analytical Grade Filter Aid. The solution was standardized by aluminum analysis (EDTA).

Reactions of CH_3Li with CuI in THF in 3:2 Ratio Followed by Addition of $LiAlH_4$. Preparation of $LiCu_2H_3$. Cuprous iodide (1.28 g, 6.76 mmol) was weighed into a 100-mL round-bottom flask fitted with a rubber septum. A THF slurry was made by adding THF to the CuI. The slurry was cooled to −78 °C and 20.2 mL of a 0.507 M solution of CH_3Li (10.14 mmol) in THF was added dropwise with continuous stirring. The reaction mixture first turned to a yellow solid, then to a yellow solution, and finally to a clear colorless solution. The mixture was stirred for 1 h at −78 °C and then $LiAlH_4$ (5.07 mmol) in THF was added dropwise. No precipitate formed at −78 °C; however, while warming the solution to 0 °C, a yellow precipitate formed. This reaction mixture was further stirred for 0.5 h and the solid was separated by centrifuging the mixture and removing the supernatant solution by syringe. The yellow solid was washed with ether and isolated as a THF slurry. This slurry gave the following analysis: Li:Cu:H:Al = 1.00:1.96:2.99:0.03. Calcd for $LiCu_2H_3$: 1.00:2.00:3.00. IR of the filtrate gave Al–H stretching at 1678 cm^{-1} [$LiAlH_2(CH_3)_2$].[14] This product as a THF slurry was stable at room temperature only for about 1 h after which time it started to turn black, indicating decomposition. When the solid was dried under vacuum at room temperature, it decomposed.

Reaction of CH_3Li with CuI in 5:3 Ratio Followed by Addition of $LiAlH_4$. Preparation of $Li_2Cu_3H_5$. A diethyl ether slurry of CuI (0.635 g, 3.34 mmol) was allowed to react slowly with 5.57 mmol of CH_3Li solution in diethyl ether at −78 °C. All the solid dissolved within a few minutes to yield a clear solution. To this solution at −78 °C was added, dropwise with continuous stirring, a diethyl ether solution of $LiAlH_4$ (2.80 mmol). No precipitate formed at −78 °C; however, while warming the solution to room temperature, a yellow precipitate formed. This reaction mixture was stirred at room temperature for 0.5 h and the solid was separated and washed with diethyl ether. The filtrate gave a band at 1708 cm^{-1} due to Al–H stretching [$LiAlH_2(CH_3)_2$]. Analysis of the diethyl ether slurry of the yellow solid gave Li, Cu, and H in ratios 2.00:2.96:5.04. Calcd for $Li_2Cu_3H_5$: 2.00:3.00:5.00. The product was stable as a diethyl ether slurry for 1 day after which time it started turning black. When the yellow solid was dried under vacuum, it decomposed at room temperature as it turned a grayish-black color.

Reaction of CH_3Li with CuI in 3:1 Ratio Followed by Addition of $LiAlH_4$. Preparation of Li_2CuH_3. A diethyl ether solution of empirical formula $Li_2Cu(CH_3)_3$ (8.08 mmol) was prepared at −78 °C by the reaction of CH_3Li (12.12 mmol) with an ether slurry of CuI (0.768 g, 4.40 mmol) at −78 °C. This solution was allowed to react with $LiAlH_4$ (6.06 mmol) at −78 °C and was warmed to room temperature during which time a white solid formed. The reaction mixture was stirred for 0.5 h at room temperature and the solid was filtered, washed with diethyl ether, and dried under vacuum. The filtrate showed an Al–H stretching band at 1708 cm^{-1} ($LiAlH_2Me_2$). The white solid was analyzed and the x-ray powder-diffraction pattern was recorded. Anal. Calcd for Li_2CuH_3: Li:Cu:H = 2.00:1.00:3.00. Found: 2.06:1.00:3.02. The white solid product (ether free) was stable at room temperature for 2 days after which time it slowly changed to a yellow and then to a black solid. X-ray pattern (Å): 4.00 w, 3.50 m, 2.25 d.

Reaction of CH_3Li with CuI in 4:3 Ratio Followed by Addition of $LiAlH_4$. Preparation of Li_3CuH_4. To CuI (0.571 g, 3.0 mmol), slurried in diethyl ether at −78 °C, was added CH_3Li (12.0 mmol) in diethyl ether, dropwise with continuous stirring. A clear solution resulted within a few minutes. To the clear solution at −78 °C was added a diethyl ether solution of $LiAlH_4$ (6.0 mmol) and the reaction mixture was allowed to warm to room temperature. The white precipitate which formed was filtered, washed with ether, and dried under vacuum. The product was analyzed and the x-ray powder-diffraction pattern was recorded. Anal. Calcd for Li_3CuH_4: Li:Cu:H = 3.00:1.00:4.00. Found: 3.05:1.00:4.03. This white solid was ether free and stable for a week at room temperature. X-ray pattern (Å): 4.05 m, 3.50 s, 2.47 m, 2.12 w, 2.02 w, 1.57 w.

