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Polyynes and cyanopolyynes synthesis from the submerged electric arc: about the role played by the electrodes and solvents in polyynes formation

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Abstract—The products of the electric arc between graphite electrodes have been investigated by high performance liquid chromatographydiode-array detector (HPLC-DAD) analysis in various media: distilled water, liquid nitrogen, methanol, ethanol, *n*-hexane and benzene. In distilled water, hydrogen capped polyynes $H-(C\equiv C)_n-H$ were the unique products demonstrating that carbon is supplied by the graphite electrodes while hydrogen is supplied by the solvent plasmalysis (in this case water plasmalysis). Arcing graphite electrodes in liquid nitrogen produces cyanopolyynes: $N\equiv C-(C\equiv C)_n-C\equiv N$ demonstrating that in this case the end groups of the polyyne chains are supplied by molecular nitrogen plasmalysis caused by the electric arc. Graphite arcing in methanol and ethanol produces very clean solutions (byproducts negligible or absent) of hydrogen-capped polyynes with C_8H_2 as the main product accounting for more than 70 mol percent of the total polyyne concentration. By replacing graphite electrodes with titanium electrodes in methanol or in ethanol, polyynes are not formed at all; only trace amounts of polycyclic aromatic hydrocarbons (PAHs) were detected. When arcing with graphite electrodes is conducted in *n*-hexane or in benzene, polyyne formation is accompanied by a significant production of PAH, especially in benzene. These results have been rationalized in terms of carbonization or coking tendency of a given solvent. The effect of using titanium electrodes in place of graphite electrodes has been investigated also in *n*-hexane and in benzene as well as the effects of very high electric current intensity employed to ignite and sustain the submerged electric arc.

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1. Introduction

In a series of papers¹⁻⁵ we have reported the discovery that polyynes having the general formula $H-(C \equiv C)_n-H$ are easily formed when graphite electrodes are arced into certain solvents. Furthermore, we have also started the investigation of the chemistry of polyynes^{3,6,7} which, for the first time, are easily available in solution, thus permitting this new exploration.

There are still many questions concerning the easy formation of polyynes from the electric arc in solution. The key question that this work intends to answer is the following: are the polyynes produced by the carbon vaporization from the graphite electrodes or instead they are produced by the plasmalysis of the solvent caused by the extremely high temperature of the electric arc? To produce an unequivocal answer, we have designed a series of key experiments ranging from replacing the organic solvent with liquid nitrogen to exclude the interference of the

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solvents and by replacing graphite with titanium electrodes in the arc.

Furthermore, we intend to analyze the work and the results of Beck and co-workers⁸⁻¹⁰ who have used electric arc and other electric discharge systems in toluene in order to produce fullerenes and instead obtained and identified a plethora of polycyclic aromatic hydrocarbons (PAH). Sometimes fullerenes were present but they failed to find polyynes.⁸⁻¹⁰

2. Results and discussion

2.1. Polyynes synthesis by arcing graphite electrodes in water

The electric arc between graphite electrodes in certain solvents like methanol, acetonitrile, *n*-hexane and decahydronaphthalene produces in a few minutes polyyne solutions at a concentration of $10^{-3}-10^{-4}$ M without any concentration operation.¹⁻⁵ This synthesis represents a new advantageous and one-shot route to polyynes as an alternative to the classic step-synthesis proposed about 30 years ago.¹¹ The basic mechanism proposed, involves

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carbon vaporization from the graphite electrodes under the extremely high temperature produced by the electric arc (estimated to be above 4000 °C), above the vaporization point of elemental carbon.^{1–5} Elemental carbon is vaporized from the electrodes and oligomerizes to form polyyne chains and then is quenched into the solvent surrounding the plasma ball of the arc. The same mechanism was proposed by Tsuji and co-workers for polyyne formation under laser ablation of graphite particles suspended in a solvent.¹²

Usually the polyynes are detected as hydrogen-terminated chains although in certain special cases²⁻⁵ (acetonitrile), we have also found other end groups derived from the solvent. In general, it is reasonable to think that the hydrogen end capping is derived from the solvent plasmalysis caused by the electric arc. In fact, the solvent plasmalysis caused by the electric arc generates atomic hydrogen, which then reacts with the diradicalic carbon chains produced by carbon vaporization from the electrodes.

To test this hypothesis, we have also studied the submerged electric arc between graphite electrodes in distilled water. Since we have a carbon source form the graphite electrodes and an hydrogen source from the plasmalysis of water we expected to produce hydrogen-capped polyynes. This was indeed the case as discussed in Section 4.1. The electronic spectrum of the crude polyyne mixture (Section 4.1) matches satisfactorily the pattern of analogous mixtures obtained by arcing graphite in other solvents.^{1–5} Furthermore, as shown in Figure 1, the HPLC analysis of the polyyne mixture formed in water reveals the presence of polyynes C_8H_2 and $C_{10}H_2$ as the major arcing products; the former polyyne was detected at an approximate concentration of 5×10^{-6} M while the latter at only 1×10^{-7} M.

