

Cuprous Compounds of Acetylene

III. Identification of Dissolved Addition Compounds in Chloride Solutions

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In a previous paper¹ of this series the subject was the equilibria between acetylene and its cuprous addition complexes in aqueous solutions of cuprous chloride and hydrochloric acid. Variations of the hydrochloric acid concentration cause considerable changes in the activity coefficients of the ions present, since HCl is the predominating electrolyte in these systems. It is therefore of interest to investigate a system, where the ionic strength can be kept constant by use of an indifferent electrolyte. This electrolyte must be a strong acid of high concentration, in order to repress the formation of acetylidic compounds. We have used *perchloric acid*, which is supposedly indifferent at the formation of cuprous complexes, and whose mixtures with hydrochloric acid show a fairly constant HCl activity coefficient at a given ionic strength².

The majority of the measurements in the present paper concerns the system



The mixture of the two acids thus remains of constant total concentration, but in the system are also present inorganic cuprous chloride complexes, acetylene and acetylene-copper compounds. However, it will be demonstrated, that even in the complete system the ionic strength, with a fair approximation, can be regarded as constant $\mu = 4 \text{ m}$, provided x is smaller than 1.

Solutions of this composition remain colourless on absorption of acetylene, and the concentration of the yellow acetylidic complex ion can be neglected in comparison with that of the addition complexes. There is no interfering irreversible acetylene reaction and no noticeable oxidation of cuprous copper.

Table 1. Solubility of cuprous chloride in 4 molal mixtures of hydrochloric and perchloric acid, 25° C.

HCl _t	S
0.1000	0.00468
0.1500	0.00708
0.199	0.00977
0.415	0.0230
0.500	0.0293
0.600	0.0368
0.800	0.0531
1.000	0.0729
1.500	0.1318
2.00	0.210
3.00	0.427
4.00	0.735

Symbols

P_A	Acetylene pressure in atm,
$[C_2H_2]_t$	Total concentration of dissolved acetylene,
$[C_2H_2]_{Cu}$	Concentration of copper-bound acetylene,
a	Absorption coefficient, accounting for the "physical" solubility of acetylene; in moles/1 000 g H ₂ O × atm,
HCl _t	Formal concentration of HCl in perchloric acid mixtures, where HCl, HClO ₄ and H ₂ O are regarded as components,
$[Cl^-]$	Concentration of "free" chloride ion,
CuCl _t	Formal concentration of dissolved cuprous chloride,
S	Solubility of cuprous chloride (acetylene absent).

All concentrations are given in m, e.g. moles/1 000 g of water.

The inorganic system

The solubility of cuprous chloride in 4 molal mixtures of hydrochloric and perchloric acid has been determined analytically (see "Apparatus and Procedure") and the results are found in Table 1. The measurements are reproducible within ± 1 %, and the analysis is so performed that the relative accuracy is approximately the same throughout the whole series. In diagrams 1 a and b the quotient S/HCl_t has been plotted against HCl_t, yielding a curve which approaches a straight line at lower HCl-concentrations. Within the interval

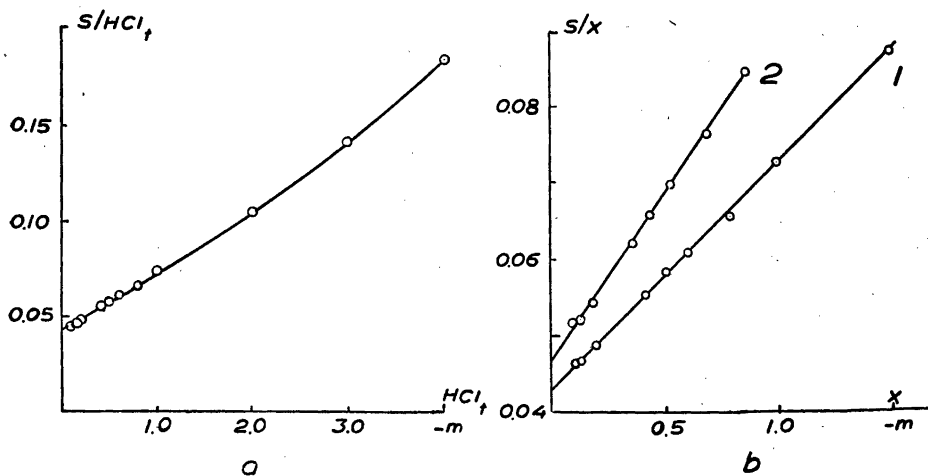


Fig 1. Relation between S and HCl_t .

Curve 1: $X = HCl_t$

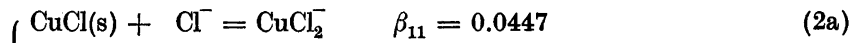
Curve 2: $X = HCl_t - 2 S$

0.1 < HCl_t < 1.5 there is no significant deviation from a linear relation, and thus:

$$S = a_1 \cdot HCl_t + a_2 \cdot HCl_t^2 \quad (0.1 < HCl_t < 1.5) \quad (1)$$

where the graphically determined constants are $a_1 = 0.0435$ and $a_2 = 0.0294$.

If the activity coefficients are assumed constant within the interval 0.1 < HCl_t < 1.0, the solubilities can be referred to the two equilibria:



which imply the following relation between the variables measured:

$$\left\{ \begin{array}{l} S = \beta_{11} \cdot [Cl^-] + \beta_{12} \cdot [Cl^-]^2 \quad (3) \\ HCl_t = [Cl^-] \cdot (1 + \beta_{11} + 2 \beta_{12} \cdot [Cl^-]) \quad (4) \end{array} \right.$$

Elimination of $[Cl^-]$ yields:

$$S = \frac{\beta_{11}}{1 - \beta_{11}} \cdot (HCl_t - 2 S) + \frac{\beta_{12}}{(1 - \beta_{11})^2} \cdot (HCl_t - 2 S)^2 \quad (5)$$

Obviously (1) and (5) are not identical functions, but within the interval mentioned no larger difference than 0.7 % is found between S -values computed from the two functions, using for the four constants the numerical values

stated above. A direct graphical check of (5) against the experimental values is included in diagram 1 b, where the quotient $S/(\text{HCl}_t - 2S)$ is plotted against $(\text{HCl}_t - 2S)$.

