From dicopper acetylide to carbyne

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Abstract: Freshly prepared dicopper acetylide, air-aged and Cu^{2+} oxidized samples have been studied by FTIR and electronic spectroscopy. There is some evidence about the polymeric and semiconductive nature of dicopper acetylide, and it is proposed to represent this compound by the general formula $(Cu_2C_2 \cdot nH_2O)_x$ in which $n = 0.5$–1 and x is unknown but large. It has been found that upon oxidation, the acetylide ion C_2^{2+} in copper acetylide undergoes a coupling reaction with formation of a diacetylene derivative and/or its higher homologues. No definitive evidence about the presence of cumulenic isomers has been found. After hydrolysis of dicopper acetylide in HCl, acetylene (the main product) together with a mixture of polyynes having the general formula $H—(C{\equiv}C)_n—H$ with $n = 1, 2, 3, 4, 5, 6$ has been identified by electronic spectroscopy. The carbonaceous insoluble matter, obtained from aged/oxidized dicopper acetylide, hydrolyzed in HCl is carbyne as indicated by the FTIR band at $2200\ cm^{-1}$. It has been shown that carbyne is also formed by oxidizing dicopper acetylide with H_2O_2 in aqueous ammonia suspension (FTIR bands at 2203 and $2139\ cm^{-1}$), and is recovered as insoluble carbonaceous matter. Carbyne is also formed by thermal decomposition of dicopper acetylide *in vacuo*. Under these conditions, carbyne is a fluffy, very fine carbon powder having a high tint strength, whose FTIR spectrum shows bands at 2220 and $2200\ cm^{-1}$ due to triple bond stretching vibrations. Volatile compounds are sublimable from carbyne and have been studied by electronic spectroscopy.
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INTRODUCTION

α-Carbyne is the fourth carbon allotrope in addition to diamond, graphite and fullerenes,[1] the structure of which can be described by carbon chains as $—(C{\equiv}C—C{\equiv}C—C{\equiv}C—)_n—$ and calculations[2] show that it is less endothermic and more stable than its cumulenic isomer β-carbyne ${=}(C{=}C{=}C{=}C{=})_n{=}$. Of course, from a thermodynamic point of view, graphite and diamond are considerably more stable than carbyne.[2] Carbyne has been found in meteoritic rests, and is believed to be part of interstellar molecular cloud complexes and circumstellar envelopes of cool carbon stars, because the related compounds cyanopolyynes and cumulenes have already been detected by rado observations.[1]

Recently, we have shown that dicopper acetylide is a key compound in the production of α-carbyne via the Glaser[3] and the Cadiot–Chodkiewicz[4] oxidative coupling reactions. The carbonaceous matter obtained by these reactions was also shown to contain some α-carbyne stabilized by end-capping of the polymeric chain by Cu(I) ions or phenyl groups.[3,4]

A recent excellent review[5] on dicopper acetylide $(Cu_2C_2 \cdot nH_2O)$ has shown that our knowledge of this compound and its oxidation/decomposition products is limited, probably because of its instability and explosiveness, despite the fact that it has been

known for a long time (probably since 1856[6]) and that it finds important applications as catalyst in various chemical reactions.[5] Moreover, it was surprising to learn that the infrared and electronic spectra of Cu_2C_2 have not been published.[5,6]

The present work is intended to fill this gap, and to present some new results on dicopper acetylide, its stability and decomposition reactions, together with its tendency to form carbyne directly, even without the occurrence of Glaser and Cadiot–Chodkiewicz coupling reactions.

EXPERIMENTAL

The FTIR spectra were recorded on a Perkin–Elmer spectrometer using KBr pellets. The electronic spectra were taken on solutions with a Shimadzu UV160A spectrophotometer in the appropriate solvent, except for the insoluble dicopper acetylide the electronic spectrum of which was recorded on a suspension in glycerol. All solvents and reagents used were from Aldrich or Fluka. Acetylene was generated from CaC_2 and water, and purified as previously described.[7]

Preparation of dicopper acetylide

Ilosvay's reagent method[6] was used. Copper(I) iodide (10.0 g) and hydroxylamine hydrochloride (13.5 g) were dissolved in 600 mol of 6% ammonia solution. A stream of purified acetylene was bubbled

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through the solution and this treatment was prolonged even after the appearance of an abundant bright-reddish precipitate. The precipitate was filtered, washed with water and left moistened to avoid any risk of explosion. The yield was judged quantitative by the fact that the ammonia solution collected after filtration was completely water-clear, i.e. all the original blue colour due to $Cu(NH_3)_n^+$ ions had disappeared.

