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Copper Compounds of Acetylene

I. Acetylene Compounds with Cuprous Chloride

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The first to report a compound of the type n CuCl · C_2H_2 were Hofmann and Küspert [1], who found when bubbling acetylene through a solution of cupric chloride in absolute ethyl alcohol that a compound of composition 6CuCl · C_2H_2 had formed. Chavastelon [2] synthetized a compound 2CuCl · C_2H_2 and determined the vapour pressure at different temperatures.

Berthelot [3] investigated the absorption of acetylene in an acid solution of cuprous chloride and assumed from the results the existence of 3CuCl · C_2H_2 and 5CuCl · C_2H_2.

Manchot, Winthers and Oltrogge [4] made further absorption measurements, found from analyses the presence of 2CuCl · C_2H_2 and assumed the compound CuCl · C_2H_2 to exist, though no analysis was undertaken.

Gilliland, Bliss and Kip [5] repeated Chavastelon's vapour pressure measurements but found much higher pressures.

The purpose of my investigation was to determine the range of existence for these compounds with regard to temperature and pressure of acetylene and to determine the crystal structures of the compounds by X-ray analysis.

They were synthetized by methods given by the various authors, but my results did not always agree with theirs. Only two compounds, 3CuCl · C_2H_2 and 2CuCl · C_2H_2, could be reproduced.

When measuring the vapour pressures of these compounds, a tensiometrical method was first used. Cuprous chloride and an alcoholic solution of hydrogen chloride in a small bulb, also containing acetylene and connected to a mercury manometer, were vigorously shaken in a thermostat. When the compound 3CuCl · C_2H_2 was produced, the acetylene pressure decreased towards a limit. In a new experiment 3CuCl · C_2H_2 was treated like the cuprous chloride in the former, but at a pressure below the previously found limit. The ace-

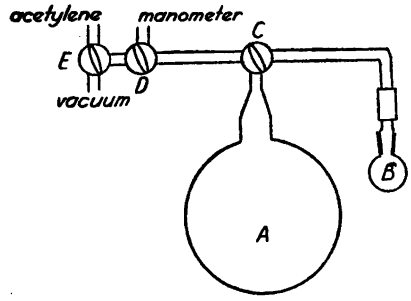

Fig. 1. Synthesis apparatus.

A. Gas container.
B. Reaction vessel.
C, D, E. Valves.

tylene compound decomposed, and the pressure increased to a limit differing from the former. Though the experiments continued for several days, no reproducible results could be reached by this method.

Instead the compounds were synthesized under controlled pressure of acetylene, and analysed immediately. A solution of hydrogen chloride in ethyl alcohol was used as reaction medium instead of aqueous solution, because the compounds could then be dried more quickly, and the disintegration diminished.

The X-ray determinations were undertaken when the range of existence had been determined for the compounds.

VAPOUR PRESSURE MEASUREMENTS

Experimental

Materials. The cuprous chloride used was of pro analysi quality. It was purified by solving in strong hydrochloric acid, the solution diluted with water and filtered. After washing with alcohol and ether, it was dried and stored in an evacuated exsiccator.

The acetylene was supplied by AGA Co., Lidingö, in a tank with their usual porous filling, but without acetone. Control analyses showed the gas containing 99 % acetylene, $\sim$ 1 % nitrogen, and traces of other gases.

The alcoholic solution of hydrogen chloride was prepared by mixing 1 part of conc. hydrochloric acid and 100 parts of ethyl alcohol of 99 % strength.

Synthesis apparatus. The apparatus constructed for the purpose is shown in Fig. 1. A small bulb B, containing 10 ml, was the reaction vessel. It was removable from the rest of the apparatus by a ground joint. The larger bulb A of 1000 ml was the gas container, and was connected to the reaction bulb, a manometer, a vacuum pump, and the acetylene storage by the valves C, D and E.

The apparatus was immersed in a thermostat, and the stirring during the synthesis achieved by vigorously shaking the small bulb, which was connected flexibly to the apparatus by a short rubber tube. This was glued to the glass and held by clamps. The ground joint was held by springs and sealed by picein.

The manometer was of mercury U-type with a steel scale. The pressure readings were corrected to 0° C of mercury, and reduced by the vapour pressure of ethyl alcohol at the temperature given.

All temperatures were measured on a mercury thermometer divided in 0.1° C.