The ionic strength of the system changes on the formation of CuCl_3^{2-} (and other, higher charged, complexes) but because of the low solubility the change remains unimportant. If only the equilibria (2) are considered, the relative change in the ionic strength amounts to $0.0075 \times \text{HCl}_t^2$. Even if other complexes are present to some extent, the ionic strength can be regarded as satisfactorily constant if $\text{HCl}_t = 1.0$ is put as the upper limit for the interval.

These solubility determinations in systems with constant ionic strength definitely support the generally accepted, but poorly verified, opinion³, derived from Bodländer's classical work (1902), that the species CuCl_2 and CuCl_3^{2-} predominate in aqueous solutions of cuprous chloride and a dissociating chloride. However, it is not to be excluded that complexes of a higher chloride content occur in amounts of some importance; the fairly arbitrary limitation of the HCl_t -interval is a condition for the interpretation according to (2). Regarding the copper content of the complexes no information of value can be extracted from these equilibrium experiments, where the cuprous chloride activity is kept constant. (Potentiometric measurements, of the same kind previously¹ described, show that, in the present system also, the main part of the dissolved copper is to be found as mononuclear complexes.) A detailed discussion of the inorganic complexes falls however outside the scope of this paper.

The physical solubility of acetylene

Table 2 records measurements of the acetylene absorption in 4 molal aqueous solutions of hydrochloric acid, perchloric acid, and mixtures of the two (CuCl absent). No deviation could be found from a proportionality between the partial pressure and the molal concentration of dissolved acetylene.

Perchloric acid has a definite salting-in effect: in 4 molal acid the absorption coefficient α is 0.0509 moles/1 000 g $\text{H}_2\text{O} \times \text{atm}$, for pure water α is 0.0424. Other electrolytes tried cause a salting-out of acetylene.

For a 4 molal mixture of hydrochloric and perchloric acid the absorption coefficient within the interval $0 < \text{HCl}_t < 1$ can be expressed by the empirical formula:

$$\alpha = 0.0509 - 3.5 \cdot 10^{-3} \cdot \text{HCl}_t \quad (6)$$

In the following it has been assumed that this absorption coefficient can be applied also to systems which contain cuprous chloride. The inorganic cuprous chloride complexes and the acetylene compounds together do not

Table 2. Solubility of acetylene in 4 molar mixtures of hydrochloric and perchloric acid, 25° C.

HCl _t	P _A	[C ₂ H ₂] _t	α	HCl _t	P _A	[C ₂ H ₂] _t	α
0.0000	0.1478	0.00724	0.049	0.494	0.1498	0.00739	0.0493
	0.2616	0.01308	0.0500		0.2998	0.01472	0.0491
	0.3141	0.01589	0.0506		0.3882	0.01920	0.0495
	0.4522	0.02289	0.0506		0.4950	0.02439	0.0493
	0.5769	0.02929	0.0508		0.6371	0.03140	0.0493
	0.6240	0.03164	0.0507		0.7573	0.03724	0.0492
	0.7177	0.03646	0.0508		0.8758	0.04301	0.0491
	0.8690	0.04406	0.0507				
	0.9285	0.04718	0.0508				
0.1115	0.1447	0.00738	0.0510	0.793	—	—	0.0481 (means)
	0.2339	0.01193	0.0510				
	0.3611	0.01837	0.0509				
	0.4745	0.02412	0.0508	1.000	0.0604	0.00279	0.046
	0.5814	0.02953	0.0508		0.1399	0.00653	0.0467
	0.7187	0.03651	0.0508		0.2683	0.01260	0.0470
	0.8581	0.04355	0.0508		0.3890	0.01827	0.0470
	0.9438	0.04787	0.0507		0.5433	0.02549	0.0469
	1.016	0.05158	0.0508		0.6764	0.03185	0.0471
0.2905	—	—	0.0497 (means)	0.7645	0.03588	0.0469	
				0.8603	0.04029	0.0468	
				0.9913	0.04648	0.0469	
			2.00	—	—	0.0437 (means)	

α = absorption coefficient in moles/1 000 g H₂O × atm.

reach a concentration higher than 0.15 m, and the change in the ionic strength will presumably not surpass 1 %. The concentration of complex bound acetylene is computed from the total absorption according to:

$$[C_2H_2]_{Cu} = [C_2H_2]_t - \alpha \cdot P_A \quad (7)$$

Acetylene absorption in the presence of cuprous chloride

The absorption experiments primarily aim at a determination of the empirical relation between the concentration of complex bound acetylene, [C₂H₂]_{Cu}, and the two variables P_A and HCl_t in a 4 m mixture of hydrochloric and perchloric acid, saturated with CuCl. The HCl concentration is varied

Table 3. Acetylene absorption in 4 molal mixtures of hydrochloric and perchloric acid saturated with cuprous chloride. 25° C.

HCl _t	P _A	[C ₂ H ₂] _t	[C ₂ H ₂] _t /P _A	HCl _t	P _A	[C ₂ H ₂] _t	[C ₂ H ₂] _t /P _A
0.1167	0.1254	0.00992	0.0791	0.199	0.1416	0.01180	0.0833
	0.2174	0.01725	0.0793		0.2037	0.01681	0.0825
	0.2885	0.02290	0.0794		0.3276	0.02692	0.0822
	0.3934	0.03109	0.0790		0.4118	0.03393	0.0824
	0.4882	0.03866	0.0792		0.5218	0.04270	0.0818
	0.5691	0.04510	0.0792		0.6187	0.05071	0.0820
	0.6889	0.05461	0.0793		0.7043	0.05788	0.0822
	0.7565	0.05994	0.0792		0.8106	0.06659	0.0821
	0.8449	0.06707	0.0794				
0.9440	0.07492	0.0794					
0.415	0.1720	0.01771	0.1030	0.494	0.0639	0.00704	0.110
	0.2381	0.02452	0.1030		0.1634	0.01762	0.1072
	0.3082	0.03169	0.1028		0.2225	0.02373	0.1067
	0.3382	0.03494	0.1033		0.3072	0.03299	0.1074
	0.4207	0.04343	0.1031		0.4010	0.04311	0.1075
	0.4710	0.04882	0.1037		0.4533	0.04878	0.1076
	0.5255	0.05434	0.1034		0.5431	0.05831	0.1074
	0.5831	0.06023	0.1033		0.6179	0.06645	0.1075
	0.6185	0.06449	0.1042		0.6787	0.07296	0.1076
	0.7062	0.07361	0.1042		0.7510	0.08074	0.1075
			0.8174	0.08785	0.1075		
0.617	0.0866	0.01025	0.118	0.793	0.0606	0.00800	0.132
	0.1353	0.01622	0.1199		0.1317	0.01751	0.1330
	0.2044	0.02463	0.1205		0.2004	0.02677	0.1331
	0.2461	0.02945	0.1197		0.2741	0.03659	0.1335
	0.2877	0.03462	0.1203		0.3509	0.04681	0.1334
	0.3479	0.04201	0.1208		0.4037	0.05388	0.1335
	0.3728	0.04507	0.1209		0.4965	0.06605	0.1330
	0.5167	0.06242	0.1208		0.6019	0.08007	0.1330
	0.6045	0.07246	0.1199		0.6696	0.08898	0.1329
	0.6553	0.07879	0.1202		0.7369	0.09786	0.1328
	0.7438	0.08941	0.1202		0.8034	0.1067	0.1328
	0.8013	0.09582	0.1196		0.8706	0.1154	0.1326
	0.8827	0.1067	0.1209		0.9289	0.1231	0.1325
	0.9433	0.1131	0.1199				
	0.9529	0.1144	0.1200				

