

UV photolysis of polyynes at $\lambda=254$ nm and at $\lambda>222$ nm

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Abstract: For the first time the kinetic rate constants of the UV photolysis of polyynes C_6H_2 , C_8H_2 , $C_{10}H_2$, $C_{12}H_2$ and $C_{14}H_2$ under rigorously inert atmosphere have been determined in three different solvents: *n*-hexane, *n*-heptane and decalin. First- or pseudofirst-order kinetics appear suitable to describe the photolysis of these molecules and k values in the range between $3.0 \times 10^{-3} s^{-1}$ and $4.6 \times 10^{-3} s^{-1}$ have been determined. The unique exception is represented by C_6H_2 which photolyses more slowly with $k = 3.2 \times 10^{-4} s^{-1}$. Two different UV sources have been used in the present study: a low-pressure mercury lamp having a monochromatic emission at 253.7 nm and a medium-to high-pressure lamp with a continuous emission between 222 nm and 580 nm. The results are of interest in the understanding, and also the modelling, of the fate of polyynes released by carbon-rich stars in the interstellar medium or the polyynes released by comets in their active phase.

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Introduction

Cyanopolyynes and polyynes are widely present in different types of astrophysical objects ranging from the circumstellar envelope of certain late-type carbon-rich stars (known also as asymptotic giant branch (AGB) stars) to post-AGB objects such as CRL-618 to dark molecular clouds (TMC-1) (Millar 2004), and to the atmospheres of planets and satellites of the Solar System (Smith *et al.* 1999; Roos-Serote 2004).

Cataldo (2004a–c, 2006a) has shown that the mechanism of polyne and cyanopolyne formation in a carbon arc may be used as a model for the study of the growth of carbon chains in the circumstellar shells of AGB stars. Although the mechanism of carbon chain formation at high temperatures and even at low temperatures seems to be reasonably understood (Kwok 2006), little is known about the stability of long polyne chains to the action of UV and other types of high-energy radiation. For instance, polyynes are released by carbon-rich stars in the interstellar medium. It has been calculated that their maximum concentration occurs at about 5×10^{11} km from the centre of the red giant carbon-rich stars (Millar *et al.* 2000). This distance represents the edge where the molecules meet the incoming interstellar UV radiation field which causes their photodissociation and photoionization. In fact, the UV field of the carbon-rich star is negligible in comparison to the UV field of the interstellar medium. At this distance from the star only photoresistant molecules are able to survive to the decomposition. It is known, for instance, that polycyclic aromatic hydrocarbons are more photostable than polyynes. Photostability may also derive

from the fact that relatively labile molecules are incorporated into solid carbonaceous particles; in such a case they may survive their journey into and through the interstellar medium followed by their incorporation into cometary bodies as organic molecules (Kwok 2004). In addition, the photochemistry of polyynes also has implications in the formation of simple organic compounds in cometary coma (Heymann 2008).

Only recently, polyynes, starting from C_8H_2 (octatetra-1,3,5,7-yne) have become easily accessible in solution through carbon arc synthesis (Cataldo 2003, 2004b, 2006b). This has paved the way for the first qualitative evaluation of the reactivity of relatively long chain polyynes towards the action of UV radiation (Cataldo 2004c) and even the first very preliminary study about their resistance to γ -photons radiolysis (Cataldo & Keheyan 2006). Previous reports on polyne photolysis were qualitative as well. For instance, Lagow *et al.* (1995) have reported the observation of the slow photolysis of these molecules under the action of light. In the present work we present quantitative data on the photolysis of polyynes with UV radiation at 250 nm from a low-pressure mercury lamp source and in a multi-wavelength range from a medium- to high-pressure mercury lamp.

Experimental results

Materials and equipment

The solvents used in this work (*n*-hexane, *n*-heptane, decalin) were all high-performance liquid chromatography (HPLC)

or spectroscopic grades and were obtained from Fluka or Aldrich. High-purity argon was obtained from Fluka.

The HPLC analysis of the polyynes was performed with an Agilent Technologies liquid chromatograph, model 1100, equipped with a diode array and fluorescence detector. The details of the HPLC analysis have been reported elsewhere (Cataldo 2006b). A C-8 column and a mobile phase of acetonitrile/water of 80/20 vol/vol was employed. The electronic absorption spectra were recorded on a Shimadzu UV160A spectrophotometer.

For the irradiation study, two types of UV mercury arc lamps from Helios Italquartz (Milan, Italy) were used in dedicated quartz reactors. The low-pressure mercury arc lamp used in this study has a nominal power of 12 W and an almost monochromatic emission at 253.7 nm which arises from the transition $\text{Hg}(^1\text{P}_1) \rightarrow \text{Hg}(^1\text{S}_0) + h\nu$ (Ninomiya & Naito 1989). The other emission line at 184.9 nm associated to the mentioned mercury atomic transition was completely filtered by the walls of the lamp and by the solvents used. The medium- to high-pressure mercury lamp employed has instead a nominal power of 125 W and is characterized by a series of emission from 222 to 580 nm (Ninomiya & Naito 1989). Two immersion-type quartz reactors were used. The reactor for the low-pressure mercury lamp was the simplest and the irradiation was made at room temperature (+25 °C) without cooling. The reactor for the medium- to high-pressure mercury lamp was instead designed for water cooling with circulation of tap water. Thus the irradiation was conducted at about +15 °C.

Synthesis of polyynes in solution

Polyynes in solution were produced through the submerged carbon arc technique (Cataldo 2003, 2004b, 2006b). The arc was struck between graphite electrodes submerged in *n*-heptane, in *n*-hexane or in decalin. In general, the polyyne mixtures obtained with such synthesis have an overall concentration of 10^{-5} – 10^{-6} M. Alternatively the synthesis of polyynes in solution was also achieved by the modified Glaser reaction starting from the oxidation of dicopper acetylide followed by acid hydrolysis (Cataldo 2005a,b). With the modified Glaser synthesis it is possible to prepare polyynes at concentrations greater than 10^{-2} M. The drawback of such solutions is their relatively low stability (Cataldo 2006c). Such solutions were used in the photolysis experiments after dilution with pure solvent.