When starting a synthesis, 0.5 g cuprous chloride and 5 ml hydrochloric alcohol was transferred to the reaction bulb. This was attached to the apparatus, and the joint carefully sealed. The system was evacuated, washed twice with acetylene, and finally filled to appropriate pressure, which had to be corrected a few times during the beginning of the synthesis. After 24—48 hours the reaction was complete. The small bulb was released, cooled to 0° C, and the contents pressed through a glass filter by acetylene of 2 atm. and immediately analysed. It was found by experiments, that when washing the compounds on the glass filter with alcohol and ether, saturated with acetylene, before analysing the losses of acetylene were larger than when analysing the compounds immediately.

Analyses. Acetylene was determined by a method given by Vestin [6]. The addition compound was decomposed by a solution of potassium cyanide, the gas evolved bubbled through 0.6 *N* solutions of silver nitrate, where the following reaction occured:

$$C_2H_2 + 3AgNO_3 = C_2Ag_2 \cdot AgNO_3 + 2HNO_3$$

The acid developed was titrated with 0.05 *N* solution of sodium hydroxide, using chlorphenol-red as indicator. The accuracy is approximately 1 per cent.

Copper was determined by electrolysis of the hot, diluted cyanide solution, using platinum electrodes, which were both weighed before and after the experiment. The accuracy was found better than 0.5 per cent.

Results

When possible, an estimation of the vapour pressure by tensiometrical measurements was made before starting the controlled syntheses. These were performed at 10, 15, 20 and 25° C at pressures up to 2 atm.

A study of the composition changes at different pressures was made, the limit pressure of two compounds being found by stepwise narrowing the pressure interval in which a change of composition occured. When the interval was a few mm mercury, the measurements were discontinued. Further narrowing is of little value, due to uncertaincies in the other experimental conditions. To avoid these as much as possible, the last intervals was determined by simultaneous synthesis at the higher and lower pressures.

The experimental results are found in Tables 1, 2, 3, and 4, where n is the number of moles acetylene per mole cuprous chloride.

Table 1. Syntheses from cuprous chloride at 10° C.

Temp. °C	Time h	p mm Hg	mM C_2H_2	mM Cu	n
10.02	24	178	0	—	0
10.03	22	188	0	—	0
10.02	24	192	0.472	3.06	0.16
10.15	24	198	0.436	1.65	0.27
10.00	24	397	0.323	0.973	0.33
10.00	24	400	0.444	1.42	0.31
10.00	24	403	0.546	1.24	0.44
10.00	18	407	1.78	2.43	0.44
10.00	18	411	0.578	1.24	0.47
10.03	16	415	0.985	2.12	0.47
10.02	16	415	0.985	2.12	0.45

Table 2. Syntheses from cuprous chloride at 15° C.

Temp. °C	Time h	p mm Hg	mM C_2H_2	mM Cu	n
15.02	16	260	0	—	0
15.02	16	263	0.281	1.03	0.28
15.11	24	577	0.963	2.88	0.33
15.10	22	591	1.06	3.47	0.33
15.08	40	594	1.30	3.62	0.28
15.10	26	598	0.742	1.69	0.44
15.06	48	642	0.530	1.12	0.48
15.09	24	790	0.677	1.48	0.46
15.09	24	825	1.46	3.14	0.47
14.87	40	1090	0.487	1.03	0.47
15.05	20	1181	1.18	2.68	0.44
14.94	30	1274	0.372	0.764	0.49
15.02	40	1496	0.630	1.29	0.49

Table 3. Syntheses from cuprous chloride at 20° C.

Temp. °C	Time h	p mm Hg	mM C_2H_2	mM Cu	n
19.98	22	350	0	—	0
19.97	16	352	0	—	0
19.97	17	353	0.206	0.716	0.29
19.99	22	355	0.518	1.58	0.33
19.99	19	357	0.531	1.74	0.31
19.98	28	364	0.515	1.55	0.33
19.94	48	749	0.521	1.62	0.32
19.89	24	752	0.469	1.42	0.33
19.89	24	757	0.504	1.09	0.46
19.90	24	762	1.558	3.38	0.46
19.90	24	764	0.511	1.06	0.48
19.90	24	765	0.720	1.58	0.46
19.84	18	774	0.540	1.11	0.49

Table 4. Syntheses from cuprous chloride at 25° C.