Continued

Table 3 continued

HCl _t	P _A	[C ₂ H ₂] _t	[C ₂ H ₂] _t /P _A	HCl _t	P _A	[C ₂ H ₂] _t	[C ₂ H ₂] _t /P _A
0.962	0.0348	0.00509	0.146	0.962	0.1145	0.01661	0.1451
	0.0839	0.01217	0.1450		0.1709	0.02437	0.1426
	0.1234	0.01786	0.1447		0.2485	0.03601	0.1449
	0.1519	0.02198	0.1447		0.3091	0.04506	0.1458
	0.2171	0.03163	0.1457		0.3350	0.04878	0.1456
	0.2717	0.03993	0.1469		0.4101	0.05992	0.1461
	0.3000	0.04410	0.1470		0.4614	0.06758	0.1465
	0.3637	0.05334	0.1466		0.5025	0.07348	0.1463
	0.4130	0.06054	0.1466		0.5565	0.08174	0.1469
	0.4521	0.06638	0.1468		0.6263	0.09182	0.1466
	0.5202	0.07655	0.1472		0.6684	0.09815	0.1468
	0.5727	0.08373	0.1462		0.7128	0.1046	0.1467
	0.7008	0.1028	0.1467		0.8304	0.1217	0.1466
	0.7469	0.1100	0.1472		0.8490	0.1243	0.1463
	0.8081	0.1188	0.1470		0.9856	0.1446	0.1467
1.000	0.1159	0.01791	0.155	1.000	0.0973	0.01476	0.1514
	0.1917	0.02885	0.1520		0.1628	0.02465	0.1514
	0.3103	0.04710	0.1518		0.2518	0.03828	0.1520
	0.3846	0.05817	0.1512		0.3270	0.04957	0.1516
	0.4937	0.07404	0.1500		0.4113	0.06191	0.1505
	0.5698	0.08575	0.1505		0.4833	0.07267	0.1504
	0.6711	0.1006	0.1499		0.5580	0.08470	0.1518
	0.7572	0.1135	0.1499		0.6049	0.09086	0.1502
	0.8764	0.1309	0.1494		0.6483	0.09758	0.1505
	0.9497	0.1416	0.1493		0.7070	0.1066	0.1508

between 0 and 1 m and the acetylene pressure between 0.1 and 1.0 atm approximately. Unfortunately the measurements cannot be extended to higher pressures, since a solid addition compound forms ¹.

There is a surface adsorption of acetylene on solid CuCl, which can cause noticeable errors in these systems, where the concentration of dissolved acetylene is low, in spite of the fact that the adsorbed amounts are quite small. The effect is most apparent at low pressures and depends of course on the relative amount of solid phase, and its particle size. The surface adsorption can be demonstrated, and also arithmetically eliminated, by a comparison between two or several experiments, differing only in the quantity ratio solid phase/solution. But the adsorption error will become negligible at 1 atm and normally also insignificant at 0.1 atm, provided a rather coarse-crystalline substance, in moderate excess, is used.

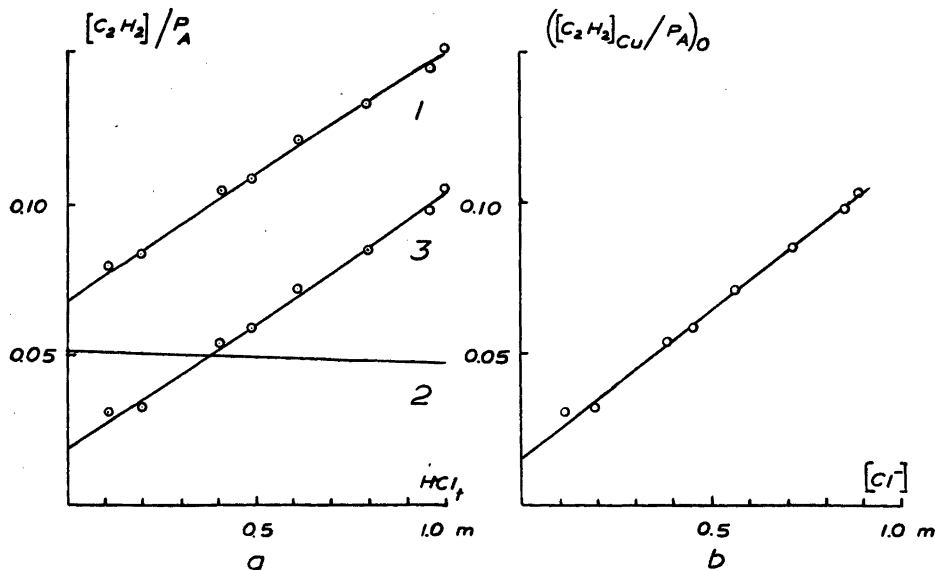


Fig. 2. The absorption quotient as a function of HCl_t and of $[\text{Cl}^-]$.