Irrespective of the synthetic pathway used, either the carbon arc or the modified Glaser reaction, the dominant polyyne species in the mixture is always C_8H_2 which represents ~80 % by mol of the total polyyne mixture (Cataldo 2005a,b, 2006b).

Photolysis of polyynes with the low-pressure mercury lamp at 253.7 nm

In a typical procedure, the reactor was filled with 220 ml of polyyne solution in *n*-hexane, *n*-heptane or in decalin. The polyynes concentration was set at about 10^{-5} M by dilution with the selected solvent, if necessary. A stream of argon was

continuously bubbled through the solution for at least 2 min before switching on the lamp and during the irradiation. After a prefixed interval of time ranging from 15 s to a few minutes the lamp was switched off and the reactor opened to take a sample of the irradiated solution. The sample was analysed both by UV spectroscopy and by liquid chromatographic analysis (HPLC; injection volume 20 μl). After sampling the reactor was closed again, continuously flushed with argon and after 2 min the lamp was switched on again. These operations were repeated numerous times until the complete disappearance of the polyynes from the solution.

Photolysis of polyynes with the medium- to high-pressure mercury lamp (emission from 222 nm to 579 nm)

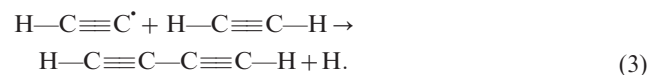
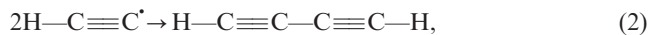
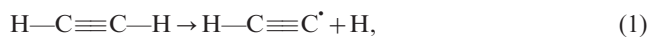
The same general procedure described for the irradiation with the low-pressure lamp was also adopted for the high-pressure lamp. Apart for the necessity to cool the lamp with water circulation, the high-pressure mercury lamp is characterized by a warm-up time to reach operational stability (Ninomiya & Naito 1989). Therefore, more concentrated polyyne solutions were employed (e.g. 10^{-4} M) and longer intervals of times between sampling (about 5 min), to take into account the stabilization time needed by the lamp after it was switched on. Also in this case the irradiation was conducted under argon atmosphere and the analysis of the samples taken was made by UV spectroscopy and by HPLC.

Results and discussion

Overview of acetylene and oligoynes photolysis

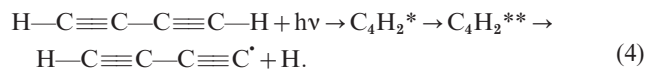
Until recently, polyynes were not easily accessible and therefore the main research works on the photolysis of acetylenic molecules were concentrated on acetylene itself (Zelikoff & Aschenbrand 1956; Okabe 1978; Laufer & Bass 1979; Seki *et al.* 1986) and on its most accessible oligomers, diacetylene or butadiyne (Glicker & Okabe 1987; Bandy *et al.* 1992; Frost *et al.* 1995; Arlington *et al.* 1999; Robinson *et al.* 2000; Wrobel *et al.* 2000; Pola *et al.* 2004) and triacetylene or hexatriyne (Wrobel *et al.* 2000).

Zelikoff & Aschenbrand (1956) reported that when acetylene is irradiated at 184.9 nm, its main product is diacetylene, although at relatively higher pressure benzene is also formed in relatively high quantities. Vinylacetylene was found as a secondary product. A free radical mechanism was proposed involving the ethynyl radical C_2H :

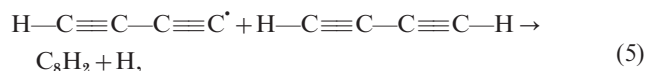


Other works have confirmed the above mechanism and the quantum yield for ethynyl radical production has been determined, as well as the formation of acetylene in the triplet state which has different deactivation pathways (Okabe 1978). Also diacetylene irradiated at 185 nm produces an excited state (a singlet state) which, through another metastable state

(a triplet state with long lifetime towards collisions), decays to a diethynyl radical (Glicker & Okabe 1987):



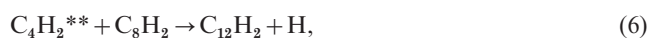
The diethynyl radical in its turn may react with other diacetylene molecules,



producing octatetrayne (C_8H_2).

The fate of $\text{C}_4\text{H}_2^{**}$ also involves many other possible reactions with other adventitious molecules that are present in the reaction environment such as methane (Glicker & Okabe 1987; Frost *et al.* 1995).

Polyynes could be formed from diacetylene through oligomerization reactions:



Triacetylene (hexatriyne) has been produced from the photolysis of diacetylene at 253.7 nm (Pontrelli 1965):



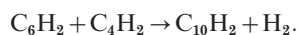
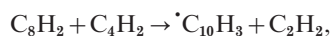
Such oligomerization reactions leading to long-chain polyynes have been proposed as the source of haze in Saturn's giant moon Titan (Smith *et al.* 1999).

Bandy *et al.* (1992, 1993) have shown that the gas-phase UV irradiation of diacetylene at wavelengths in the regions between 220 nm and 245 nm does not cause a direct photolysis but yields a metastable excited state C_4H_2^* . The formation of higher polyynes passes through the following reaction paths always involving the excited triplet state C_4H_2^* :



etc.

and as secondary reactions the following are, for instance, also reported (Bandy *et al.* 1992, 1993):



Thus, all the data suggests that under opportune UV irradiation conditions smaller polyynes like C_4H_2 or even acetylene can produce higher polyynes with oligomerization reactions which may or may not involve primary free-radical intermediates.

