An NMR Investigation of the Acetylene—Cu(I)— π -Complex in Homogeneous Aqueous Solution

A. BORG, T. LINDBLOM and R. VESTIN

Department of Physical Chemistry, Arrhenius Laboratory, University of Stockholm, Fack, S-104 05 Stockholm, Sweden

^1H NMR and ^{13}C NMR spectra of the π -complexes acetylene—Cu(I) and ethylene—Cu(I) are recorded. The solutions used contain the systems $\text{HCl—CuCl—C}_2\text{H}_2$ and $\text{DCl—CuCl—C}_2\text{H}_4\text{—D}_2\text{O}$, prepared in specially designed devices for gas saturation of air-sensitive NMR-samples. The chemical exchange between complexed and dissolved hydrocarbon is rapid and only one narrow peak is seen in the spectrum, and the ^1H NMR frequency of the pure complex is determined by means of extrapolation. The acetylene resonance is shifted 2.6 ppm to lower field from its uncomplexed frequency in ^1H NMR, the ethylene 0.77 ppm to higher field. In ^{13}C NMR the acetylene resonance is shifted 1.1 ppm, the ethylene 31.1 ppm. Since shift of the acetylene resonance on complexing is restricted to protons, the molecule is believed to be bent, *cis* or *trans*, in the complex.

Our studies of the ^1H NMR properties of π -complexes between olefines and Ag(I) and olefines and acetylenes and Cu(I) have shown that, in some cases, the resonance frequencies of the hydrocarbons are shifted considerably on complex formation. Measured shifts are listed in Table 1, where ΔK symbolizes the

coordination shift according to $\Delta K = \Delta(\text{uncomplexed}) - \Delta(\text{complexed})$. The ethylene shows a quite normal behaviour with a change of 0.77 ppm to higher field, but the large shift of the acetylenic protons on complex formation with Cu(I) is quite exceptional¹ and therefore submitted to more careful studies in order to clarify its causes.

For the determination of the ^1H NMR shift of the Cu(I)— π -complex with acetylene, two series of measurements have been carried out in homogeneous systems with the components $\text{H}_2\text{O—HCl—CuCl—C}_2\text{H}_2$, where the acetylene is distributed between physically dissolved and complexed to Cu(I). One of the series contains samples where the total concentration of CuCl, CuCl_2 , is varied, and is called the CuCl_2 series. In the other series the acetylene resonance is studied at varied acetylene pressures, P_A , and otherwise constant conditions, and is called the P_A series. The equilibria in these systems, where the acetylenic components are mainly $\text{C}_2\text{H}_2\cdot\text{CuCl}$ and $\text{C}_2\text{H}_2\cdot\text{CuCl}_2^-$, have been carefully studied by Vestin and Löfman.² Water has been chosen as solvent instead of the normally preferred D_2O for two reasons. Firstly, we have found that a chemical exchange takes place between the protons, which in deuteriated solution leads to a decrease in the intensity of the acetylene signal until an equilibrium mixture between the two deuteriated species is established. Secondly, the water signal in these strongly acidic solutions (8–9 m) is shifted so far downfield as to remain outside the region of interest. Moreover, the results of the measurements can be evaluated using the relations be-

Table 1. ^1H NMR coordination shifts of some olefines and acetylenes
 $\Delta K = \Delta(\text{uncomplexed}) - \Delta(\text{complexed})$.

Ligand	Central atom	ΔK (ppm)
Ethylene	Ag^+	– 0.1
Vinyl acetate	Ag^+	– 0.09
Ethylene	Cu^+	+ 0.77
Acetylene	Cu^+	– 2.62
Propyne	Cu^+	– 2.4

tween the components of the systems which have been found by Vestin and Löfman.² For comparison, a series of ^1H NMR measurements of the corresponding ethylene-Cu(I)- π -complex was performed. (Unfortunately an acetylene series with silver is impossible because the acetylide formation predominates.) The samples of this series contain the system $\text{DCl}-\text{C}_2\text{H}_4-\text{CuCl}-\text{D}_2\text{O}$, where the total concentration of the copper(I) chloride is varied but the ethylene partial pressure, P_E , and the deuterium chloride concentration are kept constant. In this series it is necessary to use deuteriated water and acid because otherwise the strong proton signal interferes with the rather weak ethylene signal, and it is this time possible because we have not found any evidence of an exchange between ethylene and water protons. The series is called the ethylene CuCl_t -series.

