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A study on ethylene and acetylene photoligomerization and photopolymerization

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Abstract

It is shown that ethylene irradiated with UV light forms divinylacetylene, benzene and a liquid oligomeric aromatic–naphthenic hydrocarbon. A similar mixture of products is obtained by irradiating acetylene in cyclohexane, demonstrating that ethylene is initially photolyzed to acetylene and hydrogen during the early stages of irradiation.

The possible implications of these results to the atmospheric chemistry of the giant planets of the solar system as well as to the atmospheric and surface chemistry of Saturn's giant moon Titan are outlined.

Moreover, it is shown that ethylene photopolymerizes in water solution giving a solid photopolymer whose Fourier tansform IR spectrum and whose elemental analysis are in good agreement with the photopolymer obtained directly from acetylene in the same environment, demonstrating once again that ethylene is firstly photolyzed to acetylene and hydrogen.

It is proposed that divinylacetylene in cyclohexane is spontaneously isomerized to benzene since it is shown that this isomerization reaction is thermodynamically favored in the reaction conditions adopted.

Keywords: Photoligomerization; Photopolymerization; Irradiation

1. Introduction

Voyager missions within the solar system have revealed unexpected atmosphere, chemical composition and dynamics of the giant outer planets such as Jupiter, Saturn and Neptune [1–4]. Particular interest has been generated in the surprisingly rich atmosphere chemistry of Saturn's giant moon Titan [3,4]. In all these atmospheric systems, methane and its photoproducts ethylene, ethane and acetylene seem to play a crucial role in the production of more complex hydrocarbon molecules as well as in the generation of haze which is observable for example in the lower stratosphere of Jupiter [5] or Neptune [2]. Moreover a more complicated situation can be depicted for the Saturn's moon Titan where also acetylene and ethylene are formed from methane photolysis and radiolysis under the action of solar UV radiation and cosmic rays respectively [3]. By further photolysis and radiolysis, ethylene and acetylene interact with Titan's other atmospheric components containing nitrogen atoms to give an orange solid with an undefined structure called tholin [3]. It is believed that tholin is responsible for the colour of Titan because it remains suspended in the atmosphere as an aerosol and also stratifies on the surface of this satellite or under its oceans of liquid ethane–methane [3]. Tholin has also been reproduced in laboratory simulations of Titan's atmosphere and surprisingly, upon hydrolysis, it gives a mixture of aminoacids [3,6,7] with possibly important implications about the prebiological formation of the constituents of DNA.

In addition to all the above observations, acetylene, ethylene and methane seem to be ubiquitous in the Universe since they have been detected in the molecular clouds in interstellar spaces and near certain stars together with other molecules [8].

Despite this renewed interest in ethylene and acetylene photochemistry, we can find in the literature a relatively abundant number of studies [9–27] in this field, many of them dating back to the early decades of this century [9–19] and dealing mainly with gas-phase photolysis and radiolysis of these molecules.

In a previous paper [28] we have studied acetylene photopolymerization in aqueous solution and have shown that the photopolymer has the same structure as a linear polyenic polyacetylene obtained over Rh(I) catalyst [29,30] and aged in humid air.

In this paper we studied ethylene photopolymerization in water solution and photoligomerization in cyclohexane solution and we shall show that the products obtained are the same as obtainable from acetylene photopolymerization and

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photoligomerization in the same solvents, demonstrating that ethylene is transformed into acetylene under the conditions adopted in the present study.

2. Experimental details

Ethylene was obtained from Aldrich (purity, 99.5+%), water was doubly distilled grade and all solvents were analytical grades from Aldrich or Fluka. Acetylene was purified as previously described [29,30] after passing into a KOH solution of pyrogallol. Perdeuteroacetylene was obtained by dissolving calcium carbide in heavy water (from Aldrich) and purifying the gas as mentioned above.

The aqueous ethylene or acetylene solutions in water and in cyclohexane were irradiated by a high pressure mercury lamp Helios Italquartz model GR.E.125 W in a water-cooled reactor of fused quartz, at room temperature.

For spectroscopic study of photoproducts, use was made of a UV–visible–near-IR spectrophotometer Shimadzu A160 while for the Fourier transform IR (FTIR) spectra a Perkin–Elmer 1710 instrument was used.

Elemental analysis on a solid photopolymer were performed at the Istituto di Chimica Farmaceutica, University of Pisa.

