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Solid Copper(I)carbonyl Complex. Composition and Equilibria

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The absorption of carbon monoxide by copper(I) chloride has been studied by manometrical methods in aqueous systems containing hydrochloric acid and dissolved potassium chloride. It turned out that the only components of the solid compound formed are carbon monoxide and copper(I) chloride, which are present in a molar ratio equal to unity. Although formed in aqueous solutions, this carbonyl complex does thus not contain H_2O as has been stated by earlier investigators.

The equilibrium pressure of carbon monoxide over solid copper(I) chloride coexistent with its solid carbonyl complex was determined with high precision. For the reaction $CO+CuCl(s)=COCuCl(s)$ thermodynamic data were calculated.

The phenomenon that copper(I) chloride in hydrochloric acid absorbs carbon monoxide has long been known.[1] Manchot and Friend[2] believed that a second ligand, *e.g.* water, was essential for the formation of a complex, and their suggestion for the composition was $CuClCO.2H_2O$. Subsequent investigators[3,4] have also accepted this formula and Manchot was not contradicted until Wagner[5] showed that under anhydrous conditions and high pressure copper(I) chloride absorbs carbon monoxide. For the complex the formula $Cu_2Cl_2 2CO$ was written. Wagner also measured the decomposition pressure, which by that time was done[4] also for the complex formed in hydrochloric acid. However, as both measurements were inaccurate, the conclusion that the complexes are identical was not drawn, and ever since then formulas for the hydrate[6–11] as well as the anhydrous complex[9–15] have appeared.

In the present work, most of the experiments have been performed in systems made up of H_2O and HCl saturated with Cu(I)Cl. In some cases dissolved KCl has also been included. A simple apparatus for absorption measurements was used (see EXPERIMENTAL).

List of symbols

- CO_{Cu} concentration of complex-bound carbon monoxide
- CO_t total concentration of carbon monoxide
- S solubility of copper(I) chloride – carbon monoxide absent
- HCl_t formal total concentration of hydrochloric acid
- $[Cl]^-$ concentration of "free" chloride ion
- $CuCl_t$ total concentration of copper(I) chloride
- P_{CO} partial pressure of carbon monoxide at equilibrium
- P_ε equilibrium pressure of carbon monoxide over copper(I) chloride and carbonyl complex as coexisting solid phases.

Pressures are given in Torr and concentrations in molal, *i.e.* mol/1000 g solvent (H_2O). Concentrations are often used in a generalized sense; that is calculations are made from the amount of substance and solvent present, regardless of whether all of the substance is dissolved or not.

RESULTS AND DISCUSSION

After every addition of carbon monoxide P_{CO} and CO_t were determined. The concentration of complex-bound carbon monoxide was then calculated according to

$$CO_{Cu} = CO_t - \alpha P_{CO} \quad (1)$$

where α (molal $Torr^{-1}$) determines the "physical" solubility in the solutions in question, *i.e.* the

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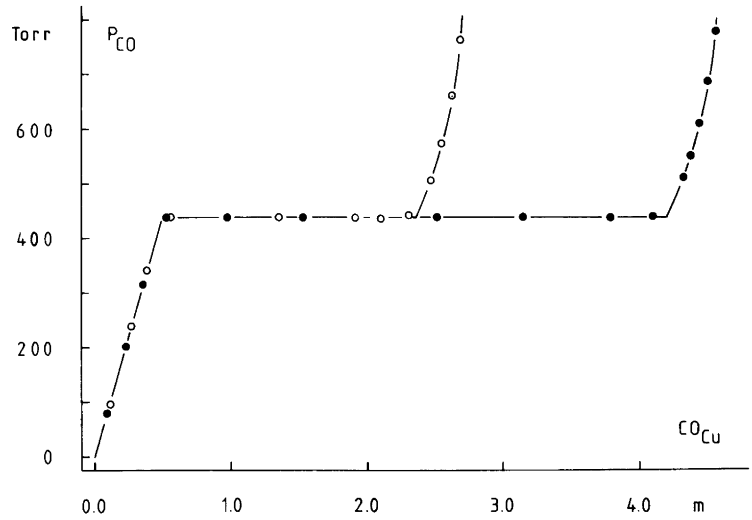

Fig. 1. Typical absorption curves in heterogeneous systems. $HCl_t = 4.00$ m. $CuCl_t = 3.101$ m (empty symbols) and $CuCl_t = 4.928$ m (filled symbols). 25.0 °C.

solubility in aqueous solutions of HCl (and KCl) of certain concentrations, with the exception of Cu(I)Cl. However, the physical solubility of carbon monoxide is quite low and in the solutions examined here it was of the same order as in pure water. The deviation from $\alpha = 1.0 \times 10^{-6}$ seems to be less than $\pm 20\,\%$. This variation in α will give rise to a maximum deviation in CO_{Cu} of 0.10 % in the experiments performed. Thus the above-mentioned value for α has been accepted and used throughout.