Heymann (2008) in his recent study on the UV photolysis of the pure polyne C_{10}H_2 has discovered that it is decomposed in part to C_8H_2 . The passage from C_{10}H_2 to C_8H_2 occurs through an excited state, which is a triplet state described as $\text{C}_{10}\text{H}_2^*$:

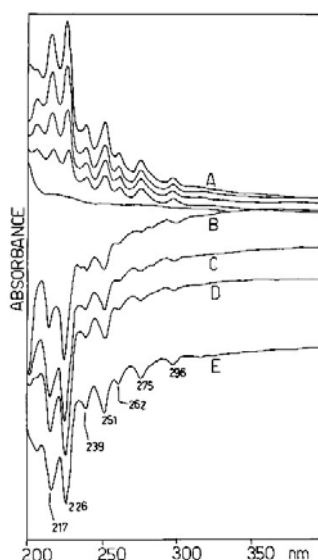
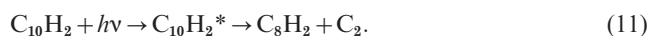


Fig. 1. Electronic absorption spectra in *n*-hexane of polyynes photolysed with a high-pressure mercury lamp under argon. A: All the spectra with peaks pointing upwards from top to bottom show the absorption spectra taken after 0, 26, 50, 75 and 160 min photolysis, respectively. B–E: All the spectra pointing downwards show the difference spectra (with respect to the pristine solution spectrum) after 0, 26, 50, 75 and 160 min photolysis.

Heymann (2008) has postulated that the molecular species C_2 is a secondary product of the photolysis and has proposed an interesting mechanism of terminal hydrogen migration to the 2,3 bond of C_{10}H_2 which leads to the 2,3 C–C bond breakage with formation of C_8H_2 . The hydrogen migration has been advocated to justify why only the formation of C_8H_2 has been observed (and not, for instance, also of C_6H_2). Such a hydrogen migration mechanism has also been advocated previously by Glicker & Okabe (1987) and by Pontrelli (1965).

Qualitative evidences of polyynes photolysis under argon

Cataldo (2004c, 2006b) in a couple of exploratory works was the first to show qualitatively that mixtures of polyynes or monocyanopolyynes are photolysed by UV photons. Figure 1A reproduces a series of electronic absorption spectra of polyne mixture from C_6H_2 to C_{14}H_2 in hexane taken at different intervals of irradiation time. A gradual reduction of the optical density of the solution as a function of the irradiation time can be observed. The difference spectra are shown in Figs 1B–1E with peaks pointing downwards. They represent the difference curves between the electronic absorption spectra of polyynes irradiated at any time and the spectrum of the starting, un-irradiated polyne solution. Also the difference spectra (which are shifted in the ordinate for clarity) show the clear trend of the polyynes disappearing under the action of the UV photons. In this case the light source employed in such an experiment was a medium- to high-pressure mercury lamp of 125 W emitting between 222 nm and 580 nm (see the experimental section). The

irradiation was always conducted under argon flow. In other words, argon was bubbled continuously through the polyynes solution during the UV irradiation to ensure the complete absence of oxygen in the reactor. In fact, the interference of oxygen from air in the polyynes photolysis was observed with a slowdown of the decomposition process (Cataldo 2004c, 2006b). However, Heymann (2008) has made a quantitative measurement of the oxygen effect on the photolysis of $C_{10}H_2$. He found that the presence of oxygen inhibits the $C_{10}H_2$ photolysis by three orders of magnitude in the pseudofirst-order kinetic rate constant. Such inhibition is due to the fact that the excited triple state $C_{10}H_2^*$ of reaction (11) derived from the UV photolysis is quenched by the presence of oxygen and therefore the subsequent reaction paths are hindered.

Quantitative measurement of the polyynes photolysis under argon

In order to obtain the kinetic rate constants of the polyynes photolysis, a series of UV irradiation experiments have been conducted in polyynes mixtures dissolved in three different solvents all transparent to UV radiation: hexane, heptane and decalin. As detailed in the experimental section, two UV lamps were employed: a powerful (125 W) medium- to high-pressure mercury lamp (main emission between 222 nm and 580 nm) and a low-pressure mercury lamp (12 W) with an almost monochromatic emission at 254 nm. To avoid any interference from oxygen all the irradiation experiments were conducted under continuous flow of argon gas into the reaction medium. After opportune intervals of time the lamps were switched off and a sample of the irradiated solution was analysed by HPLC. Figure 2 illustrates the case of the polyynes mixture irradiated in *n*-hexane with a low-pressure mercury lamp. The chromatogram at the top of Fig. 2 shows the peak due to C_8H_2 (identified from its electronic absorption spectra recorded by the diode array detector) with a retention time $R_t=1.89$ min. The UV irradiation reduced the intensity of the peak as shown in the chromatograms in the middle and at the bottom of Fig. 2. Thus, the molecular species associated with the peak is consumed and there is no evidence of the growth of other peaks. In each case the absorbance of C_8H_2 was measured in the electronic absorption spectrum associated with each chromatogram reported in Fig. 2 and recorded at the wavelength of 225 nm. The chromatograms recorded at 250 nm are reported in Fig. 3 and they show the peaks associated with the $C_{10}H_2$ and $C_{12}H_2$ polyynes with $R_t=2.59$ min and 3.71 min, respectively. Also in this case, the irradiation with a low-pressure mercury lamp under argon leads to the gradual disappearance of these two polyynes as testified by the change in the intensity of the peaks associated with these molecular species in the chromatograms of Fig. 3.

From each chromatogram it is possible to get the relative electronic absorption spectrum associated with each peak in the chromatogram and hence with each molecular species. From these spectra it is possible to follow the absorbance of each polyynes species after irradiation. If A_i is the

absorbance of a certain polyynes (for instance, C_8H_2) in hexane solution at a certain wavelength before irradiation and A_f the absorbance at the same wavelength at any time after irradiation, applying first-order kinetics (Yeremin 1979),

$$\ln(A_f/A_i) = kt, \quad (12)$$

which is the integrated form of the first-order reactions, where the speed of the reaction is dependent of the concentration of the reactant:

$$v = dC/dt = kC \quad (13)$$

since from the Lambert and Beer law the concentration C is linked to the absorbance A through two constants: the molar extinction coefficient and the light pathlength b ,

$$A_i = \epsilon b C_i \text{ and } A_f = \epsilon b C_f. \quad (14)$$

By integration of (13) we get

$$\ln(C_f/C_i) = kt \quad (15)$$

and by substituting Equation (14) into Equation (15), making the necessary simplifications, we get Equation (12). Thus, by plotting the quantity $\ln(A_f/A_i)$ against the time t (in s), from the slope of the graph we get the first-order rate constant k (in s^{-1}).