2.1. Ethylene photo-oligomerization in cyclohexane

250 ml of cyclohexane were saturated with a stream of ethylene by bubbling this gas into the reactor charged with the solvent. Saturation was supposed to be complete after 15 min of ethylene bubbling. The reactor was sealed without any use of silicone-based grease or other types of grease to avoid any contamination. Light irradiation was conducted for 23 h and a slight overpressure was noticed; it was discharged every hour at the beginning of irradiation. Then the reaction mixture was saturated again with ethylene and irradiated for an additional 15 h.

The mixture was then distilled at atmospheric pressure; it boiled in the range 77–90 °C and was subdivided into five fractions. Each fraction was studied by UV spectroscopy as shown in Fig. 1.

The distillation residue consisted of a yellow oil with a mild fatty smell (yield, 0.42 ml) and was studied by FTIR spectroscopy.

2.2. Acetylene photo-oligomerization in cyclohexane

2.2.1. Run 1

250 ml of cyclohexane were saturated with a stream of acetylene and the solution was irradiated with the UV lamp. No glass joints was treated with any grease to avoid contaminations. With a peristaltic pump the irradiated solution was pumped through Teflon tubing into a quartz flow cell, and periodically the spectra of the reaction mixture were recorded as reported in Fig. 2 to follow the early stages of reaction.

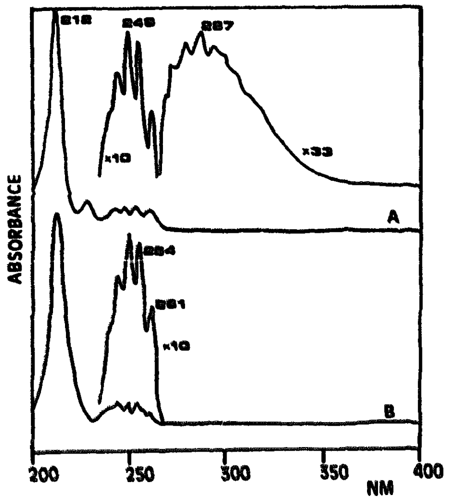

Fig. 1. Electronic spectrum (curve A) of distillation head of ethylene in cyclohexane after irradiation for 38 h (divinylacetylene concentration, approximately 1.9×10^{-6} mol l^{-1}; benzene concentration, approximately 3.4×10^{-4} mol l^{-1}) together with bulk distillation fraction (curve B) (benzene concentration, approximately 5.0×10^{-4} mol l^{-1}).

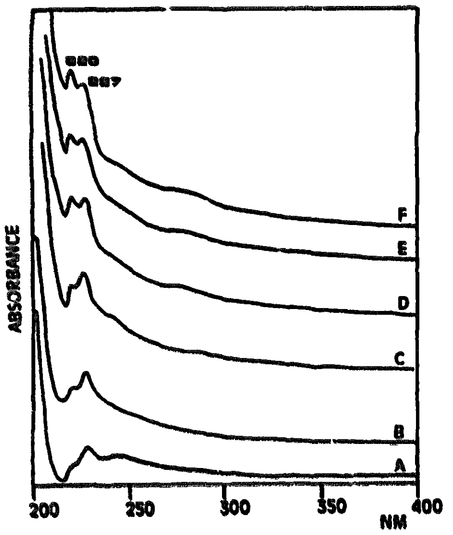

Fig. 2. Electronic spectrum of acetylene irradiated in cyclohexane for various irradiation times: curve A, 30 min; curve B, 60 min; curve C, 90 min; curve D, 120 min; curve E, 150 min; curve F, 180 min (vinylacetylene concentration for F, approximately 6.5×10^{-5} mol l^{-1}).

2.2.2. Run 2

250 ml of cyclohexane were saturated with a stream of acetylene, and the sealed reaction mixture prepared as described above (without using any grease for the glass joints) was irradiated for 32 h. No overpressure was noticed during the irradiation period. The reaction mixture was distilled as described above and also here the distillate (boiling point (b.p.), 72–80 °C) was divided into five subsequent fractions and studied by UV spectroscopy (Fig. 3). The light-yellow oily residue (yield, about 1.0 ml) had a mild fatty smell and was studied by FTIR spectroscopy.