Thus, it appears clear that the hydrogen atoms present as end groups in the polyyne chains in this specific case are derived from water dissociation at the high temperature of the arc, while elemental carbon is supplied by the graphite electrodes.

2.2. Formation of polyynes by arcing graphite electrodes in liquid nitrogen

Once it was clarified that the polyyne chains are produced with hydrogen end groups in water, it does not appear surprising that the polyynes produced between graphite electrodes submerged in liquid nitrogen are also hydrogenterminated (see Section 4.2). In fact, in our electric arc in liquid nitrogen, we have excluded the presence of any organic solvent but not the presence of humidity. Therefore, the arc between graphite electrodes in liquid nitrogen necessarily involves the plasmalysis of small amounts of water, which supplies the hydrogen necessary for endcapping the polyyne chain.

As expected, the graphite arc in liquid nitrogen produces cyanopolyynes as main products, while the hydrogencapped polyynes are only minor products. This is shown in Figure 2 and implies that the nitrogen molecules are activated by the electric arc and plasmalyzed to atomic nitrogen. The carbon vapour reacts with atomic nitrogen forming cyanopolyynes; the formation of cyanopolyynes (and polyynes) in the electric arc in liquid nitrogen represents a clear indication that the elemental carbon for the polyyne chains is supplied exclusively from the graphite electrodes and not from the solvent. This conclusion was quite expected since we know that the electric arc in vacuum conditions between graphite electrodes produces polyyne ions.^{13,14} Instead, when the electric arc between graphite electrodes is struck under a low pressure of cyanogen gas (N=C-C=N) under Kraetschmer-Huffmann conditions,¹⁵ cyanopolyynes belonging to the general formula: $N \equiv C - (C \equiv C)_n - C \equiv N$ were obtained.¹⁶

When the graphite electrodes were arced in liquid nitrogen



Figure 1. Electronic absorption spectra of polyynes C_8H_2 and $C_{10}H_2$ produced by arcing graphite electrodes in distilled water and detected by HPLC-DAD analysis. The first absorption spectrum in the left is due to C_8H_2 which has a retention time of 1.685 min and the other spectrum is due to $C_{10}H_2$ with a retention time of 2.205 min. The absorbance scale in the ordinate is normalized and is in mAU units.



Figure 2. Individual electronic absorption spectra of each molecular species separated by the liquid chromatographic analysis. From bottom to top of Figure 2 it is possible to distinguish the spectrum of C_6N_2 with $t_R=1.55$, then C_8H_2 with $t_R=1.64$ followed by C_8N_2 ($t_R=1.87$), $C_{10}H_2$ ($t_R=2.11$) and $C_{10}N_2$ ($t_R=2.39$).

the cyanopolyynes (and polyynes) formed were quenched into the very cold reservoir of the liquid nitrogen surrounding the plasma ball. When liquid nitrogen vaporizes, it drags the cyanopolyynes and polyynes, which presumably are insoluble but are embedded in liquid nitrogen, outside the reactor into the gas washing bottle filled with a solvent like *n*-octane. When nitrogen bubbles into the bottle, it releases the polyynes into the octane solvent, which acts as a trap. The HPLC separation of the cyanopolyynes and polyynes trapped in the octane solvent was made using a C8 column and each molecular specie eluted was detected with a diode-array detector (DAD) detector. Figure 2 reports the spectra of each specie eluted. From bottom to top of Figure 2 it is possible to observe the detection of $N \equiv C - (C \equiv C)_2 - C \equiv N$ followed by $H - (C \equiv C)_4 - H$. Then the spectra of $N \equiv C - (C \equiv C)_3 C \equiv N$ followed by $H - (C \equiv C)_5 - H$ are observed and finally $N \equiv C - (C \equiv C)_4 - C \equiv N$ was also detected. Elsewhere we



Figure 3. Electronic absorption spectra of the polyynes formed from graphite arcing in liquid nitrogen. In this figure the products are shown at their real absorption intensity in mAU scale. The liquid chromatographic analysis (HPLC) was able to separate the mixture into its components. The electronic spectrum of each component eluted was recorded by the diode-array detector (DAD). The three main components are easily and definitively identified from their electronic absorption spectra and are, respectively, C_6N_2 (light green line), C_8N_2 (dark green line) and $C_{10}N_2$ (blue line). The spectra of these three dicyanopolyynes in this figure are easily identifiable from the longest wavelength absorption band lying at 233, 260 and 283 nm, respectively. There are also two other minor components in Figure 3: the hydrogen-terminated polyynes C_8H_2 (pink line), $C_{10}H_2$ (red line). Furthermore, $C_{12}H_2$ has also been identified although at very low concentration (not shown in Figure 3).