Reaction of CH_3Li with CuI in 5:1 Ratio Followed by $LiAlH_4$. Preparation of Li_4CuH_5. A diethyl ether solution of CH_3Li (10.0 mmol) was added dropwise to a well stirred CuI (2.0 mmol) slurry in diethyl ether at −78 °C. A clear solution resulted in a few minutes. To this solution was added $LiAlH_4$ (5.0 mmol) in ether and the reaction mixture was stirred at room temperature for 1 h during which time a white crystalline solid formed. The insoluble solid was filtered, washed with ether, and dried under vacuum. The product was analyzed and the x-ray powder-diffraction pattern was recorded. Anal. Calcd for Li_4CuH_5: Li:Cu:H = 4.00:1.00:5.00. Found: 4.10:1.00:5.09. X-ray pattern (Å): 4.05 m, 3.51 s, 2.47 m, 2.13 w, 2.02 w, 1.57 w. The white solid was stable at room temperature for over a week.

Reaction of CH_3Li with CuI in Diethyl Ether in 6:1 Ratio Followed by Addition of $LiAlH_4$. Preparation of Li_5CuH_6. Methyllithium and CuI were allowed to react in 6:1 molar ratio in the same manner as reported above. The resulting clear solution was allowed to react with $LiAlH_4$ to produce a white solid. The solid was filtered, washed with ether, and dried under vacuum. The resulting solid was stable at room temperature over a 30-day period. Anal. Calcd for Li_5CuH_6: Li:Cu:H = 5.00:1.00:6.00. Found: 5.07:1.00:6.03. X-ray pattern (Å): 4.04 m, 3.50 s, 2.48 m, 2.12 w, 2.02 s, 1.57.

Results and Discussion

When CH_3Li was allowed to react with CuI in THF in the ratio 3:2, a clear solution resulted. Recent low-temperature NMR studies showed that a single species of composition $LiCu_2(CH_3)_3$ was formed (eq 1). Reaction of $LiAlH_4$ with this solution (eq 2) resulted in the formation of a yellow solid which was found by elemental analysis to have the empirical formula $LiCu_2H_3$. However, the product was only stable as a THF slurry at 0 °C and decomposed when the solvent was removed under vacuum at room temperature. X-ray powder diffraction and DTA–TGA studies could not be carried out because of the instability of the product. (DTA–TGA data and elemental analyses obtained on all other compounds are reported in Tables I and II.) Because CuH is very unstable in ether solvents even at −80 °C, it is clear that slurries in ether of the complex metal hydride products cannot contain CuH. Therefore it does not seem that the product designated as $LiCu_2H_3$ could be a mixture of $LiCuH_2$ and CuH. We have previously prepared $LiCuH_2$ and it is stable at 0 °C for several weeks, whereas under the same conditions CuH is in a state of rapid decomposition producing a distinct black solid (Cu^0).

$$3CH_3Li + 2CuI \xrightarrow{THF} LiCu_2(CH_3)_3 + 2LiI \tag{1}$$

$$2LiCu_2(CH_3)_3 + 3LiAlH_4 \xrightarrow{THF} 2LiCu_2H_3 + 3LiAlH_2(CH_3)_2 \tag{2}$$

Table I. Thermal Decomposition of Complex Metal Hydrides of Copper

Compd (sample wt, mg)	Thermicity	Range of transition (peak max), °C	% wt loss
Li_2CuH_3 (81.02)	Exo	80–94 (89)	(Phase change)
	Endo	80–95 (90)	0.42
	Endo	105–112 (110)	0.21
	Endo	118–130 (120)	0.16
	Endo	135–148 (145)	0.43
	Endo	270–320 (290)	1.10
	Endo	420–475 (440)	(Increase in wt ?)
Li_3CuH_4 (90.10)	Endo	100–114 (110)	0.29
	Endo	116–128 (120)	0.18
	Endo	135–145 (140)	0.60
	Endo	280–325 (308)	1.04
	Endo	395–430 (410)	(Increase in wt ?)
	Endo	430–470 (450)	(Increase in wt ?)
Li_4CuH_5 (95.74)	Endo	110–129 (120)	0.28
	Endo	130–150 (145)	0.70
	Endo	275–315 (300)	0.95
	Endo	355–375 (365)	0.20
	Endo	420–450 (430)	(Increase in wt ?)
	Endo	480–above 500	(Continued wt loss)
Li_5CuH_6 (98.54)	Endo	125–148 (140)	0.95
	Endo	280–320 (305)	0.97
	Endo	425–455 (440)	(Increase in wt ?)
	Endo	480–above 500	(Continued wt loss)