Figure 4 illustrates this operation for the data obtained from the photolysis of polyynes mixture in hexane under argon using a low-pressure mercury lamp as light source. It can be observed that the experimental data can be fitted by straight lines and from the slope of these lines the rate constants have been determined; these are reported in Table 1. The same procedure was also adopted for the treatment of the experimental data derived from the polyynes photolysis in heptane or in decalin using the medium- to high-pressure mercury lamp as light source; all the data are reported in Table 1.

Table 1 shows the kinetic rate constant of polyynes photolysis under different conditions. There are no significant differences between the constants measured in different solvents: *n*-hexane, *n*-heptane or decalin. In addition, there are no differences in the rate constants measured on polyynes prepared through the modified Glaser reaction and those prepared by carbon arc synthesis. It is known that the synthesis through the carbon arc produces numerous impurities and by-products such as carbon soot and mixtures of polycyclic aromatic hydrocarbons (Cataldo 2005b). The data in Table 1 shows that such impurities do not play any role in affecting the rate constant of polyynes photolysis.

Furthermore, the data in Table 1 demonstrates that there are no differences in the rate constant of polyynes photolysis by using a medium- to high-pressure mercury lamp of 125 W or a low-pressure mercury lamp of 12 W with almost monochromatic emission. The point is the energy of the photons involved; for the latter lamp the monochromatic photons at 254 nm have an energy of 112.7 kcal/mol while the most energetic photons emitted from the medium- to high-pressure lamp at 222 nm have an energy of 128.7 kcal/mol.

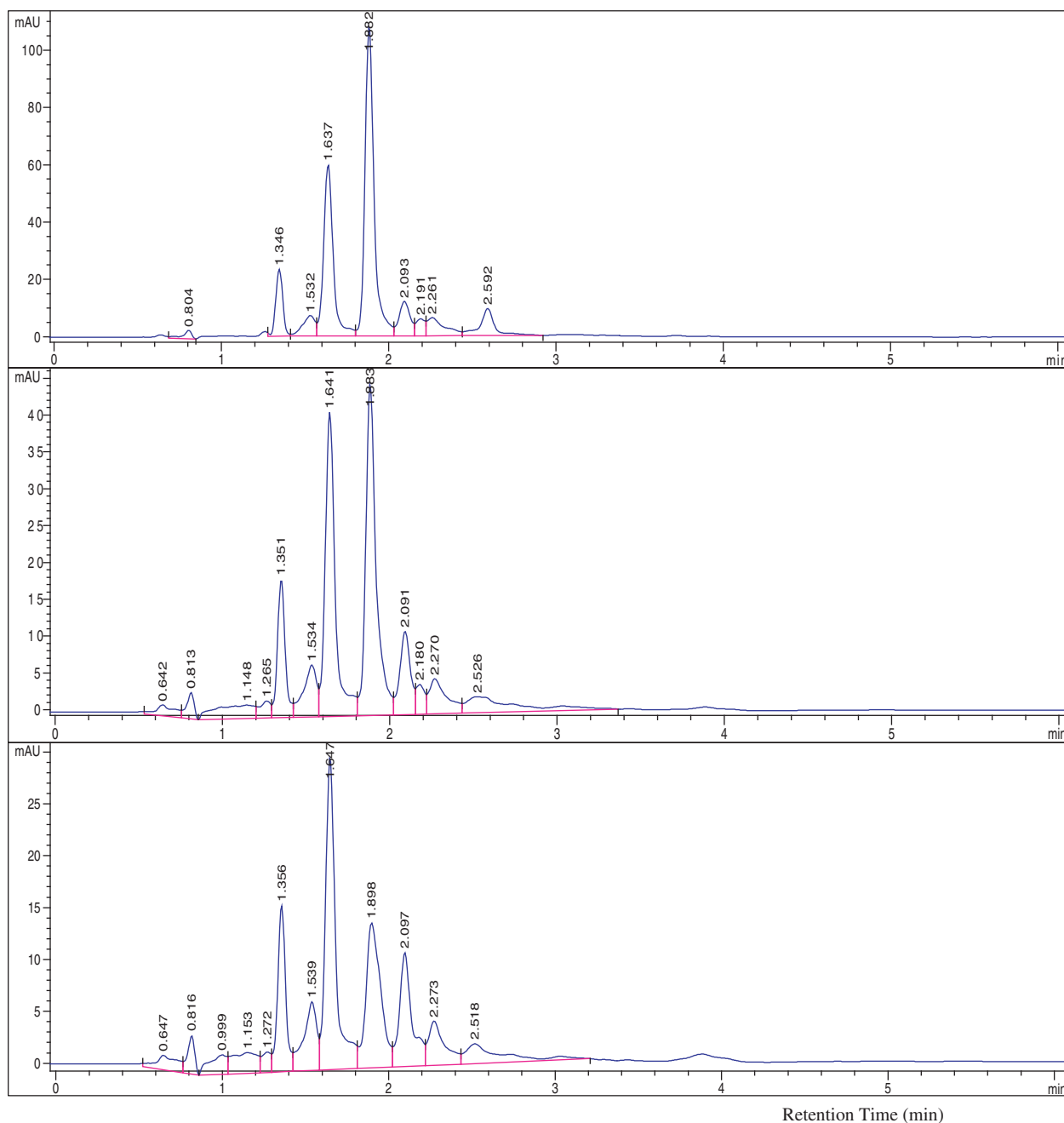


Fig. 2. HPL chromatograms recorded at 225 nm. From top to bottom are shown three chromatograms taken before photolysis, after 508 s photolysis and after 958 s photolysis respectively. The irradiation was conducted in *n*-hexane with a low-pressure mercury lamp under argon. The peak with a retention time of 1.898 is due to the polyne C₈H₂. The reduction of intensity as a function of the irradiation time can be observed. The other peaks are due to impurities and by-products of the polyne arc synthesis. On the ordinate axis the detector response in mAU = absorption units/10³ is reported.