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| Table 1. | Syno | psis o | f products | formed by | arcing | graphite o | r titanium | in selected | solvents |
|----------|------|--------|------------|-----------|--------|------------|------------|-------------|----------|
| | | | | | | 0 1 1 1 | | | |

| Solvent Electrodes | Hexane Graphite (% mol) | Hexane Titanium (% mol) | Benzene Graphite (% mol) | Benzene Titanium (% mol) | Methanol Graphite (% mol) | Methanol Titanium (% mol) | Ethanol Graphite (% mol) | Ethanol Titanium (% mol) |
|---------------------------------|-------------------------------|-------------------------------|--------------------------------|--------------------------------|---------------------------------|---------------------------------|--------------------------------|--------------------------------|
| Polyvne C6 | 20.3 | 23.9 | 13.8 | Detected | 7.2 | n.d. | 8.9 | n.d. |
| Polyvne C8 | 61.2 | 72.7 | 68.3 | 83 | 77.8 | n.d. | 73.5 | n.d. |
| Polyyne C10 | 14.8 | 3.4 | 12.6 | 17 | 12.8 | n.d. | 12.3 | n.d. |
| Polyyne C12 | 2.9 | n.d. | 3.2 | Traces | 2.2 | n.d. | 3.7 | n.d. |
| Polyyne C14 | 0.63 | n.d. | 2.1 | Traces | Detected | n.d. | 1.5 | n.d. |
| Polyyne C16 | 0.17 | n.d. | Traces | n.d. | n.d. | n.d. | 0.1 | n.d. |
| Polyyne C18 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Benzene | n.d. | Traces? | | | n.d. | Traces | n.d. | Traces |
| Indene | n.d. | Traces | n.d. | n.d. | n.d. | n.d. | n.d. | n.d |
| Naphthalene | Traces | Traces | Detected | Detected | Traces | Traces | Traces | Traces |
| Acenaphthene | Traces | n.d. | Detected | n.d. | n.d. | Traces | n.d. | Traces |
| Acenaphtylene | Traces | Traces | Detected | Detected | n.d. | n.d. | n.d. | n.d. |
| Biphenyl | n.d. | n.d. | Detected | Detected | n.d. | Traces | n.d. | n.d. |
| Phenanthrene | n.d. | n.d. | Detected | Detected | n.d. | Traces | n.d. | n.d. |
| Anthracene | n.d. | n.d. | Detected | Detected | n.d. | Traces | n.d. | n.d. |
| Perylene | n.d. | n.d. | Detected | Detected | Traces | Traces | n.d. | n.d. |
| Pyrene | Traces | n.d. | Detected | n.d. | n.d. | n.d. | n.d. | n.d. |
| Crysene | Traces | n.d. | Detected | n.d. | n.d. | n.d. | n.d. | n.d. |
| Fluoranthene | n.d. | n.d. | Detected | Detected | n.d. | Traces | n.d. | n.d. |
| Benzo[b]fluoranthene | Traces | Traces? | Detected | Detected | Traces | n.d. | n.d. | n.d. |
| Benzo[b]naphto[2,1-cd]thiophene | n.d. | n.d. | Traces | Traces | n.d. | n.d. | n.d. | n.d. |
| Total polyyne conc. (mol/l) | 4×10^{-4} | 2×10^{-6} | 5×10^{-4} | 2×10^{-5} | 5×10^{-4} | None | 3×10^{-4} | None |
| Carbon black formation | Yes | Yes | Abundant | Abundant | Small | Small | Small | Small |

n.d.=not detected.

have discussed both the spectra and the assignments of the molecular species just reported.¹⁷ Figure 3 shows that the cyanopolyynes were the dominant species in the synthesis from the graphite arc in liquid nitrogen while the normal polyynes are only present as a minority and can be considered by-products derived from the humidity as discussed previously.

2.3. About the role played by organic solvents when the submerged arcing is made between graphite electrodes

The discussion about the formation of cyanopolyynes and polyynes in liquid nitrogen and in water, respectively, underlines the key role played by the electrodes during graphite arcing and suggests a minor to negligible contribution from the solvent as elemental carbon source. Instead the solvent clearly supplies the end groups of the polyynes chains.

When the graphite electrodes are arced into a solvent like *n*-hexane, as described in Section 4, although by far the main reaction product consists of a mixture of polyynes, it is possible to detect other by-products by HPLC-DAD analysis. These by-products are not found when graphite electrodes are arced in liquid nitrogen or are present in extremely small trace amounts when the arc is made in certain solvents like methanol, ethanol or water (see Table 1).