Temp. °C	Time h	p mm Hg	mM C_2H_2	mM Cu	n
25.02	24	256	0	—	0
25.05	24	373	0	—	0
25.03	24	400	0	—	0
25.05	16	440	0	—	0
25.04	24	460	0	—	0
25.02	24	470	0	—	0
25.02	24	473	0.434	1.45	0.31
25.05	22	484	1.31	3.92	0.33
25.05	24	496	0.525	1.69	0.31
25.03	24	517	1.24	4.04	0.31
25.03	24	540	0.780	2.69	0.30
25.05	24	693	1.27	4.51	0.28
25.05	24	790	0.225	0.705	0.32
25.01	24	820	0.598	2.00	0.30
25.01	24	860	0.482	1.71	0.28
25.04	21	874	0.455	1.52	0.30
25.04	22	930	0.652	2.12	0.31
25.03	15	952	0.498	1.52	0.33
25.08	24	961	0.729	2.31	0.32
25.00	20	988	0.650	2.06	0.32
25.05	22	1003	0.536	1.73	0.31
25.05	22	1007	0.710	1.56	0.46
25.05	14	1020	0.582	1.27	0.46
25.03	13	1180	1.01	2.21	0.46
25.05	20	1250	0.785	1.79	0.44
25.00	48	1490	0.623	1.32	0.47

As is seen from the tables, the number of moles acetylene per mole of copper averages to 0.31 and 0.47 instead of 0.33 and 0.50, as would be expected for the compounds $3CuCl \cdot C_2H_2$ and $2CuCl \cdot C_2H_2$. This discrepancy can be explained:

1. by losses of acetylene due to disintegration between syntheses and analyses, though the period was only a few seconds.
2. by incomplete reactions.

The moist compounds were found to decompose very fast, but when carefully dried they were comparatively stable. Precautions were taken to decrease the losses of acetylene between synthesis and analysis to a minimum.

To investigate the second possibility, series of experiments were performed to determine the composition at different times during the synthesis under the same conditions as in earlier experiments. Tables 5 and 6 show the results.

Table 5. Studies of the time required to synthesize $3CuCl \cdot C_2H_2$ at 25° C.

p mm Hg	Time h	mM C_2H_2	mM Cu	n
490	8	0.575	2.48	0.23
490	16	0.503	1.53	0.33
490	24	0.526	1.69	0.31
490	36	0.691	2.26	0.31

Table 6. Studies of the time required to synthesize $2CuCl \cdot C_2H_2$ at 25° C.

p mm Hg	Time h	mM C_2H_2	mM Cu	n
1 500	10	0.671	1.78	0.38
1 500	20	0.934	2.02	0.46
1 500	30	0.785	1.64	0.48
1 500	40	0.630	1.29	0.49

It was sometimes observed that the reaction was inhibited for a long time, even 12 hours, before it started and could then be almost completed in a few more hours. The reason could not be found.

In order to make sure that the compositions were reproducible and the equilibrium real, a few reactions were performed, starting from materials richer in acetylene than the product, *e. g.* $3CuCl \cdot C_2H_2$ from $2CuCl \cdot C_2H_2$. The results are given in Table 7.

The contents of Tables 1, 2, 3 and 4 show the existence of only two compounds, $3CuCl \cdot C_2H_2$ and $2CuCl \cdot C_2H_2$, in the pressure range up to 2 atm. at

Table 7. Decomposition of $2CuCl \cdot C_2H_2$ at 25° C.

Time h	p mm Hg	mM C_2H_2	mM Cu	n
18	363	0.078	2.25	0.03
22	700	0.795	2.32	0.34

temperatures between 10 and 25° C. The sudden pressure steps between these compounds show that the addition compounds of cuprous chloride and acetylene have distinct compositions and are not berthollides with continuously varying compositions. The vapour pressures are given in Table 8.

Table 8. Vapour Pressures of acetylene-cuprous chloride compounds.

Compound	Temp. °C	p mm Hg
$3CuCl \cdot C_2H_2$	10.02	190
»	15.02	262
»	19.97	353
»	25.02	472
$2CuCl \cdot C_2H_2$	10.00	402
»	15.09	596
»	19.89	755
»	25.05	1005

The enthalpy change $\Delta H°$ of the decompositions:

$$3CuCl \cdot C_2H_2 = 3CuCl + C_2H_2 \quad (1)$$
$$2CuCl \cdot C_2H_2 = 2\ 3CuCl \cdot C_2H_2 + C_2H_2 \quad (2)$$

have been calculated by plotting the logarithms of the vapour pressures found against $1/T$. The slope of the curve is $-0.43\ \Delta H°/R$. The points lie close to two straight lines, the divergences are less than 3 per cent of the pressure values.