The absorption curves from measurements in heterogeneous systems show a characteristic pattern, as is evident from Fig. 1. There the results from two experiments are plotted, with the only difference being the amount of CuCl(s) present. To begin with, successive additions of carbon monoxide in systems saturated with Cu(I)Cl will cause P_{CO} to increase almost proportionally to CO_{Cu}. After the complex containing CO has precipitated, P_{CO} will keep a constant value as long as there is CuCl(s) left, and thereafter increase as is shown in Fig. 1. Because of the abrupt change in absorption it is easy to determine when the complex containing CO precipitates.

Constant equilibrium pressure

The results from the determination of the equilibrium pressure over solid Cu(I)Cl and solid carbonyl complex in different reaction media at 25.0 °C are presented in Fig. 2. In most experiments the reaction medium was made up of HCl and H_2O, with HCl_t being varied from 0.67 to 8.73 m. In three experiments dissolved KCl was also included. These mixtures had the concentration of "free" chloride ion in common (4.00 m) but contained different amounts of H^+ and K^+, the values of HCl_t being 0.10, 0.19 and 0.40 m, respectively. Twenty-five measurements gave a mean value of $P_\varepsilon = 436.6$ Torr with a standard deviation of no more than 0.6 Torr. No significant difference is observed for P_ε determined in experiments in different reaction media. However, values of P_ε determined after synthesis seem to be significantly higher than those made after splitting of the carbonyl complex.

As will be shown later in this paper, the equilibrium pressure depends rather strongly on the temperature. From formula (9) it follows that the maximum difference in P_ε (*ca.* ± 1 Torr) corresponds to a difference in temperature of no more than ± 0.04 degrees. As the thermostat used (Haake E52) can maintain a constant temperature only within ± 0.03 degrees, the observed difference in P_ε can be explained by minor temperature variations. The accepted value of P_ε at 25.0 °C was 436.6 ± 1.0 Torr.

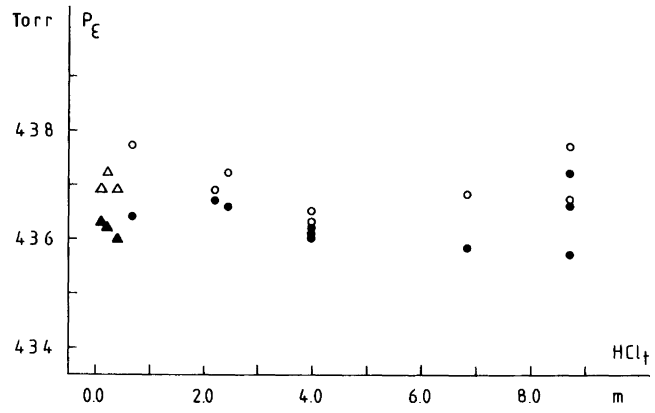

Fig. 2. Equilibrium pressure at 25.0 °C over copper(I) chloride and its carbonyl complex as coexisting solid phases measured after synthesis (empty symbols) and splitting (filled symbols) of the complex. ○ and ● denote systems where HCl is the sole dissociating chloride and △ and ▲ denote mixtures of HCl and KCl.

Components of the complex

As P_ε was found to be independent of $[H]^+$ when $[Cl^-]$ was kept constant, a solid CO-complex formed in solutions containing both H^+ and K^+ should not contain HCl. Furthermore, as P_ε is the same for solutions without K^+, neither should HCl be contained in a solid carbonyl complex formed there. Thus HCl is not a component of the solid complex in the systems investigated. In experiments with HCl as the sole dissociating chloride, HCl_t was varied from 0.67 to 8.73 m. Even though in this range water activity decreases by about 50 % the equilibrium pressure remains at a constant value. Therefore also H_2O is excluded as a component of the solid carbonyl complex and only CO and CuCl are parts of this compound.

Molar ratio by three methods

I. Measurements in systems differing only with respect to $CuCl_t$ will give absorption curves that are identical except for the length of the interval where the equilibrium pressure is constant, provided of course that sufficient Cu(I)Cl for two solid phases to be coexistent is used. Fig. 1 shows absorption curves from two such experiments performed in 4.00 m HCl at 25.0 °C.