A very small amount of freshly prepared acetylide was placed on a filter paper and kept in a stream of air at 45°C for several minutes in order to dry it sufficiently for the preparation of a pellet with KBr, and record its FTIR spectrum (100 scans) (Fig 1, curve A). The electronic spectrum of freshly prepared material was recorded using a glycerol suspension (Fig 2).

Caution! Do not dry dicopper acetylide in a desiccator under vacuum; explosions have been reported.[5]

Ageing of dicopper acetylide

A sample of dicopper acetylide prepared as described above was left for 14 days on filter paper exposed to air at 15–20°C, 50–60% relative humidity. During this period, the sample lost its brightness but no apparent changes occurred. The FTIR spectrum was recorded in KBr pellet (Fig 1, curve B).

Preparation of dicopper acetylide in the presence of Cu^{2+} ions

Copper(I) iodide (4.0 g) was dissolved/suspended in 100 ml of 6% ammonia solution. Separately 2.9 g of
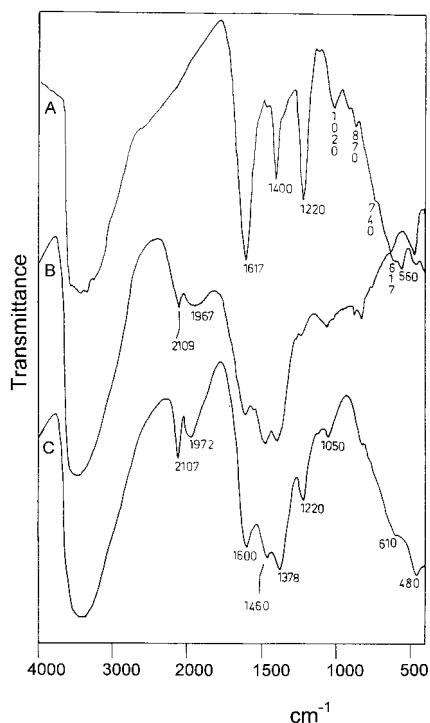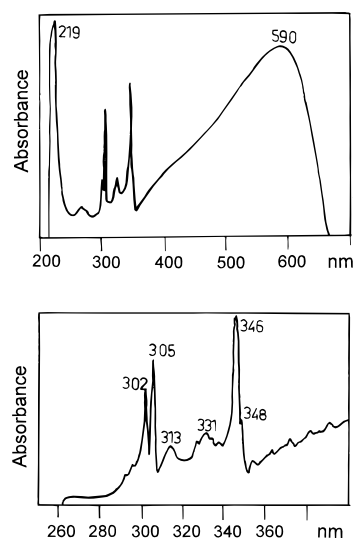
Figure 2. (Top) Electronic spectrum of freshly prepared dicopper acetylide in glycerol suspension. (Bottom) Expansion of the top spectrum.

copper(II) chloride was dissolved in 100 ml of 6% ammonia solution. The two solutions were then mixed together and a stream of purified acetylene was passed into this solution. The precipitated acetylide was brown in colour. It was stirred overnight at room temperature in its supernatant and then filtered, washed with water and left moistened (yield 9.0 g of moistened product). A small sample was dried on filter paper as described above to prepare KBr pellets for recording of the FTIR spectrum (Fig 1, curve C).

Decomposition of dicopper acetylide by hydrochloric acid

Fresh sample

About 8.0 g (moistened) of freshly prepared dicopper acetylide was stirred in a conical flask with 260 ml of a 15.5% solution of hydrochloric acid at room temperature. The aqueous solution was covered during the dissolution by a layer of cyclohexane (100 ml). An evolution of gas took place that was partly absorbed by cyclohexane and partly evolved and collected in an IR cell (10 cm long). The FTIR spectrum of the evolved gas showed that, as expected, it was acetylene only ($\equiv$C—H asym stretching): 3305 and 3260 cm^{-1}, 1350 and 1305 cm^{-1} (comb bands), and 735 cm^{-1} ($\equiv$C—H asym bending). Diacetylene and superior homologues were detected as cyclohexane extracts by UV spectroscopy (see Fig 3, curve A; and Results and Discussion). No residual carbonaceous matter was collected, but only Cu_2Cl_2 as an insoluble fraction.