Calculations were also made of the free energy or enchresy [7] change $\Delta G°$ and the entropy change $\Delta S°$. The results are given in Table 9.

Table 9. Thermodynamical constants at 25° C.

Reaction	p atm.	$\Delta G°$ cal mole	$\Delta H°$ cal mole	$\Delta S°$ cal mole · degree
$3CuCl \cdot C_2H_2 = 3CuCl + C_2H_2$	0.621	277	10 200	34
$3\ 2CuCl \cdot C_2H_2 = 2\ 3CuCl \cdot C_2H_2 + C_2H_2$	1.32	771	10 200	32

DISCUSSION

In relation to earlier investigations my experiments show:

1. In the range of temperature and pressure investigated only two compounds $3CuCl \cdot C_2H_2$ and $2CuCl \cdot C_2H_2$ exist. The compounds $6CuCl \cdot C_2H_2$[1] and $5CuCl \cdot C_2H_2$[3] are probably mixtures. The compound $CuCl \cdot C_2H_2$[4] has not been found in this range.

Syntheses at — 30° C and an acetylene pressure of 750 mm Hg. have resulted in a compound $CuCl \cdot C_2H_2$, which will be subjected to further investigation.

2. The vapour pressures of $2CuCl \cdot C_2H_2$ were found to be much higher than those found by Gilliland and co-workers [5] and even much higher than those Chavastelon [2] reported.

The former used a tensiometrical method, withdrawing acetylene and measuring the limit pressure. The vapour pressures of $2CuCl \cdot C_2H_2$ they give are about 65 per cent lower than those I have observed and about 25 per cent lower than mine for $3CuCl \cdot C_2H_2$. The differences decrease somewhat at higher temperatures.

My experiencies of the tensiometrical method of measuring the vapour pressures are that in this case it is not possible to reach the equilibrium pressure at given temperature from higher or lower pressures in reasonable time, owing to the low reaction rate. Nor is it possible to detect the existence of two compounds by this method.

My conclusions are that due to the deficiencies of the method they used, Gilliland and co-workers happened to measure the vapour pressures of $3CuCl \cdot C_2H_2$ instead of $2CuCl \cdot C_2H_2$ and that these readings are too low, because after withdrawing acetylene the pressure reaches equilibrium only after a very long time.

Chavastelon does not report how he measured the vapour pressures.

X-RAY INVESTIGATIONS

These were characterised by the efforts to overcome difficulties in preparing a stable powder for the X-ray analyses and to record diffraction lines of lowest intensities.

Experimental

A holocylindrical powder spectrograph of 19 cm diameter was used. X-ray radiation was produced by a discharge tube with a copper target at 46 kV and 6 mA. No monochromator was used. Ilford Red Seal X-ray Film, ex-

posures of 36—48 hours, and maximum energy developer were employed to obtain photograms, recording as many diffraction lines as possible with the comparatively feeble source of radiation.

Thin Pyrex glass tubes were drawn to capillaries 0.5 mm in diameter and with walls 0.01—0.02 mm thick. They were broken into two pieces, the synthesized suspension of acetylene — cuprous chloride poured through the wider opening of the tube and then pressed down through the capillary by acetylene of 2 atm. Some crystals blocked the capillary, and the liquid could be pressed out. The crystals were dried in the flowing gas, and the capillary, having been cooled on the middle, was sealed at both ends in a small flame.

Comparative exposures of cuprous chloride were performed in a similar way.

Results

No discrepancy could be found between photograms of $3CuCl \cdot C_2H_2$ and $2CuCl \cdot C_2H_2$. The only difference detected between these and photograms of cuprous chloride is they very weak lines 100 and 110 found in the former. The line 110 is doubtful. Both lines have, however, been found at repeated experiments. In all, two exposures of each acetylene compound and cuprous chloride were made, using newly prepared powders. Unfortunately the lines are too weak to appear on a photometer curve.

The intensities have been calculated assuming a cuprous chloride structure with acetylene interstitially placed in the hollow spaces of the pattern. The actual intensities of the lines 100 and 110, caused by the presence of acetylene, must be less than the corresponding intensities, if the reflection waves from all carbon atoms were of the same phase. These latter intensities can, however, be calculated without knowing the positions of the carbon atoms in the pattern, so it is possible to give an upper limit for the intensities of the lines 100 and 110 in comparison with the other lines in the photogram.