Table II. Elemental Analysis of Ether-Free Complex-Metal Hydrides of Copper

Compd	% found (calcd) Li	Cu	H
Li_2CuH_3	17.49 (17.26)	77.85 (79.00)	3.83 (3.75)
Li_3CuH_4	23.85 (23.55)	70.46 (71.89)	4.67 (4.56)
Li_4CuH_5	29.05 (28.81)	64.65 (65.95)	5.42 (5.23)
Li_5CuH_6	33.46 (33.27)	60.04 (60.93)	5.85 (5.80)

When a diethyl ether solution of CH_3Li was allowed to react with CuI in 5:3 ratio in diethyl ether at −78 °C, a clear solution resulted (eq 3). When $LiAlH_4$ was allowed to react with this solution, a yellow solid was formed which was stable at room temperature as a diethyl ether slurry but which decomposed slowly when the diethyl solvent was removed. Since a CuH slurry in ether is not stable at room temperature, it seems that the compound of empirical formula $Li_2Cu_3H_5$ could not be a mixture of $LiCuH_2$ and CuH. Furthermore, the cuprate $LiCu_2(CH_3)_3$ does not exist in diethyl ether thus lessening the possibility that the compound of empirical formula $Li_2Cu_3H_5$ is actually a mixture of $LiCu_2H_3$ and LiH. More definitive proof for the integrity of this compound was not possible since we were not able to obtain x-ray diffraction and DTA–TGA data on this compound because of its instability.

$$5MeLi + 3CuI \xrightarrow{Et_2O} Li_2Cu_3(CH_3)_5 + 3LiI \tag{3}$$

$$2Li_2Cu_3(CH_3)_5 + 5LiAlH_4 \rightarrow 2Li_2Cu_3H_5 + 5LiAlH_2(CH_3)_2 \tag{4}$$

Preparation of $LiCuH_2$ has been reported earlier by us.[8] It was prepared by the reaction of $LiAlH_4$ with a solution of $LiCu(CH_3)_2$ (eq 6) which was prepared in diethyl ether by the reaction of CH_3Li with CuI in 2:1 molar ratio (eq 5). The slightly yellow insoluble solid was characterized by elemental

$$2CH_3Li + CuI \rightarrow LiCu(CH_3)_2 + LiI \tag{5}$$

$$LiCu(CH_3)_2 + LiAlH_4 \rightarrow LiCuH_2 + LiAl(CH_3)_2H_2 \tag{6}$$

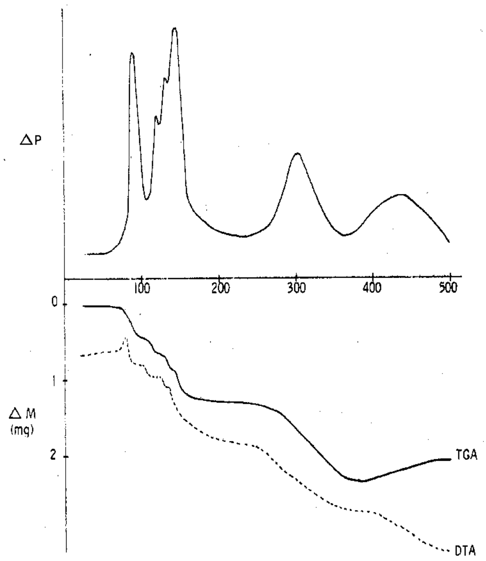

Figure 1. Vacuum DTA–TGA of Li_2CuH_3.

analysis and x-ray powder-diffraction analysis (showed only two diffuse lines). DTA–TGA studies showed that $LiCuH_2$ decomposed at 70 °C with gas evolution. At the time it was prepared, this compound was the most stable Cu–H compound known.