To elucidate the nature of these by-products, as described in Section 4.3, we precipitated all the hydrogen-terminated polyynes present in an *n*-hexane solution as acetylides by treatment with a Cu(I) reagent.^{1–5} After this treatment, it was possible to observe a profound alteration of the electronic absorption spectrum of the hexane solution (see Fig. 4). Before the precipitation, the electronic absorption spectrum of the graphite arced hexane solution (Fig. 4A)

was dominated by the absorption bands due to the polyynes,¹⁻⁵ but after their precipitation as Cu(I) acetylides it was possible to observe the spectrum (Fig. 4B) of the nonprecipitable by-products. Of course, if the unique result of arcing between graphite electrodes in hexane would have been the polyynes, after their precipitation the hexane solution should have appeared completely clean and free from absorption bands. This is not the case, because the HPLC-DAD analysis of such a solution freed from polyynes reveals a plethora of products but no trace at all of the polyynes. This is shown in Figure 5A and B. In Figure 5A the polyynes are clearly distinguishable as a sharp and intense peak in the chromatogram but they are completely absent from Figure 5B after their complete separation as acetylides. The molecular species of Figure 5B are a mixture of polycyclic aromatic hydrocarbons (PAHs). This



Figure 4. (A) Electronic absorption spectrum of polyynes obtained in *n*-hexane after arcing with graphite electrodes. (B) Spectrum after polyyne precipitation from solution as acetylides. The residual absorption bands are due to PAHs formed as secondary products during arcing. The two spectra have been shifted for clarity. The absorbance units in the ordinate are in arbitrary scale.



Figure 5. (A) Normalized HPLC Chromatogram showing the polyynes formed in *n*-hexane in standard conditions at 10 A. Each sharp peak is a polyyne. The polyynes detected at C_8H_2 , $C_{10}H_2$, $C_{12}H_2$, $C_{14}H_2$ and even $C_{16}H_2$ as the broad peak after 10 min of retention time. The abscissa is reporting the elution time in minutes, the ordinate reports the DAD response in milli-absorption units (normalized). The blue line was detected at the fixed wavelength of 225 nm, the red line at 250 nm, the green line at 274 nm, the pink line at 295 nm and the grey line at 350 nm. (B) HPLC chromatogram of molecular species non-precipitable as acetylides, identified as PAHs on the basis of their electronic spectra. Note the absence of the C_8H_2 , $C_{10}H_2$, $C_{12}H_2$ polyynes which appear at about 2, 2.7 and 4 min in the Figure 5A. The abscissa is reporting the elution time in minute, the ordinate reports the DAD response in milli-absorption units. The blue line was detected at the fixed wavelength of 225 nm, the red line at 250 nm.

has been established on the basis of their retention time in the chromatogram and on the basis of their electronic absorption spectra in comparison to the spectra of our standards or of Agilent PAHs library spectra. For instance, we unequivocally identified the presence of naphthalene, acenaphthalene, benzo[b]fluoranthene, pyrene and crysene of a total of 17 different compounds eluted, all with spectra suggesting a PAH nature, although in some case some cyclic polyynes and ene-ynes cannot be excluded, because of the lack of standard and reference spectra.

The presence of PAH in solvents subjected to the electric arc is not a surprise or a novelty. For instance Beck and colleagues^{8–10} have already investigated the effect of electric discharges in toluene with the aim of producing C_{60} fullerene. Instead they found in all cases the formation of mixtures of PAH, and in some cases fullerenes were present but only in trace amounts. The mentioned authors^{8–10} have explored different conditions of electric discharges in hydrocarbon solvents ranging from arc between graphite electrodes to scintillysis, from radiofrequency plasma to silent electric discharges, conditions which are completely different from those used in our previous works¹⁻⁵ and in the present work. Only in one case have Beck et al. adopted the electric arc in conditions very close to ours⁸ using an electric arc at 10-15 A, but also in that case they failed to detect polyynes and obtained instead a complex mixture of PAH. The reason for this failure may be attributed to the workup used for product isolation and analysis: the toluene solution after two-hour arcing was distilled under reduced pressure to dryness after the addition of dichloromethane. The residue after solvent evaporation was used for the GC-MS analysis.⁸ However, we know from our studies 1-7 that polyynes are only stable in solution. When solvent is distilled off the polyynes decompose into other products. This justifies completely the failure to detect linear polyynes by Beck et al.⁸ Since, we have used HPLC techniques coupled with a diode array detector for the analysis of the products of the arc, we have not caused any alteration of the components of the crude mixture of products which was injected as it was produced after a simple filtration. Furthermore, as shown in Figure 6, when arcing in hexane is conducted at 20 A, the polyynes are still present and detectable but the fraction of other products

(PAH) increases significantly. Under these conditions PAH may become the dominant products.