Aged samples

Similar results were achieved by dissolving a sample of dicopper acetylide which had been air aged for more than 1 day in 12% HCl solution (acetylene main product: UV spectrum of cyclohexane extract similar to that shown in Fig 3(A) for fresh product). However, dissolution of the acetylide required more

Figure 1. FTIR spectra of: (A) freshly prepared dicopper acetylide; (B) dicopper acetylide aged 14 days in air at room temperature; (C) dicopper acetylide oxidized at room temperature by Cu^{2-} ions.
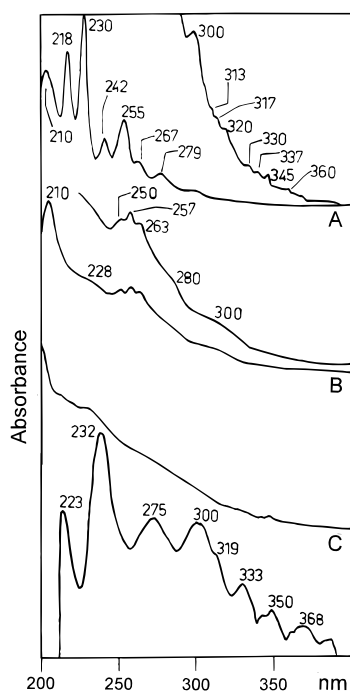
Figure 3. (A) Electronic spectrum in cyclohexane of diacetylene and superior homologues (polyynes) of general formula H—(C≡C)$_n$—H with n = 1, 2, 3, 4, 5, 6, formed by dissolving dicopper acetylide in hydrochloric acid solution. (B) Electronic spectrum in ethanol of yellow-white sublimate from carbyne produced by Glaser coupling reaction. (C) Electronic spectrum in ethanol of sublimate from carbyne produced by oxidation of dicopper acetylide with hydrogen peroxide (bottom curve is the first derivative).

Figure 4. (A) Electronic spectrum in cyclohexane of magenta-coloured solution formed on standing, from the mixture of polyynes originally generated from dicopper acetylide hydrolysis. (B) Electronic spectrum of red sublimate obtained from carbyne prepared by the Glaser coupling reaction.

time, and in addition to the formation of insoluble Cu_2Cl_2, there was formation of small amounts of insoluble carbonaceous matter which could be isolated by washing the filtered Cu_2Cl_2 with an excess of 6% ammonia solution to dissolve the Cu(I) salt thus leaving the insoluble and purified carbonaceous matter. This study was repeated with 14 days aged and Cu^{2+} oxidized dicopper acetylide. The longer the ageing time of the acetylide sample in air, the larger the amount of carbonaceous matter recovered as described, confirming previous results.[8] Oxidation with Cu^{2+} ions increased the amount of insoluble carbonaceous matter. The IR spectrum of the carbonaceous matter recovered was similar to that of the carbyne produced by the Glaser reaction[3] and those reported in Fig 5 below: FTIR in KBr (absorption bands in cm^{-1}): 2230 (sh), 2185 (mw), 2105 (w), 1970 (sh), 1700 (sh), 1618 (vs), 1400 (s), 1250 (s), 540 (br), 440 (m), 415 (m).

Note that the cyclohexane solutions of polyynes obtained as described above, both from freshly prepared or aged dicopper acetylide, stirred in air in the presence of their acidic mother-solution containing Cu^+/Cu^{2+} ions, became magenta in colour provided that they were not exposed to light for a long time. The spectrum of this solution is reported in Fig 4, curves A. The magenta solution was readily bleached if shaken with sodium hypochlorite (NaClO) 6% aqueous solution or sodium hydroxide solution.

Oxidation of dicopper acetylide with hydrogen peroxide

Moistened dicopper acetylide (8.8 g), was suspended in 300 ml of 6% ammonia solution. An aqueous solution of hydrogen peroxide (30%) was added dropwise to the stirred suspension. A total of 38 ml of 30% hydrogen peroxide was added. During each addition, the decomposition of H_2O_2 was observed through the evolution of O_2. At the end of the addition, the mixture was diluted with 120 ml of 6% ammonia solution and left under stirring for 48 h. Then it was filtered and a brown–black residue was recovered, while the aqueous solution was deep blue in colour. The brown–black residue was then washed with acetone, which became orange–brown, and left to dry in air. The yield was 0.93 g; FTIR spectra are reported in Fig 5, curves A and B. The acetone extract was left to evaporate in air leaving 0.09 g of a brown residue which was soluble in absolute ethanol. The FTIR spectrum of the extractable fraction was as follows: (in KBr, bands in cm^{-1}): 2920 (m), 2869 (m), 2158 (m), 2110 (sh), 2079 (sh), 1925 (vvw), 1869 (vvw), 1605 (s), 1560 (s), 1470 (s), 1385 (s), 1245 (m), 1160 (w), 1130 (m), 1025 (m), 960 (w), 855 (m), 725 (mw), 470 (mw). The electronic spectrum of the soluble fraction (in absolute EtOH, absorption bands in nm) was as follows: 215 (max), 268, 315, 336 (shoulders): first derivative spectrum (peaks in nm): 228, 289, 328, 385, 422, 455, 493.