For two absorption curves (1 and 2) as described above and with partial pressure $P_{CO} > P_\varepsilon$, the quotient

$$r = (CuCl_{t2} - CuCl_{t1})/(CO_{Cu2} - CO_{Cu1}) \quad (2)$$

will give a direct measure of the molar ratio CuCl/CO of the solid carbonyl complex. Calculations of this ratio using the technique described were performed for experiments in 4.00 m HCl and the results are presented in Table 1. The absorption curves were compared for the experimentally determined partial pressures $P_{CO} > P_\varepsilon$. This means that in both experiments every second value of CO_{Cu} had to be obtained by interpolation. This was done nonlinearly using each absorption curve's unique interpolation polynomial determined from the experimentally obtained points at $P_{CO} > P_\varepsilon$. From Table 1 it is evident that the molar ratio deviates only slightly from unity. As will be shown below, the deviations observed are due to experimental uncertainty.

II. If results from a separate experiment are to be used to determine the molar ratio CuCl/CO, it is necessary to know the composition of the liquid phase in order to estimate the amount of Cu(I)Cl dissolved. From preliminary measurements there is reason to assume that in dissolved CO-complexes exactly one molecule carbon monoxide is bound per copper atom. Furthermore, the amount of dissolved Cu(I)Cl, not in complex with carbon monoxide, is given by its solubility S when carbon monoxide is absent. The molar ratio CuCl/CO for the solid CO-complex can then be calculated according to

Table 1. Molar ratio CuCl/CO in solid carbonyl complex calculated from experiments differing only with respect to the amount of copper(I) chloride used. $HCl_t = 4.00$ m.25.0 °C. Pressures are given in Torr and concentrations[a] in molal.

P_{CO}	CO_{Cu} $CuCl_t =$ 3.101	$CuCl_t =$ 4.928	CuCl/CO
504.1	2.466	4.319[b]	0.986
549.6	2.522[b]	4.382	0.982
573.2	2.547	4.408[b]	0.982
609.7	2.582[b]	4.444	0.981
660.0	2.623	4.487[b]	0.980
686.7	2.642[b]	4.508	0.979
761.1	2.686	4.557[b]	0.976
779.5	2.695[b]	4.564	0.978

[a] Concentrations are used in the generalized sense mentioned above (see List of symbols). [b] Denotes that the value was calculated by interpolation.

$$r' = (CuCl_t - S - CO_{Cu\,a})/(CO_{Cu\,b} - CO_{Cu\,a}) \quad (3)$$

where the indices a and b denote the end points of the CO_{Cu}-interval where $P_{CO} = P_\varepsilon$. The numerical values of $CO_{Cu\,a}$ and $CO_{Cu\,b}$ have been obtained using the nonlinear interpolation technique mentioned above. Calculations of the molar ratio using formula (3) were made for the experiments in 4.00 m HCl referred to earlier. Table 2 also includes results from measurements in different reaction media – HCl_t from 0.670 to 4.79 m.

III. Upon absorption of carbon monoxide at $P_{CO} > P_\varepsilon$ the activity of Cu(I)Cl will decrease. At equilibrium one can, however, write

$$\{CuCl\} = P_\varepsilon/P_{CO} \quad (4)$$

provided that the sole solid phase present is the carbonyl complex with molar ratio equal to unity. It has been shown [16] that in hydrochloric acid at the concentrations used here the activity of copper(I) chloride is proportional to its concentration and that

$$\{CuCl\} = [CuCl]/S \quad (5)$$

For the molar ratio CuCl/CO in the solid carbonyl complex one can therefore write

$$r'' = (CuCl_t - SP_\varepsilon/P_{CO} - CO_{Cu\,a})/(CO_{Cu} - CO_{Cu\,a}) \quad (6)$$

assuming as before that in dissolved CO-complexes exactly one molecule carbon monoxide is bound per copper atom. Calculations according to (6) have been made and the results are presented in Table 3. The values of P_{CO} and CO_{Cu} are those experimentally determined. Only slight variation in the molar ratio can be observed for values determined at different partial pressures. Furthermore, the variation is not systematic and therefore does not indicate the existence of a solid carbonyl complex with molar ratio other than 1:1.

From Table 3 in particular, it is clear that there is a significant difference in the values determined from the two experiments made in 4.00 m HCl. The discrepancies are, however, such that they readily explain the deviation from unity when the molar ratio is calculated according to (2).