- a 1: In the presence of solid CuCl ; $[\text{C}_2\text{H}_2]_t/P_A$
 2: CuCl absent - a according to (6)
 3: $[\text{C}_2\text{H}_2]_{\text{Cu}}/P_A$, computed as $[\text{C}_2\text{H}_2]_t/P_A - a$
 b : $[\text{Cl}^-]$ computed according to (4)

Each separate experiment of Table 3 ($0.1 < \text{HCl}_t < 1.0$) will give a relation between $[\text{C}_2\text{H}_2]_t$ and P_A at a constant HCl_t . This relation is a proportional one in all cases. The tendency of the quotient $[\text{C}_2\text{H}_2]_t/P_A$ to diminish with increasing P_A , observed in some experiments (e.g. one of the experiments at $\text{HCl}_t = 1.000$), can be explained completely by the surface adsorption. Otherwise the variations in the quotient values are within the experimental error. Supposing that a is independent of P_A the same thing holds for the quotient $[\text{C}_2\text{H}_2]_{\text{Cu}}/P_A$, computed according to (7). For these systems thus holds the same rule as for solutions containing only hydrochloric acid, saturated with CuCl , i.e.:

$$[\text{C}_2\text{H}_2]_{\text{Cu}}/P_A \text{ constant at } \begin{cases} \text{CuCl (s)} \\ \text{HCl}_t \text{ constant} \end{cases} \quad (8)$$

The quotients $[\text{C}_2\text{H}_2]_t/P_A$ and $[\text{C}_2\text{H}_2]_{\text{Cu}}/P_A$ thus are functions of HCl_t only, under the conditions stated. Curve 1 in Fig. 2 a shows that the relation between $[\text{C}_2\text{H}_2]_t/P_A$ and HCl_t is linear (with a constant term). The quotient values are taken from Table 3, and are mean values of all the readings which

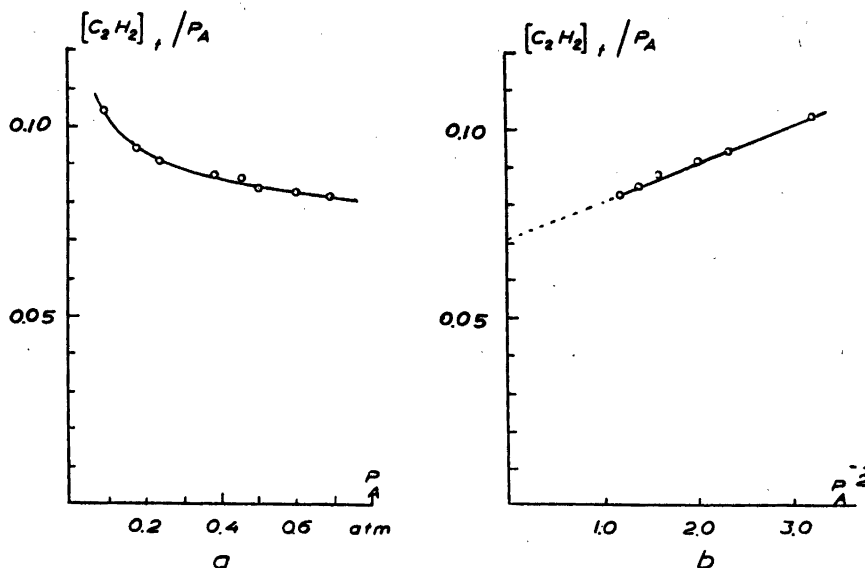


Fig. 3. Relation between acetylene absorption and partial pressure in 4-molar perchloric acid saturated with CuCl .

correspond to pressures over 0.1 atm. The absorption coefficient α which accounts for the "physical" solubility, is given by curve 2, representing the empirical function (6). Curve 3 corresponds to the difference 1–2 and thus gives $[\text{C}_2\text{H}_2]_{\text{Cu}}/P_A$ as a function of HCl_t .

The absorption measurements in systems with solid CuCl , within the interval $0.1 < \text{HCl}_t < 1.0$, can thus be summarized in the following empirical formula:

$$[\text{C}_2\text{H}_2]_{\text{Cu}} = P_A \cdot (A + B \cdot \text{HCl}_t) \quad \begin{cases} A = 0.016 \\ B = 0.086 \end{cases} \quad (9)$$

For the quantity $([\text{C}_2\text{H}_2]_{\text{Cu}}/P_A)_0$, previously¹ defined as the limit value of the quotient when P_A tends to zero at a constant HCl_t , an analogous formula holds:

$$([\text{C}_2\text{H}_2]_{\text{Cu}}/P_A)_0 = A + B \cdot \text{HCl}_t \quad (10)$$

Measurements of the acetylene absorption in 4 m perchloric acid (with solid CuCl), *i.e.* at $\text{HCl}_t = 0$, gives quite different results. As is obvious from Table 4 the absorption is larger than to be expected from (9). The absorption is not proportional to the pressure; the quotient $[\text{C}_2\text{H}_2]_t/P_A$ decreases by about 20 % when the pressure is raised from 0.1 to 0.7 atm, *cf.* Fig. 3 a.

Table 4. Acetylene absorption in 4 molar perchloric acid saturated with cuprous chloride, 25° C.

P_A	$[C_2H_2]_t$	$[C_2H_2]_t/P_A$
0.0967	0.01004	0.1038
0.1844	0.01743	0.0945
0.2439	0.02232	0.0915
0.3902	0.03412	0.0874
0.4598	0.03970	0.0863
0.5052	0.04232	0.0838
0.6087	0.05047	0.0829
0.6977	0.05717	0.0819
0.7244	(0.06417)	(0.0886)

To perform a more complete investigation of the acetylene absorption within the interval $0 < HCl_t < 0.1$ does not seem very inviting. The concentration of complexbound acetylene cannot be computed with satisfactory accuracy, since the physical solubility predominates. A solid acetylidic compound (violet complex) precipitates even at low pressures in most experiments. (Thanks to supersaturation it was possible to raise the pressure, in the experiment of Table 4, unto 0.72 atm before the violet complex began to precipitate.)

Table 5 shows the results of an absorption experiment in a *homogenous system*, where the $CuCl$ concentration lies close to the solubility, S , for the mixture of acids employed. In this case $[C_2H_2]_{Cu}$ is not proportional to P_A but to the parameter

$$\pi_A \equiv P_A (1 - [C_2H_2]_{Cu}/CuCl_t) \quad (11)$$

as in the previous experiments¹ with homogenous solutions of cuprous chloride in hydrochloric acid only. The accuracy of the $[C_2H_2]_{Cu}$ value decreases with rising pressure, since physically dissolved acetylene will become a greater portion of the total absorption, at the highest pressure corresponding to 61 %. If HCl_t and $CuCl_t$ fall below the extreme values, chosen for the experiment of Table 5, it would be difficult to determine $[C_2H_2]_{Cu}$ with reasonable accuracy. Thus a complete investigation of the acetylene absorption in homogenous solutions is out of the question.