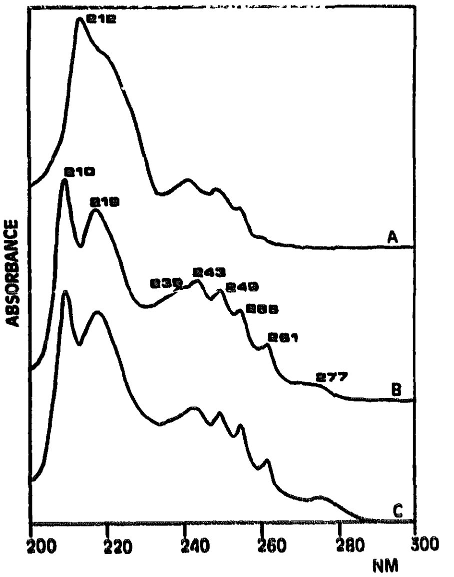

Fig. 3. Electronic spectrum of acetylene irradiated in cyclohexane for 32 h: curve A, crude reaction mixture; curves B and C, two consecutive distillation fractions (vinylacetylene concentration, approximately 4.2×10^{-4} mol l^{-1}; benzene concentration, approximately 2.0×10^{-3} mol l^{-1}; divinylacetylene concentration, 3.3×10^{-6} mol l^{-1}.

2.3. Perdeuteroacetylene photoligomerization in cyclohexane

250 ml of cyclohexane were saturated with $CD\equiv CD$ obtained by dissolving calcium carbide in heavy water and purifying the gas as described above for acetylene. The sealed reactor (without greased joints) was irradiated for 32 h. The resulting reaction mixture was fractionated by distillation at ambient pressure (b.p., 72–80 °C) and the UV spectrum of each fraction was recorded and appeared completely analogous to those reported in Fig. 3. The yellow oily residue was studied by FTIR spectroscopy.

2.4. Ethylene photopolymerization in aqueous solution

Ethylene was bubbled into 200 ml of doubly distilled water for 15 min. After this treatment, water was completely saturated with this gas and all air displaced. The solution was irradiated for 8 h and after 1.5 h it started to appear opalescent. Then ethylene was bubbled again into the reaction mixture for 15 min and light irradiation was prolonged for an additional 8 h. The white mixture was left for 2 days, and a large part of the photopolymer precipitated at the bottom of the reactor and was collected by filtration. An additional amount of photopolymer was scratched from the sheath of the lamp. The yield was 0.018 g. The polymer was yellow-brownish; it did not melt or soften up to 270 °C. Elemental analysis: C, 77.10; H, 11.51; O, 11.39% (as difference). FTIR bands are reported in Table 1.

Table 1
IR bands of solid photopolymers obtained in water medium

IR (cm^{-1})		Assignment [28]
Acetylene photopolymer [28]	Ethylene photopolymer (this work)	
3450 vs	3450 s	-OH stretching
2964 vs	2960 vs	Methyl, C–H stretching
2935 vs	2930 vs	Methylene, C–H stretching
2875 vs	2880 vs	Methyl, C–H stretching
1712 s	1710 s	Isolated, C=O stretching
1645 sh	1645 sh	α,β unsaturated, C=O stretching
1460 m	1460 ms	Band due to methyls and methylene
1381 m	1380 ms	Band due to methyls and methylene
1265 m	1260 m	Band due to methyls and methylene
	1240 sh	
1150 sh	1150 bd	C–O due to alcohol, ethers
1100 ms		C–O due to alcohol, ethers
1032 m		
987 sh	980 mw	Residual =C–H bending?
922 w	920 w	
870 vw		
804 m	805 w	
600 bd	600 vw	
	570 vw	
509 w	540 vw	

vw, very weak; w, weak; m, medium; s, strong; vs, very strong; sh, shoulder; bd, broad.

2.5. Acetylene photopolymerization in aqueous solution

The same procedure adopted above was used to prepare the solid photopolymer. For more details see [28].

2.6. Synthesis of reference vinylacetylene and divinylacetylene

For the synthesis of these two acetylenic compounds use, was made of a Nieuwland catalyst. It was prepared by heating at 80 °C for 24 h the following mixture in a tightly closed flask, under stirring: 15.0 g of CuCl, 10.0 g at ammonium chloride, 1.5 g of copper powder, 1.0 ml of HCl (37%) and 10 ml of distilled water. After this treatment the mixture became dark brown and viscous. It was cooled at 30 °C and then a stream of purified acetylene (free from oxygen) was bubbled into the mixture and the gas coming out from the flask was bubbled in a Drechsell flask containing cyclohexane. In this way the vinylacetylene formed was trapped in a cyclohexane solution and the spectrum of this molecule is reported in Fig. 4, curve A.