The energies involved are not sufficient to break a C—C bond of an acetylenic chain whose energy is about 150 kcal/mol (Platner *et al.* 1995) and even the acetylenic $\equiv\text{C—H}$ bond whose energy is 128.7 kcal/mol (Shi & Ervin 2000). Therefore, both lamps generate a photon flux which is able only to excite to the triplet state the polyynes in solution, in line with the suggestion already made by Heymann (2008). From the excited state the polyynes undergo a fragmentation

reaction probably with the hydrogen shift to the 2,3 bond as proposed by Heymann (2008).

Figure 5 provides evidence for the fact that both the photons at 254 nm from the monochromatic light source or the photons from the continuous emission from 222 nm are able to photolyse simultaneously all polyynes in the mixture. In fact, the polyne overlapped spectra of Fig. 5 suggest that at the concentration employed in the photolysis experiments

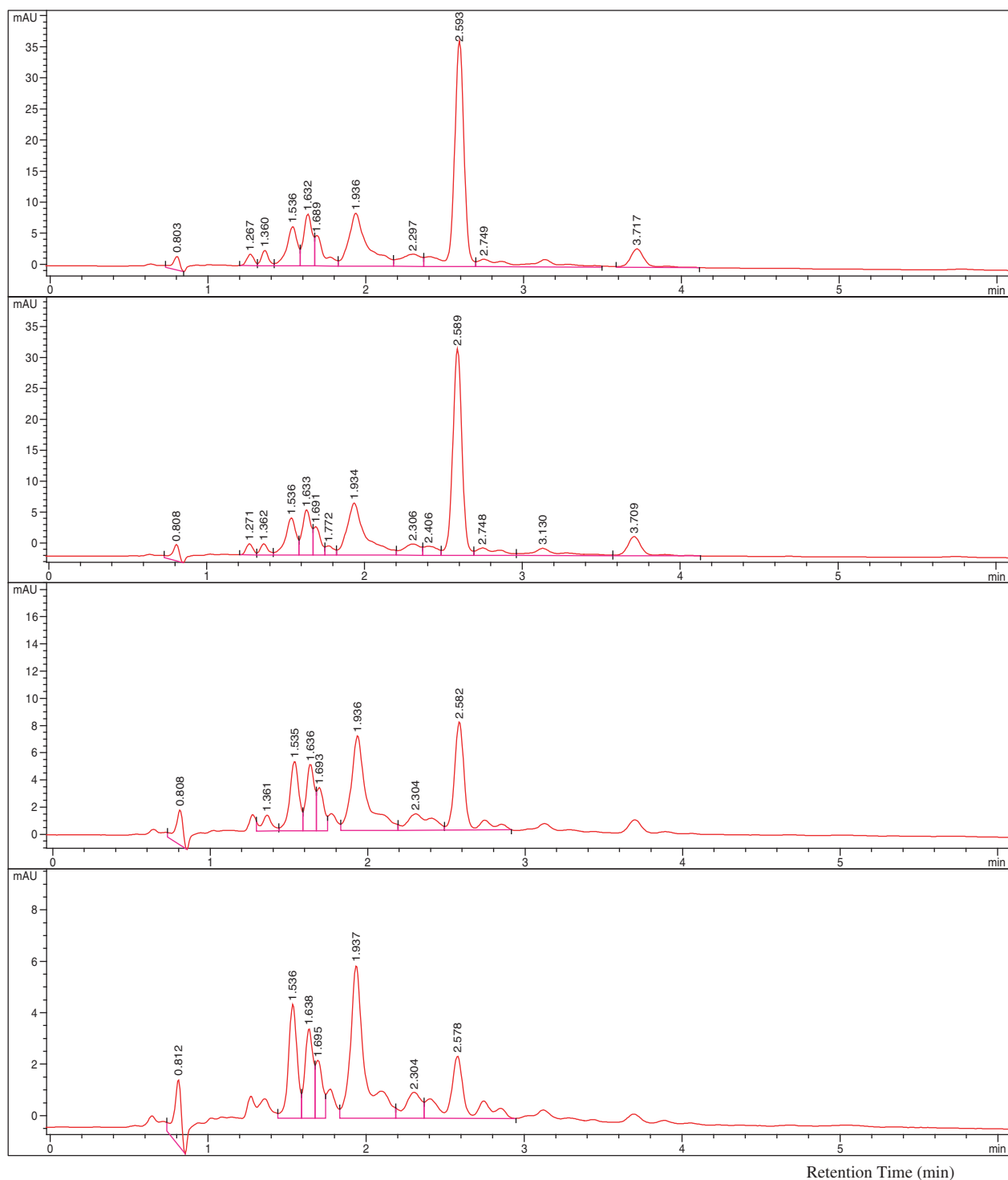


Fig. 3. HPL chromatograms recorded at 250 nm. From top to bottom are shown three chromatograms taken before photolysis, after 100 s, after 300 s and after 508 s photolysis, respectively. The irradiation was conducted in *n*-hexane with a low-pressure mercury lamp under argon. The peak with a retention time of 2.59 min is due to the polyne $C_{10}H_2$ and the peak at 3.71 min is due to $C_{12}H_2$. The reduction of intensity as a function of the irradiation time can be observed. The other peaks are due to impurities and by-products of the polyne arc synthesis. On the ordinate axis the detector response in mAU = absorption units/ 10^3 is reported.

all the polyynes from C_8H_2 to $C_{14}H_2$ are able to absorb photons and hence to be directly photolysed. Even the polyne C_6H_2 has secondary absorption bands at 254 nm (see Fig. 5 bottom) and in fact it is photolysed as well although

with a kinetic rate constant one order of magnitude smaller than the other polyynes (see Table 1).