Ordinary ^1H NMR standard substances cannot be used in these solutions, because they either form complexes with Cu(I), like DMSO, or they are insoluble in water, like TMS. Instead in the CuCl_t series the water signal was used as a shift reference and acetic acid as a concentration reference, CH_3OH in the P_A series, and DSS in the ethylene CuCl_t series. Since CuCl is very sensitive to oxidation, especially when moist, and since trace of paramagnetic contamination produces a deleterious effect upon the spectra (line broadening), the samples have been prepared with the help of the devices for preparation and gas saturation at atmospheric and higher pressures of air sensitive samples, which have been developed in this laboratory.³ In these devices the addition of the solvent and the saturation by the gas at atmospheric pressure is performed in an argon atmosphere ('Sondett') and addition of gas to higher pressures is carried out after evacuation in special sample tubes equipped with valves ('Bombett'). CuCl is, on the other hand, stable enough in the dry state to allow its weighing without any special precautions.⁴

EXPERIMENTAL

Preparation of the acetylene CuCl_t series (constant P_A). CuCl of a very high degree of purity was weighed into well dried, ordinary NMR sample tubes. These were placed in the

Sondett, and 0.500 ml of a stock solution, containing 8.42 m HCl and 0.0369 m CH_3COOH in water, was added with the help of an all-glass syringe ('Agla'), which allows accurate volume readings. The solutions were afterwards saturated with acetylene, free from acetone, according to the instructions for the device. The tubes were closed and the NMR spectra were recorded immediately.

Preparation of the acetylene P_A series (constant CuCl_t). 0.0605 g CuCl (purity as above) was weighed into a high pressure NMR sample tube of wall thickness 0.6 mm, with the valve device removed. The tube was placed in the Sondett. 0.500 ml of a stock solution, containing 8.1 m HCl and 0.273 m CH_3OH , was added as described above. The valve was fitted and the tube connected to the Bombett and evacuated. Acetylene was added to the required pressures under simultaneous equilibration by vibrating the tube in a thermostatic bath at 25°C.

Preparation of the ethylene CuCl_t series (constant P_E). The CuCl was weighed into well dried NMR sample tubes, which were afterwards placed in the Sondett. An amount of 0.500 ml of a stock solution of 8.95 m DCl and 0.0142 m trimethylsilylpropanesulfonic acid (DSS) dissolved in D_2O was added, and finally the solution was saturated with ethylene. ^1H NMR measurement was made directly after closing the tube.

Measurement of the spectra. The ^1H NMR spectra were recorded at 25°C on a Varian A60-A spectrometer, and the resonance frequencies were read in Hz directly from the spectrum. However, the spectrometer is such that it does not allow more accurate determination of the frequencies than 1 Hz, due to drifting of the scale during the recording. The accuracy of the integral peak is limited by the reproducibility of the integral, which, according to the specifications of the instrument, is approximately 98 %. The height of the integral peak has been read from the mm scale of the chart paper. The ^{13}C NMR spectra were recorded on a Varian XL 100 spectrometer at about 40°C.

