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The simplest approach to prepare solutions of polyynes in hydrocarbons

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Abstract—Polyynes solutions having as main components C_6H_2 and C_8H_2 can be prepared in hydrocarbon solvents by hydrolyzing calcium carbide in an NH_4Cl aqueous solution containing Cu(I)/Cu(II) salts. The polyynes are released into a hydrocarbon solvent by acidification with concd. HCl. Heptane solutions with polyynes concentration as high as 0.1 M can be easily prepared.

Recently, we have discovered that polyynes mixtures having the general formula $H–(C{\equiv}C)_n–H$ with n an integer can be prepared in solution by arcing two graphite electrodes submerged in a hydrocarbon or alcohol solvent.[1] The versatility of the synthesis of polyynes with the submerged electric arc has been demonstrated in the preparation of dicyanopolyynes by arcing graphite electrodes in liquid nitrogen.[2]

The mixture of polyynes formed in hydrocarbon solvents consists of the complete homologous series from C_6H_2 to $C_{16}H_2$.[1] In some special cases, $C_{18}H_2$ has also been detected.[1] The dominant specie in the polyynes mixture produced by the submerged carbon arc consists of the polyyne C_8H_2 (see Table 1).

One of the drawbacks of the synthesis of the polyynes with the submerged carbon arc is the simultaneous formation of a mixture of PAHs (polycyclic aromatic hydrocarbons) and soot.[3] Apparently, the PAHs and soot are formed mainly by the plasmalysis of the solvent caused by the arc. In any case, the HPLC analysis has shown that the PAHs concentration is two orders of magnitude lower than the polyynes concentration and for some synthetic purposes this could be a sufficient condition.[3] It is possible to purify the polyynes separating them from the PAHs and the soot by precipitation as acetylides but this operation is relatively complex and not completely satisfactory.[4] The best purification way remains the preparative HPLC.[5]

Another drawback suffered by the polyynes solution prepared by the submerged electric arc technique is the relatively low concentration achievable. Usually, concentrations as high as 10^{-5}–10^{-6} M can be reached. Higher concentrations can be reached by prolonging

Table 1. Polyynes in mol% (data from HPLC-DAD analysis)

Polyyne	**ARC**[a]	From CaC_2 (this work)				
	Ref. 1	RUN 1 [Cu(I)/Cu(II)]	RUN 2 [Cu(I)/Cu(II)]	RUN 3 [Cu(I)/Cu(II)]	RUN 4 [Cu(II)]	RUN 5 [Cu(I)]
C_6H_2	**20.3**	56.8	48.7	67.4	80.9	83.3
C_8H_2	**61.2**	35.8	49.1	31.2	18.7	15.6
$C_{10}H_2$	**14.8**	6.6	2.2	1.2	0.4	1.1
$C_{12}H_2$	**2.9**	0.7	Traces	0.2	0.0	0.0
$C_{14}H_2$	**0.6**	0.1	0.0	0.0	0.0	0.0
$C_{16}H_2$	**0.2**	0.0	0.0	0.0	0.0	0.0
Total conc.	**0.01 mM**	85.5 mM	53.4 mM	97.7 mM	56.1 mM	28.7 mM

[a] Absence of Cu species.

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arcing for hours.[5] Alternatively, it is also possible to concentrate the solutions by distillation under reduced pressure.[4] Under these circumstances, it is also possible to increase the relative concentration of C_8H_2 and higher polyynes chains at the expense of C_6H_2 which, being more volatile, distils away with the solvent.[4]

The synthesis of polyynes by arcing graphite electrodes remains a very simple synthetic approach and has also many implications in different fields of science from astrochemistry to soot formation mechanism.[4]