The fact that the rate constant for the polyynes photolysis is almost similar for all the polyynes from C_8H_2 to $C_{14}H_2$

Table 1. Pseudofirst rate constants of polyynes photolysis (under argon)

| | C_6H_2 (s^{-1}) | C_8H_2 (s^{-1}) | $C_{10}H_2$ (s^{-1}) | $C_{12}H_2$ (s^{-1}) | $C_{14}H_2$ (s^{-1}) |
|--|--------------------------|--------------------------|-----------------------------|-----------------------------|-----------------------------|
| Hexane, argon, low-pressure mercury lamp | 3.23×10^{-4} | 2.42×10^{-3} | 5.52×10^{-3} | 4.42×10^{-3} | |
| Heptane, argon, low-pressure mercury lamp | | 2.09×10^{-3} | 3.74×10^{-3} | 2.61×10^{-3} | |
| Decalin, argon, high-pressure mercury lamp | | 5.16×10^{-3} | 4.57×10^{-3} | 1.87×10^{-3} | 4.62×10^{-3} |

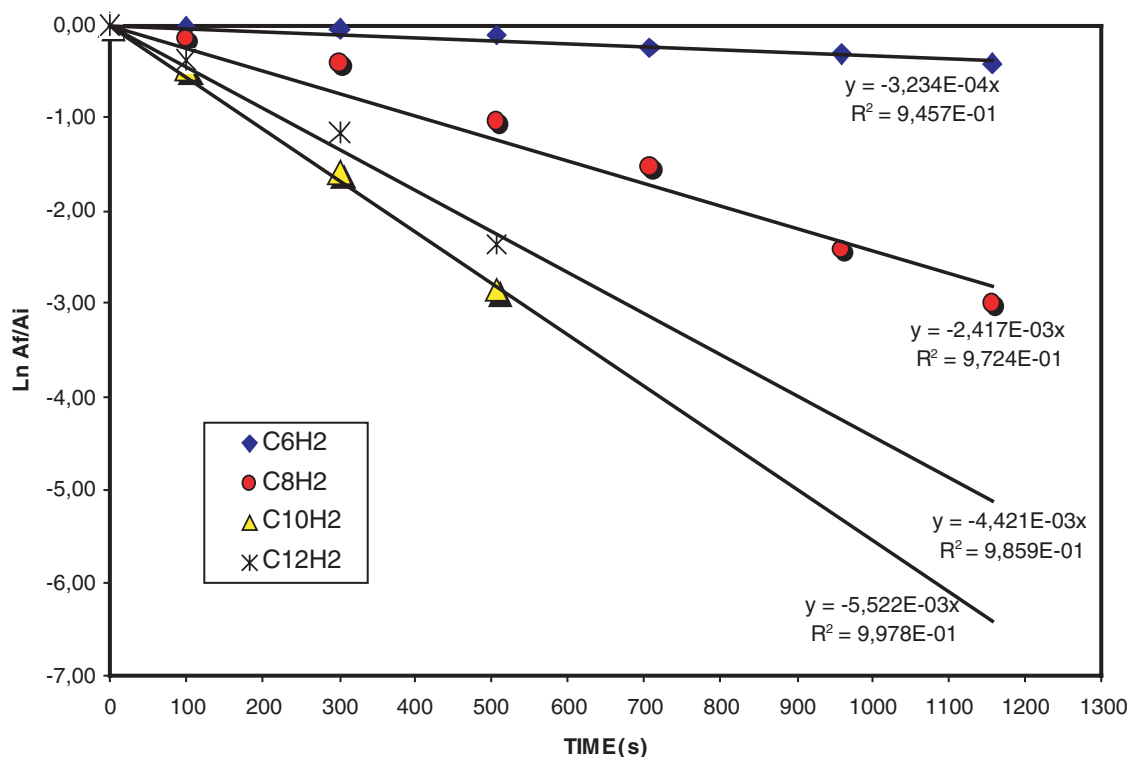


Fig. 4. Polyyne photolysis under argon flow in *n*-hexane. The data plotted in the graph are derived from the spectra recorded from the HPLC chromatogram. In this case the photolysis was conducted under the action of UV light from a low-pressure mercury lamp. The main emission was at 254 nm.

(see Table 1) implies that the reaction mechanism should be the same. In fact, a k value for all the polyynes considered of the order of $10^{-3} s^{-1}$ has been found. More precisely, the averaged data for polyyne species taken from Table 1 seems to suggest that both C_8H_2 and $C_{12}H_2$ are photolysed at the same rate constant of $\sim 3 \times 10^{-3} s^{-1}$ while $C_{10}H_2$ and $C_{14}H_2$ are photolysed at $\sim 4.6 \times 10^{-3} s^{-1}$.

Another important point to underline is the comparison of the rate constant found by Heymann (2008) in the photolysis of $C_{10}H_2$ in the absence of air and our results under argon: $k_{\text{Heymann}} = 6.37 \times 10^{-2} s^{-1}$ in comparison to an average value found in the present work (Table 1) $k_{C_{10}H_2} = 4.61 \times 10^{-3} s^{-1}$. There is a difference of one order of magnitude which could be attributed to the different experimental conditions and also to the different photon emission from the UV sources employed.

Concerning the kinetic rate constant, the polyyne photolysis can be described by first-order kinetics, but as stated by Heymann (2008): ‘Processes were either first order or pseudo

first order but second order processing could not be decisively ruled out’.