Beck and co-workers¹⁰ also made an interesting comparative study between the products formed by solvent thermal pyrolysis above 1000 °C and the products formed by electric discharges in organic solvents like scintillysis,⁹ radiofrequency plasma treatment and silent electric discharges. In all cases examined, more or less the same PAH mixtures are produced, together with the formation of thermal carbon black or, which is the same, pyrocarbon. Thus, it appears clear that electric discharge in solvents causes their carbonization. The PAHs detected are the by-products and the intermediates which lead to the formation of carbon black,^{18–21} but also polyynes are considered the key intermediates which lead both to PAH and soot formation.^{18,19}

Based on the preceding discussion, it appears clear that the PAH observed by arcing graphite electrodes in hexane are derived from the solvent pyrolysis in the plasma ball of the arc while the polyynes are released by the graphite electrodes. Since polyynes are also considered the precursors of PAH and soot formation^{18,19} it cannot be excluded that a fraction of them, once formed are converted into PAH and soot during the arcing operation. This may explain why the concentration of polyynes grows proportionally to the arcing time in the early stages of arcing but after a certain concentration is reached, say 10^{-3} - 10^{-4} M, it is impossible to further increase their concentration. Probably an equilibrium is reached at that point between the concentration of the polyynes and their transformation into other products by incorporation into the PAH and pyrocarbon or by consumption by the pyrolysis/plasmalysis and/or by the photolysis, since we have demonstrated that the polyynes are photolyzed by the action of the UV light.⁶ Thus, the light emitted by the arc may be one of the contributory factors which limits their maximum concentration in a given solution.

2.4. About the role played by the electrodes: results obtained by arcing with titanium electrodes in place of graphite electrodes

Once the role of the graphite electrodes in the production of the polyynes had been clarified, a couple of crucial tests were made by replacing the graphite electrodes with titanium electrodes.

The first study was conducted in *n*-hexane arcing with titanium electrodes. Surprisingly, and contrarily to all the partial conclusions of the preceding sections, C_6H_2 , C_8H_2 and $C_{10}H_2$ polyynes where found in the hexane solution arced between titanium electrodes (Table 1). Five other products were found in comparable concentrations to the two polyynes mentioned. All were PAH and three of them were identified as naphthalene, acenaphthalene and indene while the remaining two presumable PAH have received only a tentative assignment (see Table 1). The formation of polyynes observed by arcing hexane with titanium electrodes seems to contradict many conclusions of the preceding sections. However, it must be noticed that the arcing in hexane produced a significant amount of carbon black. Since no carbon electrodes were used, it appears clear that all the carbon black formed derived from the pyrolysis and carbonization of *n*-hexane. To explain the polyyne formation, it is possible to think that the pyrocarbon particles formed from hexane plasmalysis entered into the plasma ball of the arc or coated the surface of the titanium electrodes as a thin layer. Under these conditions, the pyrocarbon acted as a source of carbon vapour in the plasma phase for the production of the polyynes.

As shown in Table 1, although the relative concentration of the polyynes detected in *n*-hexane arced with Ti electrodes appears comparable to the distribution of polyynes in *n*-hexane prepared with graphite electrodes, the overall polyyne concentration in the solution prepared with graphite electrodes exceeds by two order of magnitudes



Figure 6. HPLC chromatogram obtained by arcing at 20 A instead of the usual 10 A in *n*-hexane. The polyynes are still produced but with significant amounts of PAHs. Compare this figure with Figure 5A. The abscissa is reporting the elution time in minutes, the ordinate reports the DAD response in milli-absorption units (normalized). The blue line was detected at the fixed wavelength of 225 nm, the red line at 250 nm, the green line at 274 nm, the pink line at 295 nm and the grey line at 350 nm.

the total concentration of the polyynes in *n*-hexane prepared with Ti electrodes under similar conditions (same current intensity and arcing time). Thus, the fundamental contribution from the graphite electrodes in supplying elemental carbon for the polyynes production is clear. Furthermore, it is remarkable that with graphite electrodes long chain polyynes $C_{12}H_2$, $C_{14}H_2$ and $C_{16}H_2$ were also formed and detected in appreciable amounts, while with Ti electrodes the longest detectable chain was $C_{10}H_2$ (see Table 1).

Approximately similar results were observed when *n*-hexane was replaced with benzene (Table 1): graphite electrodes produced a higher concentration of polyynes with a wider distribution of detectable chains in comparison to titanium electrodes. A striking peculiarity of benzene is the formation of a plethora of HPLC-DAD detectable PAHs as reported in Table 1 (plus others separated by HPLC but not identified on the basis of the electronic absorption spectra), the distribution of the PAHs was richer and more complete with graphite electrodes rather than with Ti electrodes. In this case, the contribution of the solvent to PAHs and pyrocarbon formation appears quite evident.