RESULTS

The ^1H NMR spectra of the individual samples of the CuCl_t -series and the P_A series contain three peaks; Fig. 1. The largest peak at 6.5 ppm is water, then follows acetylene at 4.25 ppm and CH_3 protons at 3.1 ppm. The appearance of one single, unbroadened peak of acetylene indicates a rapid exchange between the two acetylenic species in the solution. Its resonance frequency, $\nu(\text{C}_2\text{H}_2)$, is determined by

$$\nu(\text{C}_2\text{H}_2) = Q[\nu(\text{C}_2\text{H}_2)_{\text{Cu}} - \nu(\text{C}_2\text{H}_2)_{\text{aq}}] \quad (1)$$

Fig. 1. ^1H NMR spectrum of the acetylene-Cu(I) complex. The peak at 6.5 ppm is water, the acetylene protons at 4.25 ppm, and CH_3COOH at 3.1 ppm. The two small peaks at 6.2 and 5.85 ppm are second sideband due to rotation and a 50 Hz perturbation; 25°C.

where $\nu(\text{C}_2\text{H}_2)_{\text{Cu}}$ is the resonance frequency of the pure complex, $\nu(\text{C}_2\text{H}_2)_{\text{aq}}$ is the resonance frequency of the acetylene protons in absence of copper(I) chloride, and

$$Q = [\text{C}_2\text{H}_2]_{\text{Cu}} / [\text{C}_2\text{H}_2]_{\text{t}}$$

where $[\text{C}_2\text{H}_2]_{\text{Cu}}$ is the concentration of the Cu(I) bound acetylene, and $[\text{C}_2\text{H}_2]_{\text{t}}$ is the total concentration of acetylene in the solution.

During the course of the CuCl_t series, the acetylene peak undergoes a negative coordination shift as the CuCl_t is increased; $\nu(\text{C}_2\text{H}_2) = 157.2$ Hz is the largest frequency measured downfield from $\nu(\text{C}_2\text{H}_2)_{\text{aq}}$. The difference $[\nu(\text{C}_2\text{H}_2) - \nu(\text{C}_2\text{H}_2)_{\text{aq}}]$ is later on referred to as $\Delta\nu(\text{C}_2\text{H}_2)$. Table 2, Fig. 2a.

Table 2. Data for the acetylene CuCl_t series. HCl_t const. = 8.42 m, P_A const. = 0.96 atm.

CuCl_t	$\nu(\text{H}_2\text{O}) - \nu(\text{C}_2\text{H}_2)$ Hz	I	$[\text{C}_2\text{H}_2]_{\text{t}}$ m	Q
0	278.4	—	—	—
0.050	249.2	0.72	0.046	0.216
0.118	219.2	1.23	0.059	0.356
0.180	204.2	1.44	0.072	0.500
0.272	188.2	1.77	0.100	0.602
0.423	171.4	1.53	0.120	0.701
0.724	154.8	3.85	0.180	0.801
0.995	145.0	5.42	0.233	0.847
2.010	126.6	9.86	0.434	0.918
2.736	121.2	13.53	0.558	0.938

Table 3. Data for the acetylene P_A series. HCl_t const. = 8.1 m, CuCl_t const. = 1.52 m.

P_A	$\nu(\text{C}_2\text{H}_2) - \nu(\text{CH}_3)$ Hz	I	$[\text{C}_2\text{H}_2]_{\text{t}}$ m	$Q(I)$	$Q(P_A)$
—	—63.2	—	—	—	—
1.42	75.6	1.47	0.600	0.878	0.888
3.90	65.4	2.49	1.018	0.829	0.843
5.31	61.4	2.79	1.143	0.810	0.820
5.42	61.7	2.84	1.163	0.807	0.818
7.04	58.9	2.98	1.219	0.797	0.793
7.64	53.8	3.31	1.354	0.772	0.784
8.91	56.6	3.00	1.229	0.795	0.765

In the P_A series the acetylene frequency is neither constant nor shifted further downfield but is shifted towards higher field by a comparatively small amount upon increasing the P_A . See Table 3 and Fig. 2b.

Ethylene is only slightly soluble in water, and thus the ratio of copperbound to total ethylene approaches unity already at very low CuCl concentrations. The resonance frequency of the ethylene peak is dependent on the concentrations of the two ethylenic species in the solution according to the formula (1) but with C_2H_4 inserted instead of C_2H_2 . During the course of the experiments the peak moves 46.0 Hz towards higher field; see Table 4.