Accurate determinations of the molar ratio in solid carbonyl complex from experiments at higher acidity than *ca.* 4 m are difficult to make. A comparision with the function

$$f(x) = (a-x)/(b-x) \qquad a,b = \text{const.} \quad (7)$$

shows that, if formula (3) or (6) is to be used, a deviation from unity in $(CuCl_t - S)/CO_{Cu\,b}$ or in $(CuCl_t - SP_\varepsilon/P_{CO})/CO_{Cu}$ will give rise to a discrepancy in the molar ratio that increases with $CO_{Cu\,a}$. Since the solubility of both the carbonyl

Table 2. Carbon monoxide absorption at constant partial pressure and corresponding molar ratio CuCl/CO in the solid carbonyl complex. CO_{Cu}-interval limits indicated by a and b. Concentrations are given in molal and used in the generalized sense mentioned above (see List of symbols).

HCl_t	S	$CuCl_t$	$CO_{Cu\,a}$	$CO_{Cu\,b}$	CuCl/CO
0.670	0.056	0.913	0.094	0.847	1.013
2.465	0.333	2.046	0.292	1.661	1.038
4.00	0.735	3.101	0.490	2.365	1.001
4.00	0.735	4.928	0.488	4.176	1.005
4.79	1.020	2.429	0.611	1.420	0.986

Table 3. Determination of copper(I) chloride and carbon monoxide in the solid complex after complete co. ersion of CuCl(s), and corresponding molar ratio CuCl/CO. Pressures are given in Torr and concentrations[a] in molal.

HCl_t	S	$CuCl_t$	$CO_{Cu\,a}$	P_{CO}	CO_{Cu}	CuCl(s.c.)	CO(s.c.)	CuCl/CO
4.00	0.735	3.101	0.490	504.1	2.466	1.974	1.972	1.001
				573.2	2.547	2.051	2.053	0.999
				660.0	2.623	2.125	2.129	0.998
				761.1	2.686	2.189	2.192	0.999
4.00	0.735	4.928	0.488	549.6	4.382	3.856	3.894	0.990
				609.7	4.444	3.914	3.956	0.989
				686.7	4.508	3.973	4.020	0.988
				779.5	4.564	4.028	4.076	0.988
0.670	0.056	0.913	0.094	461.2	0.852	0.766	0.758	1.011
				558.2	0.864	0.775	0.770	1.006
				674.3	0.869	0.783	0.775	1.010
				743.7	0.872	0.786	0.778	1.010
2.465	0.333	2.046	0.292	472.8	1.698	1.446	1.406	1.028
				647.4	1.795	1.529	1.503	1.017
				713.8	1.812	1.550	1.520	1.020
				851.1	1.848	1.583	1.556	1.017

[a] Concentrations are used in the generalized sense mentioned above(see List of symbols). The amount of substance in solid carbonyl complex is indicated by (s.c.). The CO_{Cu} interval limit where this complex first precipitates is indicated by a.

complex and copper(I) chloride increases with HCl_t, the numerical instability of (3) and (6) makes it necessary to use large amounts of copper(I) chloride. However, the use of large amounts of solid phases may make it difficult to attain an accurate equilibrium.

Anyway, as the equilibrium pressure P_ε is the same in experiments with different HCl_t, the same solid carbonyl complex should be present, and its formula is simply COCuCl.

Temperature dependence

To obtain thermodynamic data for the reaction

$$CO + CuCl(s) = COCuCl(s) \quad (8)$$

the temperature dependence of P_ε was determined. Results from measurements in 8.73 m HCl are presented in Fig. 3. These measurements of P_ε were supported by a separate determination of the temperature dependence of the vapour pressure. The linear relation in Fig. 3 can be expressed by

$$\ln P_0 = \ln (436.6/760.0) - 5481.2(1/T - 1/298.15) \quad (9)$$

where P_0 denotes the standardized equilibrium pressure of carbon monoxide (760.0 Torr as standard state). To obtain the pressure at 298.15 K, the mean value of all measurements of P_ε at 25.0 °C was used. The value of the temperature coefficient was obtained by fitting a least-squares straight line to the values in Fig. 3. The value obtained is 5481.2 ± 12.8 K^{-1}. At 25.0 °C expression (9) gives the following thermodynamic data: $\Delta G° = -1.374 \pm 0.006$ kJ; $\Delta H° = -45.58 \pm 0.11$ kJ; $\Delta S° = -148.3 \pm 0.4$ JK^{-1}.