Previously¹ it has been shown that, in *saturated* solutions of $CuCl$ in hydrochloric acid, $CuCl_t$ increases equimolarly with $[C_2H_2]_{Cu}$ when the acetylene pressure is raised. The high concentration of inorganic $CuCl$ -complexes,

Table 5. Acetylene absorption in homogenous solution. 25° C.

System: 0.962 m HCl; 3.038 m HClO₄; 0.0713 m CuCl.

P_A	$[C_2H_2]_t$	$[C_2H_2]_t/P_A$	$[C_2H_2]_{Cu}/P_A$	$[C_2H_2]_{Cu}/\pi_A$
0.0431	0.00589	0.1367	0.0891	0.0941
0.0911	0.01225	0.1345	0.0869	0.0979
0.1636	0.02074	0.1268	0.0792	0.0970
0.1981	0.02481	0.1252	0.0776	0.0989
0.2715	0.03220	0.1186	0.0710	0.0974
0.3623	0.04084	0.1127	0.0651	0.0974
0.4373	0.04748	0.1086	0.0610	0.0976
0.5351	0.05537	0.1035	0.0559	0.0964
0.6175	0.06187	0.1002	0.0526	0.0967
0.7110	0.06869	0.0966	0.0490	0.0958
0.7783	0.07340	0.0943	0.0467	0.0952
0.8729	0.08004	0.0917	0.0441	0.0960
0.9307	0.08386	0.0901	0.0425	0.0956
1.0066	0.08879	0.0882	0.0406	0.0954
1.149	0.09782	0.0851	0.0375	0.0945
1.308	0.1074	0.0821	0.0345	0.0939
1.512	0.1197	0.0792	0.0316	0.0959
1.654	0.1281	0.0775	0.0299	0.0978

however, causes the relative change in $CuCl_t$ to become quite small. But in the mixtures of hydrochloric and perchloric acid studied here, $CuCl_t$ attains values much higher than the initial one, S . A direct analytical examination of the relation between $CuCl_t$ and $[C_2H_2]_{Cu}$ has therefore been carried out.

The system 0.5 m HCl; 3.5 m HClO₄; CuCl (s) has been chosen for such a measurement. A nitrogen-acetylene mixture of known composition is passed through the solution until equilibrium is attained; a sample is taken for analysis after the solid phase has been allowed to sediment. Table 6 shows that the difference $CuCl_t - S$ closely coincides with $[C_2H_2]_{Cu}$.

Apparatus and procedure

The performance of the acetylene absorption experiments has been described in a previous paper¹ of this series.

Determination of CuCl solubility

Long-necked Kjeldahl-flasks, provided with a stopper and in the middle of the neck a side tube with a stopcock, are charged with fine-crystalline CuCl and after a careful evacuation the acid-mixture, freed from air by stripping with nitrogen, is added through the side tube. In those cases where the solubility is slight ($HCl_t < 0.5$ m) the

Table 6. Solubility of cuprous chloride in the presence of acetylene, 25° C.

System: 0.500 m HCl; 3.500 m HClO₄; CuCl (s).

P_A	Analysis after	CuCl _t	[C ₂ H ₂] _{Cu}	CuCl _t -S	[Cu] _{C,H}
0.000	45 min.	0.0286	—		—
	75 »	0.0289			
0.778	35 »	0.074 ₃	0.047	0.046	0.048
	75 »	0.074 ₃			
	100 »	0.075 ₀			
0.974	25 »	0.086 ₀	0.058	0.057	0.060
	55 »	0.086 ₅			

CuCl_t according to analysis[C₂H₂]_{Cu} from the empirical function (9)

S from the empirical function (1)

[Cu]_{C,H}, calculated as CuCl_t-[CuCl]₀₀, with [CuCl]₀₀ from (2) and (16).

substance is washed twice; the liquid being decanted and sucked out through the side tube. The flask is placed in a 25° C thermostat with a shaking device.

For sampling a swift stream of nitrogen is passed through the side tube venting through the neck and an immersion filter (Pyrex F) is introduced, enabling a suitable quantity to be sucked into an evacuated weighing bottle. The quantity is so adapted that each time about 1 millimole (minimum 0.5 millimole) of dissolved CuCl is taken for analysis, and by addition of perchloric acid the composition of the solutions is approximately standardized. Hydrochloric acid, and the main part of the water and the perchloric acid are distilled off, Cu^I simultaneously being oxidized to Cu^{II} quantitatively⁴. After cooling water is added and the solution is boiled free of chlorine and chlorine oxides. The copper content is determined iodometrically in an acetate buffer with 0.02 N thiosulphate after addition of thiocyanate⁵. This obviously is a method for the determination of the total copper content, but by checking the colour of the sample and comparison with solutions where a known amount of Cu^{II} has been added, it is easy to state that the contribution from Cu^{II} is negligible.

There is no significant difference between samples taken after 2½ and 5 hours respectively, nor on comparison with checks where the equilibrium is reached from a supersaturated solution (prepared by preheating to 30°). Experiments with and without metallic copper give coinciding values. The results in Table 2 are means from two or more analyses.

Nitrogen-acetylene mixtures of known composition for the determination of the CuCl-solubility at a given acetylene pressure (Table 6) are prepared by a previously described⁶ technique, where constant gas flow is adjusted with the aid of "critical orifices".

The gas is introduced into the cylindrical reaction vessel either through its fritted disc bottom or through a tube above the surface of the liquid. The gas escapes through an open vertical tube, used for sampling of liquid. The velocity in the tube is great enough to prevent back diffusion of air. The samples are taken without filtering to avoid precipitation of acetylene-bound CuCl which might result from a pressure drop. Before sampling complete sedimentation is awaited and checked in side-light. The analysis is then performed as described above.