A most unusual and important observation regarding $LiCuH_2$ was recently made. When $LiCuH_2$, prepared as an insoluble solid in diethyl ether, was placed in THF, it dissolved immediately. This colorless solution was found to be stable at room temperature for about 1 h after which time it started to decompose producing a brownish-black solution. This is the first complex metal hydride, other than those containing aluminum and boron as the central metal atom, that we have found to be soluble in any solvent. The THF solubility makes this compound a candidate as a reducing agent for organic substrates as long as the reagent solutions are kept cold (–20 °C) prior to use.

When CH_3Li in diethyl ether was added to a well-stirred diethyl ether slurry of CuI in 3:1 ratio at –78 °C, a clear colorless solution resulted within a few minutes, having the composition $Li_2Cu(CH_3)_3$ (eq 7). Previous NMR studies have

$$3\mathrm{CH_3Li} + \mathrm{CuI} \xrightarrow{\mathrm{Et_2O}} \mathrm{Li_2Cu(CH_3)_3} + \mathrm{LiI} \qquad (7)$$

shown[4] that a complex of composition $Li_2Cu(CH_3)_3$ does form but is in equilibrium with CH_3Li and $LiCu(CH_3)_2$ (eq 8).

$$\mathrm{Li_2Cu(CH_3)_3} \rightleftharpoons \mathrm{CH_3Li} + \mathrm{LiCu(CH_3)_2} \qquad (8)$$

However, when the above solution was allowed to react with $LiAlH_4$, a white insoluble solid was formed which is stable at room temperature. As can be seen from eq 9, the resulting

$$\begin{array}{l} 2\mathrm{Li_2CuH_3} + 3\mathrm{LiAlH_2(CH_3)_2} \\ \quad \uparrow 3\mathrm{LiAlH_4} \\ 2\mathrm{Li_2Cu(CH_3)_3} \rightleftharpoons 2\mathrm{CH_3Li} + 2\mathrm{LiCu(CH_3)_2} \\ \qquad\qquad\qquad\qquad \downarrow 3\mathrm{LiAlH_4} \\ 2\mathrm{LiH} + 2\mathrm{LiCuH_2} + 2\mathrm{LiAlH_2(CH_3)_2} \end{array} \qquad (9)$$

white solid could be Li_2CuH_3 formed by the reaction of $LiAlH_4$ with $Li_2Cu(CH_3)_3$, a mixture of LiH and $LiCuH_2$ formed by the reaction of $LiAlH_4$ with CH_3Li and $LiCu(CH_3)_2$, or a mixture of LiH, $LiCuH_2$, and Li_2CuH_3 formed by the reaction of $LiAlH_4$ with the equilibrium mixture of CH_3Li, $LiCu(CH_3)_2$, and $Li_2Cu(CH_3)_3$. When the white solid was dried under vacuum, its elemental analysis corresponded to ether free Li_2CuH_3 (or LiH + $LiCuH_2$). If it was a mixture of LiH and $LiCuH_2$, then the x-ray powder-diffraction pattern should show lines due to LiH especially since $LiCuH_2$ does not give sharp, strong lines. However, the white solid gave a unique x-ray pattern which does not correspond either to $LiCuH_2$ or LiH. These results suggest that although $Li_2Cu(CH_3)_3$ in diethyl ether does exist as an equilibrium mixture of CH_3Li and $LiCu(CH_3)_2$, nevertheless, $Li_2Cu(CH_3)_3$ is more reactive toward $LiAlH_4$. Furthermore, Li_2CuH_3 is insoluble in THF. If Li_2CuH_3 is a mixture of LiH and $LiCuH_2$ then the $LiCuH_2$ should have dissolved in THF and only LiH should have remained insoluble.

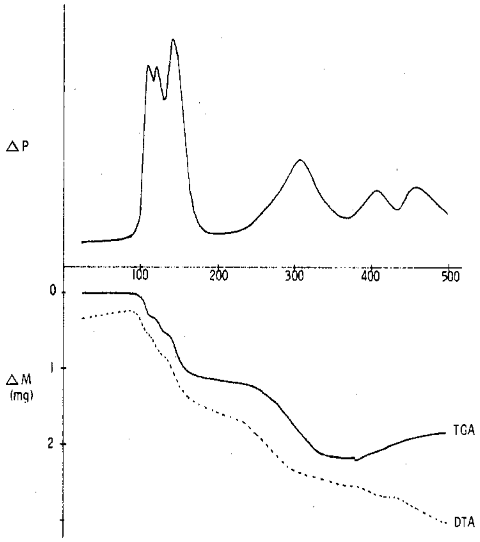

Figure 2. Vacuum DTA–TGA of Li_3CuH_4.