Completely opposite results to those discussed in the case of *n*-hexane and benzene have been observed in the case of alcohols like methanol and ethanol (Table 1).

When methanol or ethanol was used as solvent for arcing with Ti electrodes, the formation of carbon black derived from solvent carbonization was reduced to a minimum. Simultaneously, the HPLC-DAD analysis revealed the complete absence of any polyynes in these oxygenated solvents. Instead, only PAHs were detected but in trace amount (Table 1). Among the PAHs detected in methanol, biphenyl, naphthalene, acenaphthalene, phenanthrene, anthracene were easily identified based both on their retention times and on their peculiar UV spectral pattern in comparison with the spectral pattern of authentic reference compounds. Perylene and fluoranthene were also reasonably identified based on the retention time and on the reasonable match of reference UV spectra. In any case, the PAHs formed under these conditions were present in at least two orders of magnitude lower concentration than the polyynes formed by arcing the graphite electrodes in methanol. Moreover, PAH formation in methanol was considerably lower than the trace amounts produced in *n*-hexane.

Arcing of graphite electrodes in methanol or even better in ethanol, produces the cleanest polyyne solution with extremely small to negligible amounts of PAHs (Table 1). Thus, these alcohols appear to date the best solvents for the cleanest synthesis of polyynes with the electric arc technique. As already reported for other solvents, also in methanol and ethanol the dominant polyyne is C_8H_2 , accounting for more than 70 mol percent of the total polyyne mixture. The yield of longer polyynes decreases as the chain length grows (Table 1). Polyynes $C_{10}H_2$ and $C_{12}H_2$ were formed in appreciable amounts together with the C_6H_2 . In ethanol also $C_{14}H_2$ and $C_{16}H_2$ were detected.

To explain the various results in different solvents as reported in Table 1, it is useful to recall a petrochemical process known as 'coking' which involves the thermal carbonization of an hydrocarbon 22,23 (or hydrocarbon mixture). The coke produced can be considered equivalent to the pyrocarbon mentioned above. The coking tendency of an hydrocarbon under pyrolytic conditions depends on its C/H ratio and the presence of oxygen in the molecule but essentially it depends from its enthalpy of formation.^{22,23} Thus, the energy necessary to produce 1 kg of carbon is +2325 kJ/kg in the case of *n*-hexane and becomes +9787 kJ/kg in the case of ethanol but reaches the very high value of +16770 kJ/kg in the case of methanol. In the case of aromatic hydrocarbons, coking is an exothermic process and occurs with the evolution of considerable amount of heat. For instance, in the case of benzene, the heat evolved in the process is -1150 kJ/kg, for naphthalene -1270 kJ/kg. The maximum value of heat emission in the coking process is offered by acetylene: -9450 kJ/kg.²² In these last three cases the coking process is spontaneous due to the exothermicity of the process. Therefore, when arcing is conducted with aromatic hydrocarbons like benzene (or toluene $^{8-10}$), because of their spontaneous tendency to carbonization, the formation of PAH mixtures in relatively large quantity can be observed together with pyrocarbon or coke. Instead the amount of PAHs and coke decreases significantly when *n*-hexane is arced and decreases further when methanol is used in place of *n*-hexane for arcing. This because of the unfavourable thermodynamics in the carbonization process. As shown above the carbonization thermodynamics of alcohols are extremely unfavourable also because these molecules contain oxygen. Thus, in the case of alcohols, PAH formation is extremely low to negligible and similarly can be concluded for pyrocarbon formation in these media.

3. Summary and conclusions

With a series of experiments, we have thrown more light on the understanding of the process of polyyne formation by the submerged electric arc between graphite electrodes.

Arcing graphite electrodes in distilled water produces hydrogen-terminated polyyne chains $H-(C \equiv C)_n-H$, and this demonstrates that the hydrogen is coming from water plasmalysis at the arc temperature while carbon is vaporized from the graphite electrodes.

Arcing graphite electrodes in liquid nitrogen with our simple apparatus permits trapping of the polyynes formed which consist essentially of cyanopolyynes $N \equiv C - (C \equiv C)_n - C \equiv N$. Under the high arc temperature molecular nitrogen is divided into atomic nitrogen, which terminates the ends of the polyyne chains formed by the association of elemental carbon vapour released by the graphite electrodes. Together with the cyanopolyynes, normal hydrogen-terminated polyynes have also been detected in the mixture produced by arcing in liquid nitrogen. The formation of the hydrogen-capped polyynes can be explained because of the presence of humidity and traces of water in the liquid nitrogen and in the reactor.