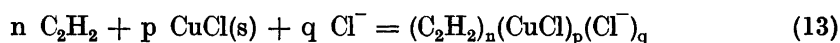
Conclusions from the equilibrium experiments

1. Interval $0.1 < \text{HCl}_t < 1.0$

To find a relation between $[\text{C}_2\text{H}_2]_{\text{Cu}}$ and the concentration of free chloride ion, $[\text{Cl}^-]$, it is necessary to compute $[\text{Cl}^-]$ from a given HCl_t by subtracting the chloride content of both inorganic complexes and acetylene compounds. But the limit value $([\text{C}_2\text{H}_2]_{\text{Cu}}/P_A)_0$ can be referred to a system, where the acetylene compounds have no influence on the chloride ion balance and where $[\text{Cl}^-]$ can be computed according to (4). If (4) is inserted in (10) a quadratic relation between $([\text{C}_2\text{H}_2]_{\text{Cu}}/P_A)_0$ and $[\text{Cl}^-]$ results, but the contribution from the second order term is so small that it cannot be determined with any degree of certainty. Fig. 2 demonstrates that the limit quotient can be given, with acceptable accuracy, as a linear function of $[\text{Cl}^-]$ also:

$$[\text{C}_2\text{H}_2]_{\text{Cu}}/P_A)_0 = 0.015 + 0.097 \cdot [\text{Cl}^-] \quad (12)$$

If we assume that the acetylene absorption can be referred to equilibria of the type



and that the ions involved have constant activity coefficients, then it follows from (12) that there must exist one complex with $q = 0$, whose concentration is independent of $[\text{Cl}^-]$, and one complex with $q = 1$, whose concentration rises proportionally with $[\text{Cl}^-]$. Other experimental data indicate that the complexes mainly occurring have $n = p = 1$.

The predominating species thus are $\text{C}_2\text{H}_2 \cdot \text{CuCl}$ and $\text{C}_2\text{H}_2 \cdot \text{CuCl}_2^-$. If then we assume that *only* these two compounds and the inorganic CuCl-complexes occur, the following relations should hold for systems with solid CuCl:

$$\begin{cases} [\text{C}_2\text{H}_2 \cdot \text{CuCl}] = k_2 \cdot P_A & k_2 = 0.015 & (14 \text{ a}) \\ [\text{C}_2\text{H}_2 \cdot \text{CuCl}_2^-] = k_3 \cdot P_A \cdot [\text{Cl}^-] & k_3 = 0.097 & (14 \text{ b}) \end{cases}$$

and

$$\begin{cases} [\text{C}_2\text{H}_2]_{\text{Cu}} = [\text{Cu}]_{\text{C}_2\text{H}_2} = P_A(k_2 + k_3 \cdot [\text{Cl}^-]) & (15) \\ \text{HCl}_t = [\text{Cl}^-] \cdot (1 + \beta_{11} + 2 \beta_{12}[\text{Cl}^-] + k_3 \cdot P_A) & (16) \end{cases}$$

It now remains to try if (15) and (16) fit the experimental results with acceptable accuracy, or if there are deviations, indicating the presence of noticeable amounts of other complexes.

a) The experiments show the quotient $[C_2H_2]_{Cu}/P_A$ to be independent of P_A . But according to (15) and (16) the quotient should diminish when P_A increases, as a consequence of the consumption of chloride ion by the formation of $C_2H_2 \cdot CuCl_2$. At a low HCl_t the computed change is small, but at $HCl_t = 1.0$ it would amount to 6 % within the interval $0.1 < P_A < 1.0$ atm, corresponding to 4 % of the directly measured quotient $[C_2H_2]_t/P_A$; the experiments show this quotient to be certainly constant within ± 0.5 %. This would indicate that complexes with $n > 1$, *i.e.* containing more than one acetylene molecule, are present to such an extent that the expected effect is compensated for. But the experiments cannot be said to prove definitely the existence of such complexes; the difference is not great, and minor variations in activity coefficients and/or acetylene's physical solubility are possible.

b) At a finite, constant P_A formulae (15) and (16) give $[Cl^-]$ values (and k -constants) which deviate slightly from the corresponding values at $P_A = 0$. But in each separate case a linear relation between $(C_2H_2)_{Cu}$ and $[Cl^-]$ is found to express satisfactorily the experimental results.

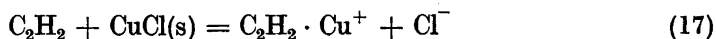
c) The difference $CuCl_t - S$ in Table 6 is only an approximate measure of the concentration of acetylene-bound copper, since the chloride ion consumption due to the formation of $C_2H_2 \cdot CuCl_2$ should cause the concentration of inorganic copper complexes to deviate slightly from S in the presence of acetylene. The values for $[Cu]_{C,H}$ in the last column of Table 6 have been calculated according to

$$[Cu]_{C,H} = CuCl_t - [CuCl]_{00}$$

where $CuCl_t$ is the analytically determined total concentration, and $[CuCl]_{00}$ is the concentration of copper bound in inorganic complexes, computed according to (2) and (16). As demonstrated by the table these $[Cu]_{C,H}$ values exceed by some per cent the empirical $[C_2H_2]_{Cu}$ values, but considering the moderate accuracy of the solubility determinations the difference cannot be regarded as significant.

2. $HCl_t = 0$

The acetylene absorption in 4 molal perchloric acid (with solid $CuCl$) will find its simplest explanation by the assumption of a cation complex whose concentration is determined by the equilibrium:



Cation complex and chloride ion thus form in equimolar amounts, and if the inorganic CuCl-complexes are neglected, we find:

$$[\text{C}_2\text{H}_2 \cdot \text{Cu}^+] = k_1^{\frac{1}{2}} \cdot P_A^{\frac{1}{2}} \quad (18)$$

Physical solubility and the uncharged complex $\text{C}_2\text{H}_2 \cdot \text{CuCl}$ further contribute to the total absorption, whereas $\text{C}_2\text{H}_2 \cdot \text{CuCl}_2^-$ can be disregarded. For the total absorption we then get:

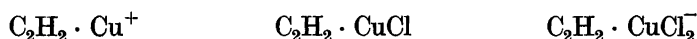
$$[\text{C}_2\text{H}_2]_t/P_A = \alpha + k_2 + k_1^{\frac{1}{2}} \cdot P_A^{-\frac{1}{2}} \quad (19)$$

A linear relation consequently is to be expected between the absorption quotient and $P_A^{-\frac{1}{2}}$, and Fig. 3 b shows that this is the case. Graphically the following values are obtained:

$$\begin{cases} k_1 = (0.011)^2 = 1.2 \cdot 10^{-4} \\ \alpha + k_2 = 0.069 \end{cases}$$

The constant k_1 thus determined will have a very low accuracy. But the experiment can be regarded as an acceptable proof of the existence of the cation compound.