Thermal decomposition of dicopper acetylide

Freshly prepared dicopper acetylide (7 mg), dried on filter paper in a stream of air (45°C) was transferred into a 50 ml flask. The flask was evacuated under dynamic vacuum and then heated using an alcohol stove. After about 10–15 s heating, complete decomposition of the sample took place (without explosion or any damage to the flask): a very fine carbon powder was spread on the walls of the flask while a
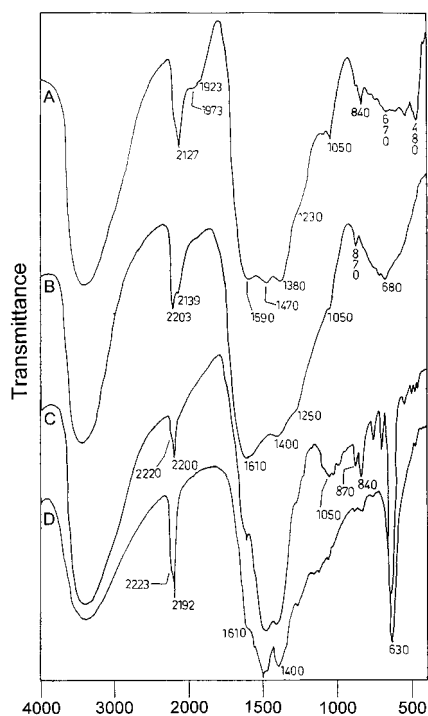
Figure 5. Carbonaceous product (carbyne) obtained by partial (curve A) and full (curve B) oxidation of dicopper acetylide by hydrogen peroxide. Carbyne obtained by thermal decomposition *in vacuo* of unaged (curve C) and Cu^{2+} oxidized (curve D) dicopper acetylide.

small copper residue remained at the bottom. The flask was cooled under dynamic vacuum and then opened. The black powder recovered from the walls of the flask was fluffy and had a very high tint strength, indicating a very small particle size: its FTIR spectrum is given in Fig 5, curve C.

This experience was repeated several times, also employing both 14 days (or more) aged samples, or dicopper acetylide, and dicopper acetylide oxidized with Cu^{2+} ions. In all cases similar results were achieved (see Fig 5, curve D).

Caution! Use a maximum of 10–15 mg of dicopper acetylide for each experiment. Be sure to evacuate the flask completely before starting to heat. Residual air in the flask could cause an explosion.

Separation of volatile hydrocarbons from carbyne by sublimation

Carbyne (0.15 g) prepared through the Glaser reaction as described in refs 3 and 4, was sealed in a flask and heated under dynamic vacuum using an alcohol stove (600°C). Heating was prolonged for a few minutes and two sublimates were collected. The first (more volatile) fraction was reddish, and was collected in the glass pipe connecting the heated flask with the pump, while the second sublimate fraction was yellow–white and condensed in the upper part of the flask. The two sublimates were readily soluble in absolute ethanol. The electronic spectrum of the red sublimate is shown in Fig 4, curves B while the

spectra of the yellowish–white sublimates are reproduced in Fig 3, curves B and C.

After this thermal treatment *in vacuo* the FTIR spectrum of carbyne remained unchanged compared with the initial spectrum. The band at $2200 \, cm^{-1}$ was still present.

RESULTS AND DISCUSSION
Dicopper acetylide: coupling reactions during ageing

In symmetrical disubstituted acetylenes, the triple bond stretching band is forbidden in the IR but is Raman active.[9] In the case of acetylene, for example, the absorption band due to triple bond stretching does not appear in the IR spectrum (see ref 9 and also the Experimental section). For this reason, the absence of triple bond stretching in an IR spectrum is not definitive proof of the absence of an acetylenic group in a given compound. The spectrum of $Cu_2C_2 \cdot nH_2O$ with $n = 0.5$–1 is shown in Fig 1, curve A. As expected no triple bond stretching band can be detected. In this spectrum the unique tentative assignment is for the bands at $480 \, cm^{-1}$ which could be due to Cu—C bond vibration.[6] The presence of water in the structure of this compound is confirmed by the IR band at $3440 \, cm^{-1}$.