EXPERIMENTAL

Apparatus. For the absorption experiments a manometrical apparatus consisting of a water-jacketed gas byrette, an open mercury manometer with a glass-scale and a reaction flask immersed in water – temperature-regulated with a thermostat – was used. The reaction flask, equipped with a three-way stopcock and a sidetube, was connected to the apparatus *via* this three-way stopcock in a

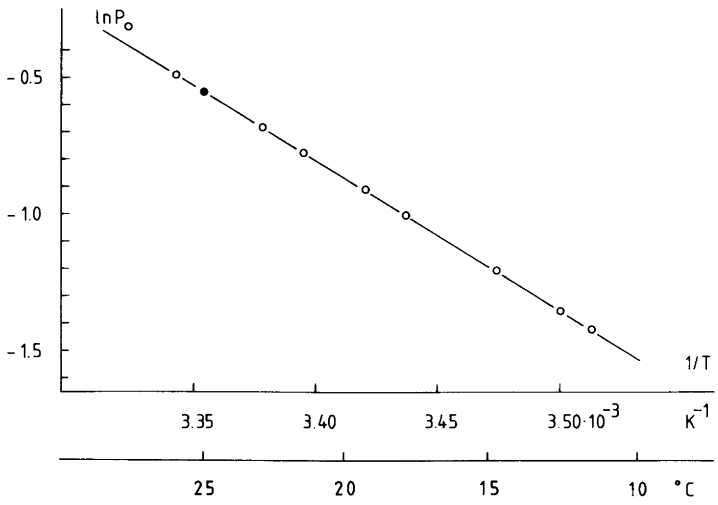

Fig. 3. Temperature dependence of the equilibrium pressure. ● denotes the mean value of all measurements at 25.0 °C. ○ denotes values from measurements in 8.73 m HCl.

Table 4. Equilibrium attainment in 4 m hydrochloric acid at 25.0 °C.

Notes	Time min	P_t [a] mmHg	P_{CO} Torr	CO_{Cu} molal
Absorption with CuCl(s) present as single solid phase.	0	270		0.0000
	1	95.7		
	5	95.7		
	10	95.8	78.4	0.0898
CuCl(s) coexisting with solid carbonyl complex.	0	590		0.4490
	4	458.8		
	9	455.8		
	21	455.4	437.1	0.5263
Absorption with the carbonyl complex present as single solid phase.	0	630		4.3301
	7	569.8		
	17	568.0		
	27	568.1	549.6	4.3815
Determination of the equilibrium pressure after	0	360		(4.038)
	1	452.4		
	4	454.3		
splitting	14	454.3	436.0	(3.850)
and	0	615		
	1	458.3		
synthesis	17	454.4	436.1	(3.944)
of the carbonyl complex				

[a] P_t denotes total pressure and is given in mmHg, uncorrected. P_t at time 0 was determined immediately after the addition or withdrawal of carbon monoxide and before shaking.

greaseless way (using "Rotulex"). In addition, it was hung up in a mechanical shaking device and by rubber tubing allowed to sway. The apparatus used was, with the exception of the slightly modified reaction flask, that described by Vestin.[17]

Procedure. At the beginning of each experiment the flask contained known amounts of copper(I) chloride and liquid. The volume of the gas phase was determined in each experiment by calibration with nitrogen. After evacuation to vapour pressure, measured quantities of carbon monoxide were added during vigorous shaking of the reaction vessel, whereby equilibrium was attained. To avoid unnecessary evaporation, a flask (vol. *ca.* 200 ml) was alternately evacuated and connected to the reaction vessel. After six or seven connections constant pressure readings were obtained. With this technique it has been shown[16] that the loss of liquid during evacuation is negligible.

After each addition of carbon monoxide the equilibrium pressure and concentration of complex-bound carbon monoxide were determined, giving one point on an absorption curve. For the determination of the equilibrium pressure over solid Cu(I)Cl coexistent with solid carbonyl complex a special routine was followed: A suitable amount of complex was synthesised. Thereafter gas was removed by a succession of withdrawals using the gas byrette. When a suitable amount of gas had been sucked out the pressure was allowed to attain a constant value. The partial pressure of carbon monoxide was then accepted as a measure of P_ε after splitting. Thereafter a small portion of gas was added and, when the pressure had become constant, the corresponding partial pressure of carbon monoxide was accepted as a measure of P_ε after synthesis.

In a typical experiment course crystalline Cu(I)Cl (5.015 g) and 4.00 m HCl (11.775 g) was used. The temperature was maintained at 25.0 °C, and the vapour pressure was found to be 19.0 Torr. Table 4 exemplifies the equilibrium attainment in different phases of this measurement.

Chemicals. Copper(I) chloride of high purity, entirely free from copper(II) and metallic copper.[18] *Carbon monoxide* of research grade (AGA 4.1 with minimum purity 99.997 % by vol.). *Hydrochloric acid* of reagent grade, prepared from constant boiling stock solution and freed from oxygen by stripping with nitrogen. Other chemicals of reagent grade.

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