The main conclusions from the equilibrium experiments will thus be: in 4 m mixtures of hydrochloric and perchloric acid acetylene and CuCl form the following three addition complexes



and their concentration in the presence of solid CuCl can be computed from the equilibrium formulae:

$$\begin{cases} [\text{C}_2\text{H}_2 \cdot \text{Cu}^+] = k_1 \cdot P_A \cdot [\text{Cl}^-]^{-1} & k_1 = 1.2 \cdot 10^{-4} \\ [\text{C}_2\text{H}_2 \cdot \text{CuCl}] = k_2 \cdot P_A & k_2 = 1.5 \cdot 10^{-2} \\ [\text{C}_2\text{H}_2 \cdot \text{CuCl}_2^-] = k_3 \cdot P_A \cdot [\text{Cl}^-] & k_3 = 9.7 \cdot 10^{-2} \end{cases} \quad (20)$$

DISCUSSION

The cuprous addition compounds of *acetylene* are probably closely related to the corresponding olefine compounds. The dissolved cuprous addition compounds of *ethylene* in chloride solutions have been the subject of a series of papers⁷ by Green, d'Angelo and Rote, and Park, all under the direction of Gilliland. The complexes formed seem to contain one atom of copper and one molecule of ethylene, as is demonstrated by experiments showing a linear relation between on the one hand the ethylene absorption and on the other

hand the activity (fugacity) of ethylene, and the concentration of "free" cuprous chloride (at a constant concentration of dissociating chloride). No definite conclusion has been reached as to the chloride content of the complexes; Green however finds it probable that the predominating complex has the composition $C_2H_4CuCl_2^-$. Similar results have been obtained for propylene.

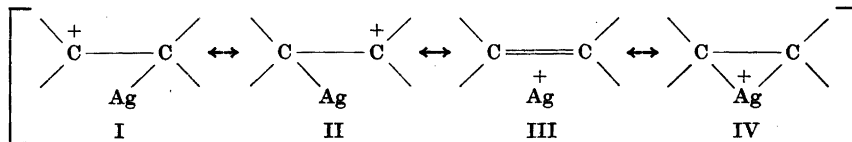
The dissolved cuprous complexes of ethylene are somewhat less stable than those of acetylene. Some preliminary measurements have shown that the constant k_c , cf. definition (13)¹, has the value 0.20 atm^{-1} for ethylene in 4 M HCl at 25° C, whereas the corresponding value for acetylene is 0.48 atm^{-1} .

Andrews, Keefer⁸ and co-workers have studied the complex formation between allyl alcohol (and several other unsaturated alcohols and acids) and monovalent copper in chloride solutions. Here also the rule seems to hold that only 1 : 1 complexes exist. The main part of their equilibrium experiments aim at a determination of the chloride content of the complexes, and the types $A \cdot Cu^+$ and $A \cdot CuCl$ are found to exist. But the experiments have not been extended to systems of higher chloride concentrations, where possibly anion complexes of the type $A \cdot CuCl_2^-$ exist in this case also.

Winstein and Lucas⁹ have shown that 1 : 1 complexes are typical of dissolved olefine complexes of silver ion also. Only for the diolefines can a tendency be observed to add two silver ions to each olefine molecule; compounds with two olefine molecules and one silver ion appear only when the olefine has an oxygen-containing group. It seems that divalent mercury also forms dissolved 1 : 1 complexes with olefines¹⁰. (Unfortunately one can hardly decide whether acetylene can form dissolved addition complexes with silver ion, since the formation of silver carbide, or complex compounds thereof, predominates entirely; silver carbide is stable¹¹ even in a strongly acid solution at a low silver ion activity.)

The question as to the nature of the metal-olefine coördination bond has been the subject of a lively discussion. On general chemical grounds a bond of the coördinate link type has been assumed, although the coördinated group has no "lone pair" of electrons. In the earlier literature¹² various suggestions are found for the solution of this difficulty. The fact that the complex formation does in no particular way favour either polymerization or isomerization of cis-trans olefines, forms a strong objection against those suggestions which involve an opening of the double bond and the formation of one carbon atom having only a sextet of electrons. Recently electronic interpretations have resulted in two ideas which, even though hypothetical, might be regarded as acceptable descriptions of the characteristics of this type of compound.

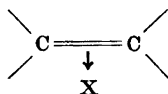
a) According to Winstein and Lucas⁹ the Ag^+ complexes of the olefines are resonance hybrids of the following four forms:



As the C-C-Ag-angle can be considerably greater than 60° the strain of the three-membered ring need not be great. The strain energy has been estimated at 3–4 kcal, and the resonance energy at 10 kcal. The four forms can contribute in varying degrees in different metal-olefine compounds. Originally IV was omitted for the silver complexes, but later on a considerable contribution of this form was assumed in order to explain the stability of the cis-trans isomers. The donor property of the metal atom towards either of the two carbon atoms in form IV has not been discussed.

The same structure has been suggested by Andrews and Keefer⁸ *et al.* for the olefine compounds of monovalent copper, excluding however form IV.

b) Werner¹³ finds that the structure of the metal-olefine compounds might best be described by that special type of bond which was independently brought forth by Walsh¹⁴ and by Dewar¹⁵; in both cases designed for compounds of quite different type. Dewar's idea has been developed from the observation that the π -orbital of ethylene closely resembles the p-orbital of a separate atom with a lone pair of electrons. There seems to be no reason why the π -orbital should not be able to coalesce with a vacant bonding orbital of a third atom, resulting in a special kind of molecular orbital covering all three nuclei. Or otherwise expressed: a bond of the coördinate link type is not confined to lone-pair electrons in the donor atom; bonding electrons, under certain conditions, may also be donated to an acceptor atom. For compounds with this type of bond Dewar has suggested the name π -complex and the designation:



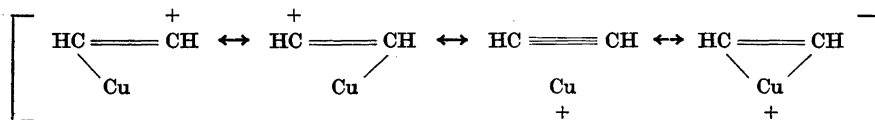
Obviously these two structure theories cannot be regarded as principally opposed; rather as two different vocabularies of resembling content. From a purely chemical view-point two similarities are obvious; both theories aim at the description of a *symmetrical* addition of the metal atom (disregarding such an obliquity as might result from an unsymmetrical structure of the olefine),

and both express that the addition will involve the multiple bond without *dissolving it entirely*.