The most interesting aspect shown in Fig 1, curve B is the alteration of the IR spctrum of dicopper acetylide upon ageing in air. This alteration is due to oxidation which could, for instance, cause coupling reactions between acetylide ions (C_2^{2-}) in the crystalline structure, in a way similar to that occurring in the Glaser reaction:[3,4] simultaneously Cu^+ ions are oxidized to Cu^{2+}. Proof of these reactions is the development of two bands at 2109 and $1967 \, cm^{-1}$ originally not present in freshly prepared Cu_2C_2, testifying that new acetylenic species have been formed. We have previously reported the general rule that the triple bond stretching vibration is forbidden in symmetrically substituted alkynes. However, frequently medium or weak bands appear in the 2300–$2000 \, cm^{-1}$ region, even for symmetrically substituted acetylenic molecules.[9,10] Because the bands at 2190 and $1967 \, cm^{-1}$ (see Fig 1, curve B) were not originally present in freshly prepared Cu_2C_2, it is obvious that these new bands should be assigned to new acetylenic species which have been formed by coupling reactions during ageing.

An additional indication that this interpretation is correct is the amount of insoluble carbonaceous matter found in Cu_2C_2: as described in the Experimental section, we have shown by dissolving it in aqueous HCl that freshly prepared Cu_2C_2 is completely free from this material. However, the amount of carbonaceous matter increases significantly upon air-ageing of Cu_2C_2, in agreement with previous results.[8] Necessarily, the carbonaceous matter was formed only by coupling reactions of acetylide ions.

In the Experimental section we have shown that this carbonaceous matter is not graphite but α-carbyne, as testified by its FTIR spectrum which is fully comparable to that of authentic carbyne produced via other synthetic routes.[3,4]

In Fig 1, curve C, we report the FTIR spectrum of freshly prepared Cu_2C_2 in the presence of Cu^{2+} ions. These ions cause direct oxidation of the freshly prepared dicopper acetylide to give the same product as that obtained by ageing in air some Cu_2C_2 prepared exclusively from Cu^+ ions (in the presence of reducing agents). In fact, the acetylenic bands in Fig 1, curve C, are the same as in Fig 1, curve B, confirming that they are formed by an oxidative coupling reaction of acetylide ions. It should be noted that acetylenic compounds having several acetylenic triple bonds normally display more than one absorption band in the $\nu_{C\equiv C}$ region as is the case of the two bands at 2109 and at 1967 cm^{-1} of Fig 1, curve B. The first one at higher wavenumber can surely be assigned to acetylenic groups, while the band at lower wavenumber lies in a spectral region already known to be typical of polymeric copper mono-acetylides:[6] for instance, $CH_3C\equiv CCu$ has a band at 1980 cm^{-1} and $PhC\equiv CCu$ a band at 1933 cm^{-1}. An alternative interpretation could assign the band at 1967 cm^{-1} to cumulenic double bonds (because allenes and cumulenes all have absorption bands in this spectral region,[9,10] thus, the formation of Cu(II)-terminated cumulenes from Cu(I)-terminated polyynes could be postulated according to the following reactions:

$$3Cu_2C_2 + 2O_2 \rightarrow Cu-C\equiv C-C\equiv C-C\equiv C-Cu$$
$$+ 4CuO$$

$$Cu-C\equiv C-C\equiv C-C\equiv C-Cu + [O]$$
$$\rightarrow Cu^{2+}[=C=C=C=C=C=C=]^{4+}Cu^{2+}$$
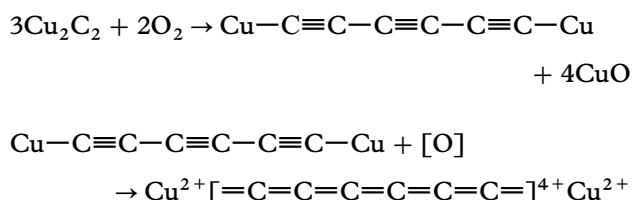
Some support for this interpretation can be advocated from the fact that allenic ions have been observed in solid carbides such as magnesium carbide (Mg_2C_3).[11] However, characterization of the products evolved during the decomposition in aqueous HCl of Cu_2C_2 (freshly prepared and aged for 14 days) has not revealed unequivocally the presence of allenic/cumulenic product (*vide infra* and Experimental section) somewhat weakening this interpretation.