As an alternative to the submerged electric arc, herein we report that polyynes can be produced simply by hydrolyzing calcium carbide (CaC_2) into an NH_4Cl aqueous solution of CuCl/$CuCl_2$, followed by acid hydrolysis of the resulting oxidized acetylides.[6] The hydrolysis of calcium carbide produces in situ acetylene, which by reacting with Cu(I) forms dicopper acetylide Cu_2C_2. The latter compound is then oxidized by the action of Cu^{2+} causing the coupling reaction. It has been observed that the presence of Cu^{2+} is not essential, since the polyynes are formed even when only Cu^+ ions are present. This is due to the fact that even the atmospheric oxygen is sufficient to cause the oxidative coupling reaction. It is also possible to start from $CuCl_2$ solutions; the addition of CaC_2 and the resulting acetylene produced causes the reduction of Cu^{2+} to Cu^+ so that the formation of Cu_2C_2 precipitate is observed. In any of the above mentioned cases, the liberation of the polyynes is caused by the addition of hydrochloric acid after the complete hydrolysis of calcium carbide. The polyynes liberated from their Cu^+ salts by the acid hydrolysis are trapped into hydrocarbon solvents by shaking the solution with *n*-hexane, *n*-heptane, or *n*-octane.[6] The polyynes are easily detected by HPLC analysis of the resulting hydrocarbon solution using a diode-array detector[7] and also by electronic absorption spectroscopy of the resulting hydrocarbon solutions.[1–4,6]

As expected, the hydrolysis of calcium carbide in an aqueous solution of NH_4Cl in the complete absence of copper ions does not produce any detectable amount of polyynes. Thus are the copper ions which are involved in the coupling reaction and polyynes synthesis.

In Table 1 is shown the distribution of polyynes formed with the electric arc synthesis in comparison with the polyynes produced by the calcium carbide hydrolysis and copper-based coupling. The relative concentration of each individual polyyne species has been measured using a diode array detector in HPLC analysis[7] and the molar extinction coefficients reported in the literature.[8] Arcing graphite electrodes in hydrocarbon solvents produces a quite constant distribution of polyynes with C_8H_2 species dominant followed by C_6H_2 and $C_{10}H_2$ with still appreciable or detectable amounts of the higher homologues. Instead, the distribution of polyynes produced by the calcium carbide hydrolysis in the presence of copper ions varies according to the conditions adopted and is always characterized by a dominant level of C_6H_2. When in solution are present simultaneously Cu^+ and Cu^{2+} ions, the concentration of C_8H_2 appears high although C_6H_2 remains dominant but also $C_{10}H_2$ is present in the solution. When instead the calcium carbide hydrolysis is conducted in aqueous solutions containing only Cu^+ or only Cu^{2+} ions, the coupling reaction appears less effective and the concentration of C_8H_2 appears much lower in comparison to C_6H_2 and $C_{10}H_2$ concentration is very low.

In any case, one of the major advantages offered by the synthetic method presented herein, apart from the simplicity and the rapidity, is represented by the high concentration reached in few minutes by the polyynes in the solution. As shown in Table 1, the total polyynes concentration obtained by arcing 5–10 minutes is about 10^{-5} M while with the new method described here, in the same time it is possible to prepare solutions having a total polyynes concentration as high as 0.1 M. By extrapolating his data on the thermal stability of polyynes in solution and especially on C_8H_2 polyyne, Heymann[5] concluded that the threshold of the instability of polyynes solution should lie at 10^{-3} M. In fact, we have found that all the solutions reported in Table 1 on standing, even when left in closed glass flasks in the dark or in diffuse light, leave a thick brown deposit on the walls and at the bottom of the flask resembling cork for its color and its consistency. There are no doubts that the precipitate is the result of a crosslinking reaction.[9]

The synthetic approach presented here is a development of our earlier observation that dicopper acetylide (Cu_2C_2) and dicopper diacetylide (Cu_2C_4) left to age in humid air undergo a slow coupling reaction.[10] When they are hydrolyzed with hydrochloric acid, they release polyynes in an extracting hydrocarbon medium[10] and a carbonaceous residue containing carbynoid structures.[11] The drawback of the described synthetic approach involved the handling of almost dry and more or less aged dicopper acetylide and dicopper diacetylide both proven to be explosive.[10] Instead, the synthetic approach described herein is completely safe because the acetylides are formed in situ in an aqueous solution. When dispersed in water solution the acetylides are completely safe and not explosive. They are oxidized and hydrolyzed always in water solution in a completely safe procedure, which is in contrast with our old approach[10] which involved necessarily the isolation of the acetylides.