The key role of the graphite electrodes in polyyne formation is underlined by the fact that when arcing in methanol and in ethanol is conducted with titanium electrodes no trace of polyynes could be detected by the HPLC-DAD analysis. Instead, with graphite electrodes, very clean solutions of polyynes can be produced up to 10^{-3} M concentration in alcohols. The cleaning of the alcohol solutions refers to the negligible presence of by-products like PAHs. Only polyynes are present and C_8H_2 is by far the dominant specie in these solutions accounting for more than 70 mol percent of the total polyyne concentration.

Arcing with graphite electrodes in *n*-hexane and in benzene produces a plethora of PAHs as secondary products together with polyynes, which remain the dominant products by two orders of magnitude in comparison to the total concentration of PAHs. Arcing *n*-hexane with very high electric current density increases the PAH concentration.

PAHs are formed essentially by solvent pyrolysis or plasmalysis. Depending on the type of solvent and its tendency to carbonize, PAH production can be very high as in the case of benzene or negligible as in the case of alcohols.

When graphite electrodes are replaced with titanium electrodes, polyynes are formed as well in *n*-hexane and in benzene and this is in contrast with the results in methanol and ethanol. However, in the case of Ti electrodes in *n*-hexane and in benzene the polyynes concentration is about two orders of magnitude lower than that achieved with graphite electrodes. The formation of polyynes in these solvents is connected with their tendency to form PAHs and pyrocarbon.

4. Experimental

Graphite rods (99.999% purity, 6 mm diameter \times 150 mm length) used as electrodes were obtained from Aldrich. All solvents used were HPLC grades from Fluka or Riedel de Haen. Titanium rods used as electrodes were from Aldrich. The titanium used as electrode had 99.7% purity. Each electrode had a length of 8.5 cm and a diameter of 0.65 cm. Liquid nitrogen was purchased from SIAD gas tecnici.

The electric arc was produced using a DC power supply Cosmo 2000 from K.E.R.T. (Italy). An electric current of 10 A was used with tension in the range of 10-30 V as already discussed previously.^{2–5} To work with 20 A, two power supply Cosmo 2000 were used conned in parallel to ignite and sustain the arc in the various liquids studied. As usual^{1–5} the electric arc was ignited and sustained by putting in contact the two electrodes and moving them up and down.

Before HPLC analysis or spectroscopy, the solutions were filtered to remove the carbon black particles formed during arcing. Fitration was made on Acrodisc 13LC syringe filters made in PVDF, 13 mm diam. Pore size 0.2 μ m.

The electronic absorption spectra were recorded on a

Shimadzu UV160A spectrophotometer on filtered solutions in organic solvents.

The high performance liquid chromatographic (HPLC) analysis of the filtered solutions was conducted on a Agilent Technologies System Model 1100 equipped with a DAD and a C-8 column Zorbax. A mixture of CH_3CN /water 80/20 v/v was used as mobile phase and pumped at a rate of 1.5 ml/min into the HPLC column. The concentration of polyynes produced was calculated on the basis of the absorption intensity of each polyyne eluted by the column using the molar extinction coefficients reported in literature.¹¹

The PAH were identified on the basis of a standard PAH library supplied by Agilent Technology together with the analytical instrument and software. An additional PAH library was constructed internally using PAH standard solutions obtained from Fluka.

4.1. The electric arc between graphite electrodes submerged in water

The arc was conducted between graphite electrodes submerged in distilled water at 10 A as detailed previously.¹⁻⁵ The electronic absorption spectrum of the crude aqueous solution of polyynes and other products showed the following absorption bands: 200, 215 and 226 nm as the most intense. Other weaker bands were observed at 238, 246, 250, 259, 274, 284, 300 and 323 nm.

The HPLC-DAD analysis revealed the presence of the following polyynes: C_6 , C_8 and C_{10} . Polyyne C_8 was by far the most abundant product.

4.2. The electric arc in liquid nitrogen between graphite electrodes

A three-necked round bottomed Duran flask of 100 ml equipped with two graphite electrodes arranged in a 'V' geometry was filled with liquid nitrogen and immersed in liquid nitrogen in a Dewar flask. The third neck of the flask was fitted with a valve connected with a Drechsel tube (a gas washing bottle) containing 50 ml of n-octane.

The electric arc was ignited and sustained at 9.5 A and 15–30 V (DC current) by putting in contact and by moving slightly up and down the two graphite electrodes submerged into liquid nitrogen into the three-necked flask. The bright light of the arc can be easily observed, and the heat generated by the arc caused the partial vaporization of the liquid nitrogen, which was forced to bubble into the gaswashing bottle attached to the reaction flask. The products formed in the electric arc were hence forced to pass into the octane solvent trap outside the reactor into the Drechsel tube. Periodically samples of the n-octane solution were collected and analyzed by electronic absorption spectroscopy and by HPLC-DAD analysis. The following polyynes and cyanopolyynes were identified based on the retention time and the electronic spectra: C_6N_2 , C_8H_2 , C_8N_2 , $C_{10}H_2, C_{10}N_2.$

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4.3. The electric arc between graphite electrodes in *n*-hexane: evidences of solvent pyrolysis with formation of PAH

The electric arc between graphite electrodes has been conducted in the three-necked round bottomed flask at about 10 A and 15-30 V as detailed elsewhere.¹⁻⁵ The flask was filled with *n*-hexane (70 ml) and was externally cooled with a water/ice bath.