Dicopper acetylide: its polymeric nature

The electronic spectra of freshly prepared dicopper acetylide in glycerol suspension are reported in Fig 2. The main feature is the broad and somewhat intense transition at about 590 nm which shows that dicopper acetylide is a semiconductor with a band gap of 2.10 eV calculated from this transition. The more interesting aspect is that the electronic spectra

of several different copper alkyl- and aryl-acetylides ($R-C\equiv CCu)_n$ show an electronic transition in the range 450–550 nm.[6] For all these alkyl- and aryl-acetylides it has already been shown that they are polymeric coordination compounds.[6] Because a similar electronic transition also occurs in dicopper acetylide it was also possible to deduce that this compound also has a polymeric structure and should be better described as $(Cu_2C_2 \cdot nH_2O)_x$ in which $n = 0.5$–1 and x is unknown but large. In our studies on highly conjugated polymers[12,13] such as *trans*-polyacetylene, we have shown that the electronic transition due to electronic conjugation along the polymeric chain occurs at 600 nm for a solid film: moreover, it is well known that there is a correlation between the degree of conjugation along the polymeric chain and the chain length, i.e. the molecular weight of a polymeric molecule. All these facts indicate that dicopper acetylide could be regarded as a polymeric coordination compound. In Fig 2 we also show a detail of the electronic spectrum of dicopper acetylide in the range 250–400 nm: this series of bands is very characteristic and can be used to identify the compound by electronic spectroscopy.

Qualitative analysis of the products evolved from dicopper acetylide by dissolution in aqueous HCl; study of sublimates obtained from carbyne

As reported in the Experimental section, freshly prepared dicopper acetylide undergoes hydrolysis upon stirring in aqueous hydrochloric acid. The main product generated from this hydrolysis is acetylene which we identified by FTIR spectroscopy; Cu_2Cl_2 is also formed, but the most interesting aspect regards the formation of a mixture of polyynes having the general formula $H-(C\equiv C)_n-H$ with $n = 2, 3, 4, 5, 6$. Fig 3, curves A, show the electronic spectrum of the cyclohexane extract of the organic products evolved during hydrolysis of dicopper acetylide. Fortunately diacetylene and its higher homologues have a very characteristic electronic spectra[14,15] which permit us to easily identify these compounds. No clear evidence for the presence of allenic compounds has been deduced from this investigation, even if the unassigned band at 317 nm is considered to be due to 1,2,3-butatriene.

Our band assignments based on reference spectra[14,15] for compounds having the general structure $H-(C\equiv C)_n-H$ are given in Table 1. The concept here is clear: during acetylene polymerization, in addition to polyenic polyacetylene, soluble carotenoid-like oligomers are also formed,[12] their presence being an indirect indication that the structure of the high polymer is analogous to that of the soluble oligomers. The same idea should be applied to the case of carbyne formation by the Glaser reaction; in fact the presence of these extractable oligomers, together with carbyne, are an indirect confirmation of their acetylenic structure and of the presence of the parent high polymer.

Table 1. Band assignments based on reference spectra for compounds of general formula H—(C≡C)$_n$—H

Abs. band (nm)	Assignment	Abs. band (nm)	Assignment
210	n = 1–5	313	n = 5
218	n = 2, 4, 5	317	CH$_2$=C=C=CH$_2$?
230	n = 2, 4	320	n = 5
242	n = 2, 3, 5	330	n = 4
255	n = 2, 3, 5	337	n = 6
267	n = 3, 5	345	n = 4, 5
279	n = 3	360	n = 6
300	n = 3	370	n = 5, 6