When the polyynes, for instance the C_8H_2 and $C_{10}H_2$, are photolysed to a certain extent, the peak in the HPLC chromatogram becomes less intense and broader. If the electronic spectra are taken across all the peaks from the beginning to the top of the peak to the end to the peak, a series of different spectra can be displayed as shown in Fig. 6, demonstrating the lack of homogeneity of the eluting species. Of course this phenomenon is not observed in the pure sample before the photolysis or at the beginning of the photolysis experiments. The spectra reported in Fig. 6 suggest for C_8H_2 and $C_{10}H_2$ that some of the photoproducts have retained the same molecular weight as the mother molecule but have a different chemical structure. This fact may also imply that some type of cyclization reaction or other rearrangements of the polyynes take place during the photolysis. This may be another pathway in competition to the fragmentation reaction already discussed.

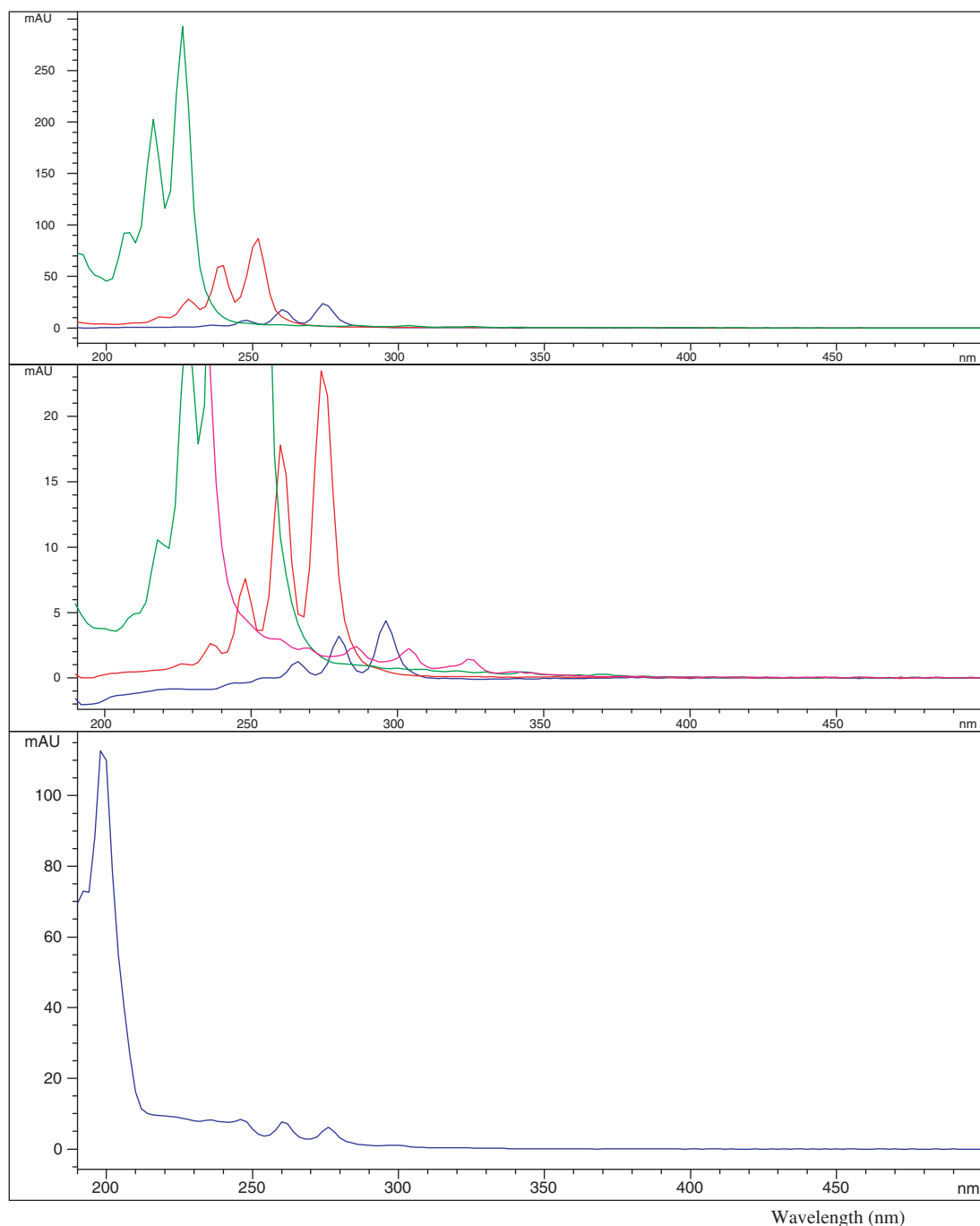


Fig. 5. Electronic absorption spectra of polyynes. Top figure (from left to right): C_8H_2 , $C_{10}H_2$ and $C_{12}H_2$. Middle figure (from left to right): zoom of the previous spectra showing the 'foot' of the C_8H_2 and $C_{10}H_2$ and the enlarged $C_{12}H_2$, as well as $C_{14}H_2$. Bottom figure: spectrum of C_6H_2 , triacetylene.

The polyynes formed with the carbon arc process are always accompanied by secondary products at two orders of magnitude lower concentrations (Cataldo 2005b). The main secondary products are naphthalene, acenaphthalene and acenaphthylene. It has been found that such molecules are completely photostable to the irradiation time needed to destroy the polyynes. This explains why the impurity peaks observed in the chromatograms reported in Figs 2 and 3 remain almost unchanged after the photolysis experiments.

Conclusions

The literature is relatively rich in reports of polyne formation from acetylene and diacetylene photolysis. Numerous mechanisms have also been proposed. Studies on the photolysis of acetylene and diacetylene have also been reported. Much less information is available about the UV photolysis of polyynes, especially long-chain polyynes which, until very recent times, were not easily accessible.