To make sure that acetylene did not escape from the powder during exposure, control analyses were made, but the small amount of sample makes the quantitative determination precarious. That at least 60 per cent of the acetylene was left is however beyond doubt.

The vapour pressures of the compounds do not exceed 760 mm. Hg at 18° C. Thermal decomposition is therefore unlikely. Disintegration due to the X-ray radiation is, however, possible and can not be prevented.

Table 10. Powder photogram of nCuCl, C_2H_2.

Cu-K radiation.

	$\sin^2\Theta$ calc.	$\sin^2\Theta$ obs.	I obs.	I calc.
100	0.0202	0.0206	v w	0.4
110	0406	0412	v v w	0.4
β111	0495	0501		
111	0606	0617	v st	10
β200	0660	0662		
200	0808	0802	v	0.6
β220	1321	1320		
220	1617	1616	v st	9
β311	1816	1815		
311	2223	2235	st	7
222	2425	2421	v w	0.2
β400	2642	2645		
β331	3137	3146		
400	3234	3242	m^-	2
331	3840	3839	m	3
β422	3962	3971		
420	4042	—	—	0.8
β511 / β333	4458	4452		
422	4850	4852	m^+	5
511 / 333	5457	5459	m	3
β531	5779	5775		
440	6467	6452	m^-	2
β620	6604	6601		
531	7074	7075	m^+	5
442 / 600	7276	—	—	0.4
620	8084	8088	m	4
533	8690	8689	m^-	4
622	8924	—	—	1
444	9701	9701	m^-	3

The cube edge a_0 is calculated to 5.406 Å.

DISCUSSION OF THE CRYSTAL STRUCTURE

On the presumption that the experimental results are correct, the crystal pattern of the addition compounds must be that of cuprous chloride with the acetylene molecules interstitially placed in the hollow spaces of the pattern. The contribution of acetylene to the lines in the photograms would then be

reflexes extinguished for the space group of cuprous chloride, T_d^2, and changed intensities for the others.

The scattering factor of carbon, f_C, decreases comparatively much faster at increasing sin Θ than f_{Cl} and f_{Cu}. Owing to geometrical configurations of the camera, the reflections are spread out over a larger surface at increasing Θ up to 45°. Perhaps it is the weakening of the "acetylene diffraction lines" by these two factors that makes it impossible to record more than the first two lines, 100 and 110.

To draw any conclusions as to how the acetylene molecules are placed in the pattern is naturally impossible under these circumstances. For cuprous chloride the structure is that of zinkblende, the atoms placed in the following way:

Space group T_d^2—$F\bar{4}3m$
4 Cu at 4(a): 000; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$.
4 Cl at 4(c): $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}\frac{3}{4}$; $\frac{3}{4}\frac{1}{4}\frac{3}{4}$; $\frac{3}{4}\frac{3}{4}\frac{1}{4}$.

Centres of the hollow spaces should be 4(b): $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}00$; $0\frac{1}{2}0$; $00\frac{1}{2}$ and 4(d): $\frac{3}{4}\frac{3}{4}\frac{3}{4}$; $\frac{3}{4}\frac{1}{4}\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}\frac{1}{4}$; $\frac{1}{4}\frac{1}{4}\frac{3}{4}$.

The shape of the hollow spaces accessible to acetylene is uncertain. From the vapour pressure investigations the conclusion must be drawn that the acetylene molecules do not move i tunnels through the pattern, as gas molecules can, in for example zeolites, because the compounds would then be berthollides and their compositions vary continually with the acetylene pressure.

Perhaps other methods or investigations of similar compounds will answer these questions.

SUMMARY

In the range of 10—25° C and pressures up to two atm. only two compounds, $3CuCl \cdot C_2H_2$ and $2CuCl \cdot C_2H_2$, are formed from acetylene and cuprous chloride in acid solution. Their vapour pressures were determined at 10, 15, 20, and 25° C. $\Delta H°$, $\Delta G°$ and $\Delta S°$ of the decompositions of the compounds were calculated for 25° C.

X-ray powder photograms of the compounds differed by only one, possibly two, new lines from that of cuprous chloride. The acetylene molecules are probably placed interstitially in the pattern of cuprous chloride.

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