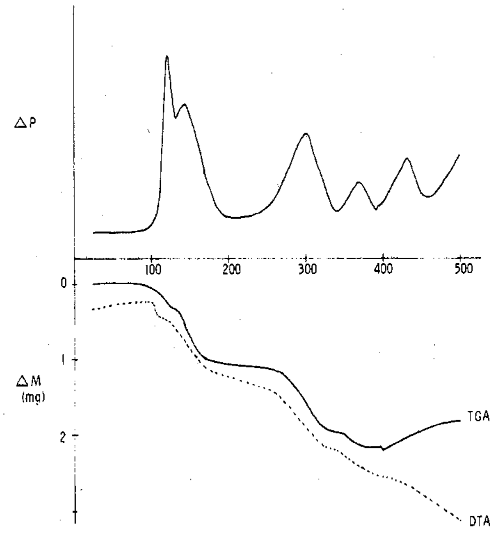

Figure 3. Vacuum DTA–TGA of Li_4CuH_5.

Results of vacuum DTA–TGA studies (Figures 1–4) are interesting and provide the following information. Li_2CuH_3 decomposes evolving noncondensable gases (H_2) at (a) 90, (b) 110, (c) 120, (d) 145, (e) 290, and (f) 440 °C (eq 10–16).

$$\text{(a) } 3\mathrm{Li_2CuH_3} \xrightarrow{90\,^\circ\mathrm{C}} 2\mathrm{Li_3CuH_4} + \mathrm{CuH} \qquad (10)$$

$$\mathrm{CuH} \rightarrow \mathrm{Cu} + {}^1/_2\mathrm{H_2} \qquad (11)$$

$$\text{(b) } 2\mathrm{Li_3CuH_4} \xrightarrow{110\,^\circ\mathrm{C}} {}^3/_2\mathrm{Li_4CuH_5} + {}^1/_2\mathrm{Cu} + {}^1/_2\mathrm{H_2} \qquad (12)$$

$$\text{(c) } {}^3/_2\mathrm{Li_4CuH_5} \xrightarrow{120\,^\circ\mathrm{C}} {}^6/_5\mathrm{Li_5CuH_6} + {}^3/_{10}\mathrm{Cu} + {}^3/_{20}\mathrm{H_2} \qquad (13)$$

$$\text{(d) } {}^6/_5\mathrm{Li_5CuH_6} \xrightarrow{145\,^\circ\mathrm{C}} 6\mathrm{LiH} + {}^6/_5\mathrm{Cu} + {}^3/_5\mathrm{H_2} \qquad (14)$$

$$\text{(e) } 3\mathrm{LiH} + 3\mathrm{Cu} \xrightarrow{290\,^\circ\mathrm{C}} 3\mathrm{LiCu} + {}^3/_2\mathrm{H_2} \qquad (15)$$

$$\text{(f) } 3\mathrm{LiH} \xrightarrow{440\,^\circ\mathrm{C}} 3\mathrm{Li} + {}^3/_2\mathrm{H_2} \qquad (16)$$

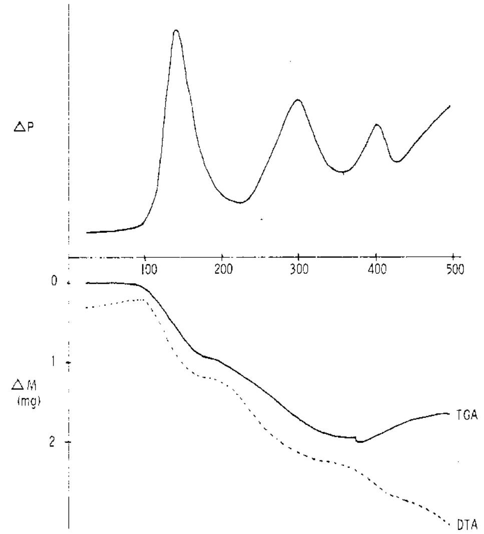

Figure 4. Vacuum DTA–TGA of Li_5CuH_6.