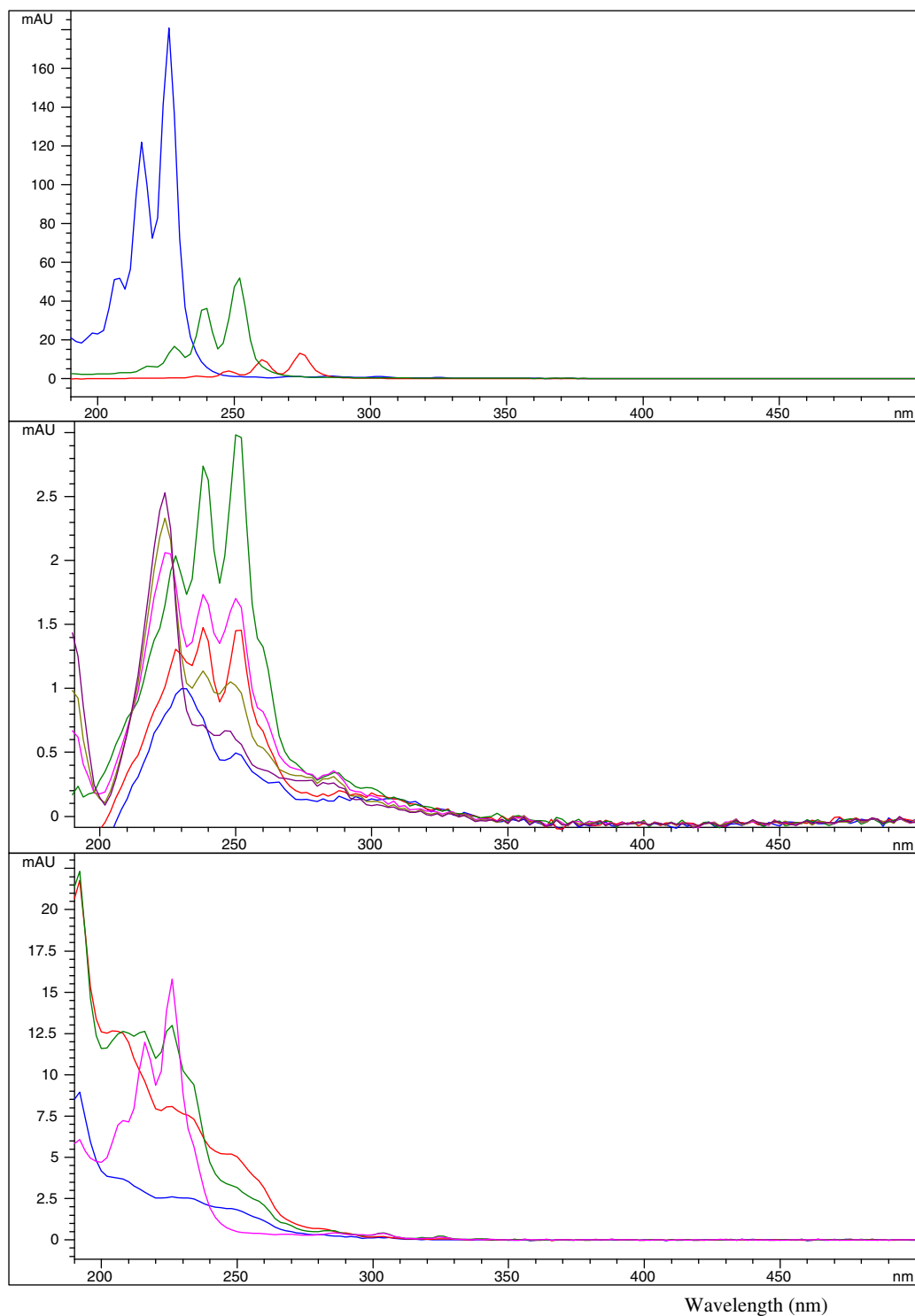


Fig. 6. Electronic absorption spectra of polyynes. The spectra at the top of the figure are due to C_8H_2 , $C_{10}H_2$ and $C_{12}H_2$ (from left to right) before photolysis. The series of spectra reported in the middle figure were taken after 508 s photolysis (with the low-pressure lamp) on the HPLC chromatogram peak eluting at 2.59 min which corresponds to $C_{10}H_2$ and its photolysis products. At this stage the products eluting are not uniform but are a mixture of different products. The series of spectra reported at the bottom of the figure were taken after 958 s photolysis on the HPLC chromatogram peak eluting at 1.898 min which corresponds to C_8H_2 and its photolysis products. Also in this case the products eluting are not uniform but are a mixture of different products.

Their easy synthesis with the submerged carbon arc method or by the modified Glaser reaction (Cataldo 2003, 2004b, 2005a, 2006b) has paved the way for new interesting

studies about the photostability of these molecules (Cataldo 2004c, 2006b; Cataldo and Keheyann 2006; Heymann 2008).

In the present work it has been found that mixtures of polyynes including C_6H_2 , C_8H_2 , $C_{10}H_2$, $C_{12}H_2$ and $C_{14}H_2$ can be easily photolysed under rigorously inert atmosphere both by a monochromatic light source at 254 nm or by a continuous UV source with $\lambda > 222$ nm to the visible.

The photolysis rate constant for all polyynes can be described by first- or pseudofirst-order kinetics. The values of the rate constant for each polyyne are affected neither by the nature of the solvent where the photolysis has been conducted (*n*-hexane, *n*-heptane and decalin have been used as inert solvents) nor by the type of light source employed.

Photolysis rate constant values in the range between $3.0 \times 10^{-3} \text{ s}^{-1}$ and $4.6 \times 10^{-3} \text{ s}^{-1}$ for all polyynes have been determined. The unique exception is represented by C_6H_2 which photolyses more slowly with $k = 3.2 \times 10^{-4} \text{ s}^{-1}$.

The presence of oxygen strongly inhibits the polyyne photolysis because it is able to quench the triplet state to which the polyynes are brought by the UV photons. This fact has been proposed by Heymann (2008) for the photolysis of $C_{10}H_2$ but it is fully extendable to all polyynes studied in the present work.

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