The individual concentrations of the copper-bound resp. physically dissolved acetylene species are calculated with the help of the relations found by Vestin and Löfman,⁶ and are, for the CuCl_t series,

$$[\text{C}_2\text{H}_2]_{\text{aq}} = 0.0357 \text{ m}$$

$$[\text{C}_2\text{H}_2]_{\text{Cu}} = \text{CuCl}_t \times 0.1982$$

and

$$Q = \frac{\text{CuCl}_t \times 0.1982}{\text{CuCl}_t \times 0.1982 + 0.0357}$$

In Fig. 3 $\Delta\nu(\text{C}_2\text{H}_2)$ is plotted against Q . The function is linear until $Q = 0.8$, whereafter the curve becomes concave upwards, with $d\Delta/dQ$ approaching 2.4×10^3 , compared to 1.5×10^3 in the lower part of the curve.

For the P_A series, where the CuCl_t is constant and the acetylene pressure varied, the Q -values are calculated according to

$$Q(P_A) = \frac{1.0047}{P_A \times 0.0242 + 1.0969}$$

Fig. 2. Acetylene frequency as a function of (a), the cuprous chloride concentration (P_A const. = 0.96 atm., HCl_t const. = 8.42 m); (b), the acetylenic pressure (CuCl_t const. = 1.52 m, HCl_t const. = 8.1 m).

However, into the P_A -term there might enter uncertainties because of insufficient equilibration, defectiveness of the manometer *etc.*, which would affect the Q -values computed in the described manner. Therefore the total concentration of acetylene of the sample is also calculated from the integral peak of the spectrum, according to

$$[\text{C}_2\text{H}_2]_t = [-\text{CH}_2] \times \frac{1}{2} \times I$$

I is the quotient between the two integral peaks, and $[-\text{CH}_2] = 0.273$ m. With the help of a calibration curve, $[\text{C}_2\text{H}_2]_t = f(Q)$, constructed from a set of P_A values chosen to fit the region of interest, the Q -values corresponding to the $[\text{C}_2\text{H}_2]_t$ values from the integral measurements can be read. These Q -values are

Table 4. Data for the ethylene CuCl_t series. DCl const. = 8.95 m, P_E const. = 1 atm.

CuCl_t m	C_2H_4 m	Q	$\nu(\text{C}_2\text{H}_4)$ Hz
0	0.0054	—	328.0
0.0133	0.0187	0.711	293.0
0.0953	0.1007	0.946	282.7
0.243	0.2486	0.978	282.0

called $Q(I)$ and are listed in Table 3. From this table it is evident that the reason why the acetylene protons are shifted towards higher field upon increasing the acetylene pressure is that the physically dissolved portion increases more rapidly than the complexed, and the ratio of complexed to total acetylene decreases in the pressure region used. In Figs. 4a and b the $\Delta\nu(\text{C}_2\text{H}_2)$ of the series are plotted against $Q(P_A)$ and $Q(I)$, resp. These functions are linear too, but the slope $d\Delta/dQ = 2.2 \times 10^2$ differs from that of the lower part of the graph in Fig. 3 and is rather in accordance with the slope of the upper part, where the CuCl_t values are high. This result may be interpreted as the indication of a species with two Cu atoms, which would be formed at high CuCl concentrations.

Extrapolation of the lower part of the graph in Fig. 3 to $Q=1$ gives $\Delta\nu(\text{C}_2\text{H}_2) = 153.3$ Hz, which is the resonance frequency for the 1:1 complex.

The lack of reliable data on the equilibria in the *ethylene CuCl_t series* and the low solubility of the hydrocarbon add up to a less accurate series of measurements. The concentrations of the species are calculated exclusively from the experimental values and listed in Table 4. The $\Delta\nu(\text{C}_2\text{H}_4)$, *e.g.* the frequencies of the

Fig. 3. Acetylene and ethylene frequencies as functions of the copperbound to total hydrocarbon ratio in the CuCl_t series.

ethylene protons in solutions with Cu(I) measured relative to the ethylene frequency in solution with Cu(I) absent, are plotted against the quotient copperbound to total ethylene in the lower part of Fig. 3. ΔK for the ethylene complex amounts to +47.5 Hz, or 0.97 ppm.