The thermal effect for the first gas evolution contains a sharp exotherm superimposed on an endotherm. The thermal effects for all other (b to f) gas evolutions are endotherms. The ratios of the weight loss for the gas evolutions from a to e, i.e., a:b:c:d:e, are 9.5:5.3:3.2:11.8:29.2. For the last decomposition (f) the gas evolution was found to be over a broad temperature range (400–480 °C) centered at 440 °C. Surprisingly, instead of a weight loss, a weight gain was observed which could not be interpreted. The first gas evolution (a) is attributed to decomposition of Li_2CuH_3 to Li_3CuH_4 and CuH with simultaneous decomposition of CuH (eq 10 and 11). The second endotherm (b) is due to the decomposition of Li_3CuH_4 to Li_4CuH_5 and CuH (Cu + $^1/_2$ H_2) (eq 12). The third gas evolution (c) is probably due to decomposition of Li_4CuH_5 to Li_5CuH_6 and (Cu + $^1/_2$ H_2) (eq 13). The fourth gas evolution (d) at 145 °C is a result of the decomposition of Li_5CuH_6 to LiH and (Cu + $^1/_2$ H_2) (eq 14). The last two decompositions (e and f) are due to LiH decomposition (eq 15 and 16). The gas evolution at 290 °C is thought to be due to LiH. This low-temperature decomposition can be explained[11] by the influence of elemental copper on the decomposition of LiH (presumably involving a solid-state reaction between LiH and Cu). Thus according to these DTA–TGA results, it seems that Li_2CuH_3 decomposes stepwise to produce different intermediate complex metal hydrides. If these are indeed intermediates, then it should be possible to prepare and isolate these compounds.

In order to prepare Li_3CuH_4, CH_3Li was allowed to react with CuI in 4:1 ratio at 0 °C (eq 17) followed by addition of

$$4CH_3Li + CuI \rightarrow Li_3Cu(CH_3)_4 + LiI \quad (17)$$

$$Li_3Cu(CH_3)_4 + 2LiAlH_4 \rightarrow Li_3CuH_4 + 2LiAlH_2(CH_3)_2 \quad (18)$$

$LiAlH_4$ (eq 18). It is interesting to note that no cuprate of composition $Li_3Cu(CH_3)_4$ has been reported. At room temperature a white solid precipitated from solution which was filtered and dried under vacuum. Elemental analysis revealed the empirical composition Li_3CuH_4 and established that the compound contained no ether. The product has very little solubility in THF. An x-ray powder-diffraction pattern showed the solid to be different from that of a mixture of Li_2CuH_3 and LiH. Vacuum DTA–TGA studies of Li_3CuH_4 showed that it decomposes evolving noncondensable gases at 110, 120, 145, 288, and 445 °C (Table I). These results suggest that the product Li_3CuH_4 is stable up to 110 °C then decomposes to produce Li_4CuH_5, which then decomposes at 120 °C to give Li_5CuH_6, which decomposes at 145 °C to give LiH, Cu, and H_2. In order to lend support to the suggestion that Li_3CuH_4 decomposes to Li_4CuH_5 and CuH, an attempt was made to prepare Li_4CuH_5.

Li_4CuH_5 was prepared by the reaction of $LiAlH_4$ with $Li_4Cu(CH_3)_5$ which in turn was prepared by adding 5 equiv of CH_3Li to 1 equiv of CuI slurry in diethyl ether (eq 19).

$$5CH_3Li + CuI \rightarrow Li_4Cu(CH_3)_5 + LiI \quad (19)$$

Although low-temperature NMR studies showed no evidence of a complex such as $Li_4Cu(CH_3)_5$ in diethyl ether, the reaction of this solution with $LiAlH_4$ produced a white solid (eq 20)

$$2Li_4Cu(CH_3)_5 + 5LiAlH_4 \rightarrow Li_4CuH_5 + 4LiAlH_2(CH_3)_2 \quad (20)$$

which was stable at room temperature for over 30 days. The DTA–TGA studies on this complex showed that it decomposes at 120 °C with noncondensable gas evolution. The other gas evolutions were at 145, 290, and 440 °C. The DTA–TGA data are given in Table I. Interestingly, although DTA–TGA analysis suggests Li_4CuH_5 to be a new compound, its x-ray powder-diffraction pattern gave lines characteristic of Li_3CuH_4. Apparently the compound was decomposed by the x rays. Most interestingly, the complex Li_4CuH_5 was found to be soluble in THF and was stable in solution when kept overnight at room temperature. However, some of the solid (analyzed for Li_4CuH_5) precipitated from solution when cooled to −15 °C. The solubility of Li_4CuH_5 indicates that it cannot be a mixture of Li_3CuH_4 and LiH though it gives an x-ray diffraction pattern similar to Li_3CuH_4.