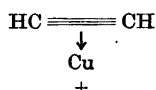
This last statement agrees well with the results from Raman measurements on dissolved olefine-silver complexes, performed by Taufen, Murray and Cleveland¹⁶ in connection with Winstein's and Lucas' investigations. The strong double bond frequency has not disappeared in the silver complexes, but shows a general lowering of approximately 65 cm^{-1} , however still remaining in the double bond region. Other frequencies of the original compound appear essentially unaltered in the complex; no new lines corresponding to a metal-carbon linkage could be discerned.

The theory on the π -complexes has already played a certain role in the recent discussions on the reactivity of the olefines, intermolecular rearrangements etc., as is obvious *e.g.* from Dewar's own monograph¹⁷. As a rule a π -complex structure has been assumed only for hypothetical reaction intermediaries. The metal-olefines are practically the only kind of stable compounds which might be regarded as π -complexes.

It may be assumed that the cuprous addition compounds of acetylene have a similar structure, which might be formulated as a resonance hybrid of the four forms:



or as a π -complex:



(Further, the copper atom may add one or more atoms of normal donor properties, as *e.g.* chloride ion.)

The two π -bonds of acetylene are perpendicular to one another and thus electronically independent. The spatial spread, which according to Walsh primarily determines the power of donation, is no smaller than for ethylene.

Complex compounds, containing copper or silver carbide and an inorganic salt of either metal can, however, hardly be explained as π -complexes. The ability to add a large number of metal atoms in aqueous solution seems to be a characteristic property of these carbidic compounds, not only of silver carbide¹⁸ and copper carbide¹⁹, but also of monoalkylacetylides (according to unpublished results obtained in this laboratory). Already this "polyvalency" indicates that other bond forces are involved.

SUMMARY

Investigations of the solubilities of acetylene and cuprous chloride in mixtures of hydrochloric and perchloric acids of constant ionic strength show that the following dissolved species occur:

inorganic complexes CuCl_2 , CuCl_3^{2-} ,

acetylene addition compounds $\text{C}_2\text{H}_2 \cdot \text{Cu}^+$, $\text{C}_2\text{H}_2 \cdot \text{CuCl}$, $\text{C}_2\text{H}_2 \cdot \text{CuCl}_2^-$.

Equilibrium constants for the five compounds have been determined.

The bond between acetylene and copper in these addition compounds is presumably similar to the coordination bond in cuprous complexes of olefines.

REFERENCES

1. Vestin, R., and Löfman, C. *Acta Chem. Scand.* **7** (1953) 398. No. II in this series.
2. Murdoch, P. G., and Barton, R. C. *J. Am. Chem. Soc.* **55** (1933) 4074.
3. Bodländer, G., and Storbeck, O. *Z. anorg. Chem.* **31**:1 (1902) 458; Náray Szabó, St. v., and Szabó, Z. *Z. physik. Chem. A* **166** (1933) 228; Kiang-Shu Chang and Ya-Teh Cha *J. Chinese Chem. Soc.* **2** (1934) 298.
4. Kolb, J. J. *Ind. Eng. Chem. Anal. Ed.* **11** (1939) 197.
5. Foote, H. W., and Vance, J. E. *Ind. Eng. Chem. Anal. Ed.* **9** (1937) 205.
6. Vestin, R., Olsson, O., and Somersalo, A. *Transactions, Instruments and Measurements Conference*, Stockholm 1949, p. 297.
7. Green, H. J. *Thesis*, Mass. Inst. Technol. 1938; d'Angelo, J. E., and Rote, J. G. *Ibid.* 1938; Park, R. H. *Ibid.* 1938; Gilliland, E. R., and Seebold, E. E. *Ind. Eng. Chem.* **33** (1941) 1143.
8. Kepner, R. E., and Andrews, L. J. *J. Org. Chem.* **13** (1948) 208; Andrews, L. J., and Keefer, R. M. *J. Am. Chem. Soc.* **70** (1948) 3261; Keefer, R. M., and Andrews, L. J. *Ibid.* **71** (1949) 1723; Andrews, L. J., and Keefer, R. M. *Ibid.* **71** (1949) 2379; Keefer, R. M., Andrews, L. J., and Kepner, R. E. *Ibid.* **71** (1949) 2381; Keefer, R. M., Andrews, L. J., and Kepner, R. E. *Ibid.* **71** (1949) 3906.
9. Winstein, S., and Lucas, H. J. *J. Am. Chem. Soc.* **60** (1938) 836; Lucas, H. J., Moore, R. S., and Pressman, D. *Ibid.* **65** (1943) 227; Lucas, H. J., Billmeyer, F. W. Jr., and Pressman, D. *Ibid.* **65** (1943) 230; Ebers, W. E., Welge, H. J., Yost, D. M., and Lucas, H. J. *Ibid.* **59** (1937) 45.
10. Lucas, H. J., Hepner, F. R., and Winstein, S. *J. Am. Chem. Soc.* **61** (1939) 3102.
11. Vestin, R., and Somersalo, A. *Acta Chem. Scand.* **3** (1949) 125.
12. Keller, R. N. *Chem. Revs.* **28** (1941) 260.
13. Werner, A. E. A. *Nature* **160** (1947) 644.
14. Walsh, A. D. *J. Chem. Soc.* **1947**, 89.
15. Dewar, M. J. S. *J. Chem. Soc.* **1947**, 406, 777.
16. Taufen, H. J., Murray, M. J., and Cleveland, F. F. *J. Am. Chem. Soc.* **63** (1941) 3500.
17. Dewar, M. J. S. "The Electronic Theory of Organic Chemistry", Clarendon Press, Oxford 1949.
18. Vestin, R., and Ralf, E. *Acta Chem. Scand.* **3** (1949) 101.
19. Vestin, R. *Acta Chem. Scand.* **3** (1949) 650.

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