^{13}C NMR spectra of acetylene and ethylene samples with and without univalent copper were recorded in the respective solvents. The large proton NMR shift of acetylene is not reflected in the ^{13}C NMR spectra, the measured ΔK being only +1.1 ppm, the copperbound to

total acetylene ratio being close to unity. For ethylene, on the other hand, ΔK amounts to +31.1 ppm, but the signal remains in the region of olefinic ^{13}C shifts.^{5,6}

DISCUSSION

Acetylene holds an exclusive position in ^1H NMR contexts, in that the resonance frequency for ethane is 0.96 ppm, ethylene 5.84 ppm, but for acetylene 2.88 ppm. The high shielding of the protons in acetylene may be qualitatively explained by considering the anisotropy of the magnetic susceptibility in the triple bond.⁷

It is now generally accepted⁸ that when disubstituted acetylenes enter into complexes, their linear geometry is abandoned in favour of a preferably *cis*-bent structure, with the substituents bent away from the central atom. In a preliminary wide band ^1H NMR measurement of the solid addition compound $\text{C}_2\text{H}_2(\text{CuCl})_3$ we have measured an intranuclear H-H distance of 2.3 Å, which indicates a bent structure. We cannot, however, tell if it is *cis* or *trans*, only that the protons remain equal. It therefore seems reasonable to seek an explanation for the large negative coordination shift of acetylene on π -complex formation with Cu(I) in a change of the acetylene geometry which involves diminished shielding of the protons.

The theory of the nature of the bonding of this type of metal-olefine and metal-acetylene π -complexes is that a σ -bond is formed by the

Fig. 4. Acetylene frequency as function of the copperbound to total acetylene ratio in the P_A series: (a), calculated from P_A ; (b), calculated from I .

overlapping of the empty $4s$ or $5s$ orbital of the metal by the filled bonding molecular π -orbital of the olefine (two in acetylene). One additional bond is formed by the overlapping by a lower filled d orbital of the metal with the empty anti-bonding π^* -orbital of the olefine or one of the empty π^* -orbitals of acetylene. As regards the acetylene it is difficult to find unambiguous proof for the formation of these π -bonds. Modified CNDO-calculations⁹ show that a *cis* or *trans* bent structure would lead to a change of the electron density such that the triple bond on coordination takes the character of a double bond, which leads to less ^1H NMR shielding. This investigation shows that the acetylene protons remain magnetically equivalent on the π -complex formation, but the ^1H NMR shift is changed with a sufficiently large amount to make a deviation from the linear geometry look probable. The ^{13}C NMR spectrum confirms that the change of geometry is restricted to the protons, and comparison with the corresponding ethylene complex shows that the effect cannot be attributed to the copper atom. Therefore the ^1H NMR behaviour can be rationalized in terms of a bending of the $\text{C}\equiv\text{C}-\text{H}$ angle.

REFERENCES

1. Keller, H. J. *NMR Untersuchungen an Komplexverbindungen* Vol. 2, *NMR Basic Principles and Progress*, Berlin 1970, p. 21.
2. Vestin, R. and Löfman, C. *Acta Chem. Scand.* 7 (1953) 398.
3. Lindblom, T. *Chem. Scr.* 4 (1973) 103.
4. Vestin, R. *Sv. Kem. Tidskr.* 66 (1954) 65.
5. Stothers, J. B. *Carbon-13-NMR-Spectroscopy*, Academic, New York 1972.
6. Beverwijk, C. D. M. and van Dongen, J. P. C. M. *Tetrahedron Lett.* 42 (1972) 4291.
7. Pople, J. A. *Proc. Roy. Soc. Ser. A.* 239 (1957) 541.
8. Glanville, J. O., Stewart, J. M. and Grim, S. O. *J. Organometal. Chem.* 7 (1967) 9.
9. Blizzard, A. C. and Santry, D. P. *J. Amer. Chem. Soc.* 90 (1968) 5749.

Received December 3, 1974.