The Nieuwland catalyst after treatment with acetylene was then stored at room temperature for 4 days and in another run for 1 month. After the above-mentioned intervals of time the

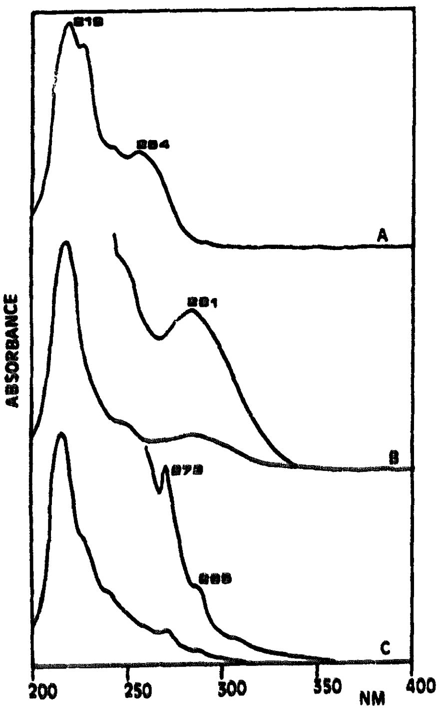

Fig. 4. Electronic spectra: curve A, vinylacetylene in cyclohexane; curve B, mainly *cis* divinylacetylene in cyclohexane after storage for 4 months over Nieuwland's catalyst; curve C, a mixture of *cis* and *trans* divinylacetylene in cyclohexane after storage for 4 days over Nieuwland's catalyst.

catalyst was extracted with cyclohexane and the spectra of divinylacetylene are reported in Fig. 4, curve B (storage for 1 month) and Fig. 4, curve C (storage for 4 days).

3. Results and discussion

3.1. General and thermodynamic observations

It has been known for a long time that under α particle irradiation in gas phase, ethylene undergoes decomposition to methane, hydrogen and a liquid hydrocarbon mixture with a turpentine-like odor [19]. It was also shown that, by irradiation with fast electrons or γ rays, ethylene is converted into acetylene and several other hydrocarbons such as methane, ethane, propane, 1-butene and hydrogen [19]. This was experimentally demonstrated notwithstanding thermodynamically (estimation of free energy of each reaction of Scheme 1 was calculated at 298 K according to Van Krevelen's [31] calculation procedure) the dehydrogenation of ethylene to acetylene is unfavoured (Scheme 1, reaction (1)). However, we should consider that acetylene, once formed in trace amount from ethylene, will be in equilibrium with the parent molecule but it is subtracted from this equilibrium by further photolysis to form another product as we shall show later so that other new molecules of ethylene should undergo transformation to acetylene to restore the original equilibrium. This explains why ethylene under UV irradiation in cyclohexane yields benzene and divinylacetylene as we show in Fig. 1, since acetylene under UV irradiation in solution reacts immediately to give vinylacetylene, benzene and divinylacetylene (see Figs. 2 and Fig. 3). Our results are in agreement with previous work on UV photolysis of acetylene in gas phase, where the same products were detected by mass spectrometry of the gas mixture [18] together with hydrogen and diacetylene which we have not detected. In fact, from a thermodynamic standpoint, dimerization of acetylene to diacetylene (1,4-butadiyne) is less favored than the dimerization to vinylacetylene (Scheme 1), reaction (2) vs. reaction (3)) and vinylacetylene once formed can react easily with another acetylene molecule to form divinylacetylene (Scheme 1, reaction (4)). Divinylacetylene formation from three acetylene molecules thermodynamically is also more favored than the trimerization to triacetylene (1,3,5-esatriyne) (Scheme 1, reaction (5) vs. reaction (6)). The isomerization of divinylacetylene to benzene is also a spontaneous reaction based on the free energy of reaction (Scheme 1, reaction (7)) and also the acetylene trimerization to benzene (Scheme 1, reaction (8)). As we

$$\mathrm{CH_2{=}CH_2 \longrightarrow CH{\equiv}CH + H_2} \qquad \Delta G_f^\circ = +33.83\ \mathrm{kcal\ mol^{-1}} \tag{1}$$

$$\mathrm{2CH{\equiv}CH \longrightarrow CH{\equiv}C{-}C{\equiv}CH + H_2} \qquad \Delta G_f^\circ = +1.56\ \mathrm{kcal\ mol^{-1}} \tag{2}$$

$$\mathrm{2CH{\equiv}CH \longrightarrow CH{\equiv}C{-}CH{=}CH_2} \qquad \Delta G_f^\circ = -35.45\ \mathrm{kcal\ mol^{-1}} \tag{3}$$

$$\mathrm{CH{\equiv}CH + CH{\equiv}C{-}CH{=}CH_2 \longrightarrow CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2} \qquad \Delta G_f^\circ = -27.93\ \mathrm{kcal\ mol^{-1}} \tag{4}$$