Reaction of CH_3Li with CuI in 6:1 molar ratio at −78 °C in diethyl ether produced a clear solution (eq 21). Reaction

$$6CH_3Li + CuI \rightarrow Li_5Cu(CH_3)_6 + LiI \quad (21)$$

of this solution with $LiAlH_4$ resulted in a white insoluble solid (eq 22). Elemental analysis of the product corresponded to

$$Li_5Cu(CH_3)_6 + 3LiAlH_4 \rightarrow Li_5CuH_6 + 3LiAlH_2(CH_3)_2 \quad (22)$$

the empirical formula Li_5CuH_6; however, the x-ray powder-diffraction pattern exhibited lines characteristic of Li_3CuH_4 (suggesting possibly a mixture of Li_3CuH_4 and LiH). However, the vacuum DTA–TGA studies showed that the first decomposition involving noncondensable gases took place at 145 °C which was different from that observed for Li_3CuH_4 (110 °C) and Li_4CuH_5 (120 °C). When this product was exposed to x rays, it turned black at the point of x-ray impact. In fact, all of the complex copper hydrides decomposed to some extent on exposure to x rays thus possibly accounting for the observation of lines due to other compounds. The compound Li_5CuH_6 is very stable at room temperature and does not decompose over a 30-day period. The compound is insoluble in THF ruling out the possibility of being a mixture of LiH and Li_4CuH_5 since Li_4CuH_5 is soluble in THF.

Reaction of these complex metal hydrides of copper with organic substrates shows very interesting results, e.g., they reduce C–I to C–H when allowed to react in 1:1 molar ratio. Furthermore, Li_2CuH_3 is more selective in the reduction of enones than any other complex in this series. Reactions of Li_4CuH_5 and Li_5CuH_6 with the same organic substrates gave dissimilar results suggesting Li_5CuH_6 is not a mixture of Li_4CuH_5 and LiH. These results will be published shortly.

Registry No. $LiCu_2H_3$, 64057-24-5; $Li_2Cu_3H_5$, 64091-65-2; Li_2CuH_3, 64010-63-5; Li_3CuH_4, 64010-64-6; Li_4CuH_5, 64010-65-7; Li_5CuH_6, 64010-66-8; CuI, 7681-65-4; CH_3Li, 917-54-4; $LiAlH_4$, 16853-85-3; $[LiAlH_2(CH_3)_2]$, 19528-78-0.

References and Notes

(1) J. F. Normant, *Synthesis*, 63 (1972); G. H. Posner, *Org. React.*, **19**, 1 (1972).
(2) E. C. Ashby and J. J. Watkins, *J. Chem. Soc., Chem. Commun.*, 784 (1976).
(3) E. C. Ashby, J. J. Lin, and J. J. Watkins, *J. Org. Chem.*, **42**, 1099 (1977).
(4) E. C. Ashby and J. J. Lin, *J. Org. Chem.*, **42**, 2805 (1977).

(5) J. A. Dilts and D. F. Shriver, *J. Am. Chem. Soc.*, **90**, 5769 (1968).
(6) S. A. Bezman, M. R. Churchill, J. A. Osborn, and J. Wormald, *J. Am. Chem. Soc.*, **93**, 2063 (1971).
(7) G. Monnier, *Ann. Chim. (Paris)*, **2**, 14 (1957).
(8) E. C. Ashby and R. Kovar, *Inorg. Chem.*, **16**, 1437 (1977).
(9) E. C. Ashby, T. F. Korenowski, and R. D. Schwartz, *J. Chem. Soc., Chem. Commun.*, 157 (1974).
(10) E. C. Ashby and R. D. Schwartz, *J. Chem. Educ.*, **51**, 65 (1974).
(11) D. F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(12) G. B. Kauffman and L. A. Teter, *Inorg. Synth.*, **7**, 9 (1963).
(13) S. Aronson and F. J. Salzano, *Inorg. Chem.*, **8**, 1541 (1969).
(14) In a separate study we have determined the Al–H stretching absorption of $LiAl(CH_3)H_3$, $LiAl(CH_3)_2H_2$, and $LiAl(CH_3)_3H$ in Et_2O and THF by reacting $LiAlH_4$ with $LiAl(CH_3)_4$. Clearly as the stoichiometry of the reaction is varied, the Al–H stretching frequency of one compound disappears and a different Al–H frequency appears representing the next redistribution analogue. The Al–H stretching frequency of the above compounds in Et_2O and THF is as follows: 1728, 1708, and 1685 cm^{-1} in Et_2O and 1685, 1678, and 1665 cm^{-1} in THF, respectively.