References and notes

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6. Typical experimental procedure: NH_4Cl (7.5 g) was dissolved in 200 mL of distilled water in a thick-walled conical flask with glass stopper equipped with a valve. $CuCl_2{\cdot}2H_2O$ (10.3 g) and CuCl (5.2 g) were added to the ammonium chloride solution and stirred to ensure the dissolution (may remain undissolved matter). Heptane (50 mL) is added to the solution followed by calcium carbide (CaC_2, 3.5 g) in small portions. After the addition of CaC_2, the flask fitted with the stopper is hand-shaken for few seconds and then the excess of acetylene is released by opening the valve. The operation is repeated several times until all calcium carbide has been added. When the first portion of CaC_2 is added the solution turns into a violet color but on further CaC_2 addition it becomes dark brown. The reaction mixture is further shaken for about 2 min and 35 mL of concd. hydrochloric acid was added to cause the hydrolysis of the acetylides. Shaking is prolonged for another 2 min and then the crude mixture is filtered with the aid of a water pump. A dark precipitate is collected on the filter paper. The filtrate consists of a green aqueous phase and the heptane layer containing the polyynes dissolved therein. The heptane solution is collected with the aid of a separatory funnel. If an assay of the polyynes heptane solution (0.1 mL) is diluted 25 times with pure heptane, it displays the following electronic absorption spectrum (in nm) 200 (s), 207 (sh), 216 (ms), 227 (s), 239 (m), 252 (m), 261 (w), 275 (mw), 297 (w). Similar results as just described can be obtained by changing the ratio of Cu^+/Cu^{2+} or even by using only Cu^+ or only Cu^{2+} as outlined in Table 1, although some change in the distribution of the products has been observed. If the polyynes solution in heptane is left in contact with the aqueous solution of copper chlorides under acidic conditions for one week, a plethora of new products can be detected by HPLC analysis. Probably coupling reactions and intramolecular cyclization as well as addition reactions have taken place.
7. HPLC analysis was conducted on an Agilent Technologies liquid chromatograph. An assay of the heptane solution recovered was diluted at least 15 times with pure heptane and 25 μL was injected. The diodes of the detector were set at 202, 225, 250, 295 and 350 nm. Use was made of a C-8 column for the separation under isocratic conditions with a mobile phase of acetonitrile/water 80:20 vol/vol. Polyynes were identified on the basis of their retention times and on the basis of their characteristic electronic absorption spectra; for quantitative analysis the molar extinction coefficients of polyynes known from the literature[8] were used. For further details on the separation and identification of polyynes see Ref. 1–4.
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9. The brown material can be recovered by decantation of the solution. It is insoluble in all common solvents and the FT-IR spectrum in KBr is as follows (absorption peaks in cm^{-1}): 3294 (s), 2956 (sh), 2929 (m), 2859 (mw), 2180 (m) 2100 (mw), 1773 (sh), 1714 (sh), 1617 (s), 1384 (ms), 1213 (s), 1122 (s), 978 (sh), 877 (w), 757 (w), 662 (mw). Particularly remarkable are the residual acetylenic bands at 3294 and 2180 and 2100 cm^{-1} testifying that it is a three-dimensional polymer derived from the crosslinking reaction of the polyynes species. Furthermore, oxidation bands can be observed at 1773, 1714 and 1122 cm^{-1} but it is unclear if they have been formed during the crosslinking reaction or after that reaction upon exposure to air during isolation and handling.
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