The cyclohexane extract containing a mixture of polyynes is a completely water-clear solution. However, on standing, upon stirring in air in the presence of its acidic mother solution containing Cu^+/Cu^{2+} ions, it becomes magenta in colour, and its electronic spectrum originally shown in Fig 3, curves A, is changed to that shown in Fig 4, curves A, with a maximum at 522 nm and a shoulder at 680 nm. We believe that a copper-mediated coupling reaction occurs, involving oligomeric polyynes with formation of cyclic polyynes and/or polyene-ynes; the spectrum observed is compatible with this hypothesis.[14,15] However, this spectrum could also be due to a non-alternant cyclic polyenic hydrocarbon formed by spontaneous cyclization and addition of the extracted polyynes. In fact, polyynes generally, and diacetylene in particular, are known to be unstable and on standing are converted to addition adducts. When carbyne prepared by the Glaser coupling reaction[3,4] is heated at very high temperature *in vacuo* (500–600°C), a yellow-white sublimate is collected together with a more volatile red sublimate. The yellow-white sublimate dissolves in ethanol and gives the electronic spectrum shown in Fig 3, curves B. This spectrum could reasonably be expected to be due to unidentified polycyclic aromatic compound(s) formed after the high temperature treatment undergone by carbyne or even during carbyne synthesis. This experiment shows that during the Glaser coupling reaction, oligomeric volatile inferior homologues of carbyne are formed, together with carbyne. Upon heating, they are sublimed or could undergo a rearrangement to more stable aromatic compounds.

Figures 4, curves B shows the electronic spectrum of the red sublimate originating from carbyne. The spectrum of this sublimate is different from that produced by spontaneous cyclization/addition of polyynes present in cyclohexane extract (Fig 4, curve A), although the formation of a similar hydrocarbon compound could be postulated.

Another hypothesis concerning the polyene-yne nature of these red–magenta adducts stems from the fact that these products are completely bleached upon shaking with NaClO or NaOH solutions, therefore should be very sensitive to isomerization.

Oxidation of dicopper acetylide with hydrogen peroxide: carbyne formation

The Glaser reaction is an oxidative coupling involving the use of air or oxygen as oxidizing agent.[3,4] In the present work we have also used hydrogen peroxide as oxidizing agent over dicopper acetylide, to prepare carbyne. Figure 5, curves A and B, testify to the success of this new route to carbyne synthesis. When dicopper acetylide is treated with H_2O_2 in ammonia suspension, the original FTIR spectrum of Fig 1, curve A, is changed to that of Fig 5, curve A, which displays a discrete similitude with the spectra of aged Cu_2C_2 (Fig 1, curves B and C). Again we observe the appearance of bands at about 2120 and 1970 cm^{-1} (Fig 5, curve A) whose nature has been discussed above. Some additional aspects observed are the development of bands at 1470 and 1380 cm^{-1} already seen with aged dicopper acetylide (Fig 1, curves B and C). The band assigned to the Cu—C vibration band at 480 cm^{-1} appears weaker than in the original Cu_2C_2 (Fig 5, curve A versus Fig 1, curve A). Upon further oxidation of dicopper acetylide with hydrogen peroxide, the Cu—C vibration band at 480 cm^{-1} disappears completely (Fig 5, curve B); all copper is now in solution as $Cu(NH_3)_n^{2+}$ (amino complex ion), the solution has acquired a deep blue colour and the insoluble residual fraction is now only carbonaceous matter. Figure 5, curve B reveals that this carbonaceous matter is carbyne with its characteristic bands at 2203 and 2139 cm^{-1} (triple bond symmetric and asymmetric stretching respectively); for reference we can mention 1,5,7,16-hexadecatetrayne CH≡C—(CH$_2$)$_4$—C≡C—C≡C—(CH$_2$)$_4$—C≡CH which shows[9] symmetrical and asymmetrical stretching of the internal —C≡C—C≡C— bonds at 2235 and 2135 cm^{-1}, while external —C≡CH groups are responsible for the absorption at 2102 cm^{-1}.

Carbyne prepared with the hydrogen peroxide route may be extracted with acetone: the infrared spectrum (see Experimental section) exhibits acetylenic bands at 2150, 2110 and 2079 cm^{-1} (whose higher frequency confirms the oligomeric nature of this extract with additional weak cumulenic bands at 1925 and 1869 cm^{-1}. Extracted carbyne prepared with H_2O_2, treated at higher temperatures releases a yellow sublimate soluble in ethanol the electronic spectrum of which is shown in Fig 3, curves C. The absorption curve does not reveal any absorption peaks, while the first derivative reveals several peaks with some analogy with the previously discussed spectra of Fig 3, curves A and B.