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Kinetics and Mechanisms of the Copper-Catalyzed Decomposition of Hypochlorite and Hypobromite. Properties of a Dimeric Copper(III) Hydroxide Intermediate

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Copper(II) hydroxide complexes catalyze the decomposition of OCl^- and OBr^- via two pathways, one first order and one second order in copper. The latter pathway produces small amounts of a yellow intermediate, B, which is a dimeric copper(III)

$$OX^- \xrightarrow[Cu(II)]{k_{AB}} B \xrightarrow{k_{BC}} {}^1/_2 O_2 + X^- \qquad k_{BC} >> k_{AB}$$

hydroxide complex. The spectrum of this complex has maxima at 270 and 362 nm (each with $\epsilon \sim 18\,800$ M^{-1} cm^{-1}). Chloride has no effect on reactions of OCl^-. Bromide suppresses both the concentration of B and the rate of oxygen evolution during the decomposition of OBr^- because of the reversibility of the formation of B. This is used to establish the stoichiometry of the dimer and its electrode potential: $Cu^{III}_2(O)(OH)_7^{3-} + H_2O + 2e^- \rightarrow 2Cu^{II}(OH)_4^{2-} + OH^-$; $E° = 0.82$ V (vs. NHE). The half-life of this dimer (producing oxygen) is 10.5 s in 1 M NaOH at 25 °C. The monomeric pathway does not produce measurable amounts of Cu(III).

Introduction

The addition of Cu(II) to alkaline solutions of hypochlorite or hypobromite results in the formation of a yellow species and the evolution of oxygen. Thenard,[1] in 1818, was the first to report this behavior in the case of hypochlorite. He suggested that the yellow species was copper peroxide. In 1953, Lister[2] claimed that the yellow species could not be a peroxide because of the rapid decomposition of peroxides by hypochlorite. He proposed that it was a copper(III) hydroxide complex, $Cu(OH)_4^-$. This formula was based on conclusions from a rough solubility study as a function of OH^-. The ability of earlier workers to precipitate red $Ba(CuO_2)_2$ from hypobromite solutions[3,4] was evidence for the existence of a copper(III) oxide salt. In 1965, Magee and Wood[5] isolated solid sodium dioxocuprate(III) ($NaCuO_2$) from alkaline solutions of OBr^- and Cu(II). Despite this, they challenged Lister's interpretation concerning the presence of an appreciable amount of a soluble copper(III) hydroxide complex. Their experiments showed the reddish brown $NaCuO_2$ to be unstable in alkaline solution and to decompose as shown in eq 1. They suggested

$$4NaCu^{III}O_2 + 2H_2O \rightarrow 4NaOH + 4Cu^{II}O + O_2 \qquad (1)$$

Lister's results could be explained by assuming that most of the copper was present as a copper(II) hypochlorite complex and only a small fraction was present as Cu(III).

The ability of copper to catalyze the decomposition of OCl^- (eq 2) is not under dispute, but there is disagreement about

$$2OCl^- \xrightarrow{Cu(II)} O_2 + 2Cl^- \qquad (2)$$

the reaction order. Lister reported the order dependence in Cu(II) to be 1.0 while Prokopcikas[6] found it to be 2.0. In the analogous OBr^- decomposition, Sakharov[7] found a $[Cu(II)]^{1.7}$ order dependence.

In the present work, the kinetics of the copper-catalyzed decomposition of hypohalite ions in strong base are investigated. The reaction order in copper varies with the concentration of Cu(II) because of the existence of two reaction pathways. Confirmation of a reactive Cu(III) complex in solution is presented. The stoichiometry, absorption spectrum, electrochemical potential, and reactivity are determined for the Cu(III) complex.

Copper(II) hydroxide is slightly amphoteric and redissolves in strong base to form $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$ complexes.[8] As the present work shows, copper(III) hydroxide complexes are not very stable in basic solution but do have a finite lifetime. Two Cu(III) complexes containing oxygen donor groups, which have long been known to exist in basic solution, are those of periodate and tellurate.[9,10] Their stability and oxidizing power have been used by Beck[11-13] and others[14] in a number of analytical determinations. Crystalline $Na_3KH_3[Cu(IO_6)_2]\cdot 14H_2O$ has four periodate oxygen atoms in a square plane around Cu(III) at a distance of 1.9 Å and a water molecule forming a fifth bond to copper at a distance of 2.7 Å.[15]

Other donor groups also are effective in stabilizing Cu(III), particularly deprotonated-nitrogen peptide donors which have been shown to form relatively stable complexes in solution.[16-18] In somewhat earlier work, electrochemical oxidation was used to prepare Cu(III) complexes of macrocyclic tetramines in acetonitrile.[19] Pulsed-radiolysis studies produced extremely reactive Cu(III) complexes of amines and amino acids in aqueous solution.[20] Solid Cu(III) complexes of biuret and of oxamide have been isolated and characterized.[21,22] The