The polyyne solution in hexane obtained after 15 min arcing was filtered, poured into 100 ml of an aqueous solution of ammonia (26%), Cu(I)Cl (2.5 g) and hydroxylamine hydrochloride (1.5 g). The organic solution was vigorously shaken with the aqueous solution for a long time and then it was left settling. All polyynes were precipitated as copper salts (acetylides) and could be observed as copper-colored precipitates. The hexane solution still showed absorption bands in the UV spectrum. The non-precipitable polyynes (non-hydrogen capped polyynes) and other species were present in the solvent. The HPLC analysis of the solution revealed the presence of PAH. About 15 components were separated by the C-8 column. One third of them show electronic spectra of ene-ynes or cyclic polyynes. The remaining two thirds of components eluted were identified as PAHs on the basis of their UV spectra. Among the PAHs, naphthalene, acenaphthalene, benzo[b]fluoranthene, pyrene and crysene were unequivocally identified.

4.4. The electric arc between graphite electrodes at very high current density

The electric arc between graphite electrodes in hexane was repeated as detailed in the preceding Section 2.3. Instead of using 10 A, by connecting in parallel two power supply, it was possible to work with 20 A at about 32 V. Enhanced formation of carbon black was observed. The filtered hexane solution was analyzed by HPLC-DAD. The polyynes C_6H_2 , C_8H_2 , $C_{10}H_2$ and $C_{12}H_2$ were clearly identified. Possibly $C_{14}H_2$ was also present. C_8H_2 was dominant in the usual conditions of arcing at 10 A. In these conditions both C_6H_2 and $C_{10}H_2$ appear to have a concentration comparable to that of C₈H₂. The concentration of the PAHs now appears dominant in comparison to the polyyne concentration, exactly the opposite conditions occurred at low current density where the polyynes are the dominant species. About 17 PAHs and other components were eluted by the C-8 column. Among them naphthalene, acenaphthalene and pyrene have been firmly identified. Some ene-yne or cyclic polyyne was present as well.

4.5. Electric arc between titanium electrodes in *n*-hexane

The electric arc between two titanium electrodes submerged in *n*-hexane was conducted in the usual manner (threenecked flask of 100 ml charged with 70 ml of *n*-hexane externally cooled by a water/ice bath; current 10 A, electrodes in contact moved up and down). The electric arc in this specific case appeared much less intense and less bright than in the case of carbon arc made by graphite electrodes under similar conditions. A gradual darkening of the solvent was noticed by progressing with the arcing time. The titanium electrodes were slightly consumed and a depot of carbon black can be observed at the bottom of the flask; its amount increased by the progress of the arcing. The analysis of the filtered solution was made as usual by HPLC-DAD. The following polyynes were clearly identified C_6H_2 , C_8H_2 , $C_{10}H_2$ with the second being largely dominant. The polyynes are accompanied by PAHs and other by-products. Indene, naphthalene and acenaphthylene were identified among the PAHs.

4.6. The electric arc between titanium electrodes in methanol; a comparison with carbon arc

The electric arc between titanium electrodes submerged in methanol (60 ml) was conducted in the three-necked round bottomed flask of 100 ml, cooled externally with a water/ice bath. The titanium electrodes were arranged in the usual 'V' geometry. The arc was ignited and sustained at 10 A by moving slowly up and down the titanium electrodes kept in contact. After 10 min arcing the polyyne solution obtained was filtered and injected into the HPLC-DAD for analysis. The formation of carbon derived from the carbonization of the solvent was much less significant than in the previous experiment made in *n*-hexane. In this case, no polyynes were detected even in trace amounts by HPLC analysis. Only a mixture of about 12 PAHs was obtained. Among them biphenyl, naphthalene, acenaphthalene, phenanthrene, anthracene, perylene and fluoranthene were identified.

For comparison the titanium electrodes were replaced with graphite electrodes and the above experiment repeated under the same conditions with fresh and pure methanol in the three necked flask. After arcing for 10 min and after filtration the solution obtained was analyzed by HPLC-DAD. The polyyne C_8H_2 was by far the most abundant molecular specie detected followed by $C_{10}H_2$ and C_6H_2 . The polyyne $C_{12}H_2$ was present in detectable amounts. The other by-products essentially made by PAHs were present in trace amount relative to C_8H_2 . Naphthalene and acenaphthalene were identified.

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