Thermal decomposition of dicopper acetylide: carbyne formation

Cu_2C_2 is well known for its explosivity.[5,6,16] After explosion, the decomposition products are essentially

carbonaceous matter and copper/copper oxides.[5,6,16] Explosion occurs in air upon heating to $T > 60°C$ and should of course involve oxidation reactions, i.e. production of CO and CO_2. We have found that by heating a few milligrams of dicopper acetylide *in vacuo*, a safe decomposition reaction occurs with emission of very fine, fluffy carbon powder (having a high tinting strength) deposited on the walls of the flask, and formation of residual copper at the bottom of the flask. This carbonaceous material was thought to be essentially graphite.[16] The FTIR spectra of Fig 5, curves C and D reveal that the carbonaceous matter formed by thermal decomposition of Cu_2C_2 is carbyne, as underlined by the intense bands at 2220 and $2200 \, cm^{-1}$ due to acetylenic stretching, fully comparable in their position to those observed for carbyne prepared by the Glaser reaction.[3,4] Other spectral features of Fig 5, curves C and D are the absence of a Cu—C band at $480 \, cm^{-1}$ and the presence of an intense band at $630 \, cm^{-1}$ due to Cu_2O formation:[17] in fact, the band at $630 \, cm^{-1}$ can be reasonably assigned to Cu_2O because the IR spectrum of this compound shows a unique absorption at this wavenumber[17] and is formed by reaction with residual air present in the flask during thermal decomposition.

Taking into account the drastic conditions under which carbyne was obtained in this work, the product described as 'carbyne' cannot be considered to be composed exclusively of pure carbon allotrope, but should be thought of as carbonaceous matter containing significant amounts of carbyne allotrope domains, together with graphite and graphene domains, i.e. we should assume that a certain degree of crosslinking occurred between adjacent chains of carbyne leading to crosslinked domains called graphene.[18]

CONCLUSIONS

It was shown by FTIR spectroscopy that pure freshly-prepared dicopper acetylide does not display a triple bond stretching transition becase it is forbidden for symmetry reasons. The Cu—C vibration is located at $480 \, cm^{-1}$.

By oxidation of Cu_2C_2 in air or with Cu^{2+} ions at room temperature, acetylide anions C_2^{2+} undergo partial coupling reactions with formation of diacetylene and superior homologues (polyynes), as suggested by the development of new bands at 2109 and $1967 \, cm^{-1}$. The band at $1967 \, cm^{-1}$ is in the range of polymeric alkyl- and aryl-acetylides,[6] but could also be due to cumulenic groups formed through isomerization of polyynes.

The polymeric and semiconductive nature of dicopper acetylide is also suggested by its electronic spectrum, so that dicopper acetylide could be better formulated as $(Cu_2C_2 \cdot nH_2O)_x$.

Freshly prepared dicopper acetylide hydrolyses easily in HCl solution releasing acetylene. Secondary products are diacetylene and superior homologues described by the general formula $H—(C≡C)_n—H$ in which $n = 1, 2, 3, 4, 5, 6$, as revealed by electronic spectroscopy. A similar distribution of products is obtained by acid hydrolysis of dicopper acetylide oxidized in air or with Cu^{2+} ions. The main difference with freshly prepared dicopper acetylide is that the former does not yield any amount of carbonaceous insoluble matter, while the other two (oxidized and hence coupled) yield variable amounts of carbonaceous matter (depending on the degree of oxidation: the higher the degree of oxidation, the higher the carbonaceous portion). This carbonaceous matter is composed of carbyne as clearly revealed by FTIR spectroscopy which reveals typical bands at about $2200 \, cm^{-1}$.

Carbyne obtained by the Glaser coupling reaction does not decompose upon heating to 500–600°C *in vacuo*, and the triple bond stretching remains unchanged. However, two sublimates are collected: the more volatile sublimate is red and the less volatile yellow-white; both are soluble in ethanol. Based on electronic spectroscopy, the red hydrocarbon is probably a non-alternant polyene, while the white hydrocarbon is a polycyclic aromatic compound. Both are presumably formed by thermally-induced cycloaddition reactions of polyynes present as oligomers adsorbed on carbyne.

In addition to the already explored Glaser coupling reactions,[3,4] it has been shown for the first time that carbyne can be formed by oxidizing dicopper acetylide suspended in ammonia solution with H_2O_2. Copper is released from acetylide as $Cu(NH_3)^{2+}$ (amino complex) and insoluble carbonaceous matter can be recovered, showing the absence of Cu—C vibration in the IR spectrum, and carbyne bands at 2203 and $2139 \, cm^{-1}$.

Thermal decomposition of dicopper acetylide *in vacuo* yields copper and fluffy carbon having a high tinting strength and hence a very small particle size. For the first time, it has been demonstrated that this carbon is not graphite or amorphous carbon (as thought in the past) but carbyne, as clearly revealed by FTIR spectra which show absorption bands at 2220 and $2200 \, cm^{-1}$.

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