$$\mathrm{3CH{\equiv}CH \longrightarrow CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2} \qquad \Delta G_f^\circ = -63.38\ \mathrm{kcal\ mol^{-1}} \tag{5}$$

$$\mathrm{3CH{\equiv}CH \longrightarrow CH{\equiv}C{-}C{\equiv}C{-}C{\equiv}CH + 2H_2} \qquad \Delta G_f^\circ = -4.86\ \mathrm{kcal\ mol^{-1}} \tag{6}$$

$$\mathrm{CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2 \longrightarrow benzene} \qquad \Delta G_f^\circ = -54.89\ \mathrm{kcal\ mol^{-1}} \tag{7}$$

$$\mathrm{3CH{\equiv}CH \longrightarrow benzene} \qquad \Delta G_f^\circ = -118.25\ \mathrm{kcal\ mol^{-1}} \tag{8}$$

$$\mathrm{3CH_2{=}CH_2 \longrightarrow benzene + 3H_2} \qquad \Delta G_f^\circ = -16.76\ \mathrm{kcal\ mol^{-1}} \tag{9}$$

$$\mathrm{2CH_2{=}CH_2 + CH{\equiv}CH \longrightarrow CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2 + 2H_2} \qquad \Delta G_f^\circ = +4.28\ \mathrm{kcal\ mol^{-1}} \tag{10}$$

Scheme 1. Scheme calculated according to Ref. [31].

show in Scheme 1, reaction (9), even the direct trimerization of ethylene to benzene with the liberation of hydrogen seems to be thermodynamically allowed. However, since we observe the formation of vinylacetylene and divinylacetylene during ethylene irradiation, it seems clear that the real intermediate to benzene from ethylene is acetylene which is formed from the latter molecule. On the contrary, the condensation reaction of two ethylene molecules with one of acetylene is more close to an equilibrium reaction and in this case, if we subtract from the equilibrium divinylacetylene because of its isomerization to benzene and/or its polymerization, the reagent molecules will be consumed (Scheme 1, reaction (10)).

3.2. Discussion of UV spectra

In Fig. 4, curve A, we have recorded for reference the spectrum of vinylacetylene. The absorption spectrum of this molecule is characterized by a maximum at 219 nm ($\epsilon \approx 6400$) with an inflection at about 228 nm and another weak maximum at 254 nm. Our data are in good agreement with previous work [32] but we observe also the weaker maximum at 254 nm not reported previously. The formation of vinylacetylene is clearly shown in Fig. 2 during early stages of acetylene photolysis in cyclohexane by the two bands growing in intensity at 220 and 227 nm. Also the distillation fractions collected after acetylene photolysis for 32 h in cyclohexane shows relatively large amounts of vinylacetylene (Fig. 3). Vinylacetylene is present in the distillation fractions of ethylene in cyclohexane after irradiation for 38 h (band at 212 nm in Fig. 1), confirming that in our conditions ethylene is photolyzed to acetylene which immediately reacts to form vinylacetylene.

In Fig. 4, curves B and C, we have reported also the spectra of divinylacetylene which is composed of two isomers. The *cis* isomer absorbs at 281–285 nm while the peak at 273 nm can be assigned to the *trans* isomer. These assignments have been made in analogy with the absorption band position of *cis* and *trans* hexatriene since a certain analogy between the spectra of conjugated polyenes and eneynes is known [32]. If we look at the spectrum in Fig. 1, curve A, we can see that divinylacetylene is present in a low concentration in the early distillation fraction (heads) of ethylene in cyclohexane after irradiation for 38 h, but it is no longer present in the following fractions (Fig. 1, curve B).

A weak and broad maximum is also visible at about 275–280 nm in Fig. 2 produced by acetylene irradiation for 1–3 h. Acetylene irradiated for 43 h shows a neat maximum at 277–280 nm (Fig. 3, curves B and C).

The most ubiquitous product is benzene which is present with its characteristic band pattern both in photolyzed ethylene (Fig. 1) and in photolyzed acetylene (Fig. 2). The band pattern is fully in agreement with literature data [32]: 234 nm ($\epsilon = 32$), 239 nm ($\epsilon = 50$), 244 nm ($\epsilon = 100$), 240 nm ($\epsilon = 178$), 255 nm ($\epsilon = 230$) and 261 nm ($\epsilon = 158$). The formation of benzene from acetylene photolysis is very interesting from the standpoint of abiogenic synthesis of aminoacids, since tyrosine and phenylalanine contain aromatic rings whose "inorganic" source should be acetylene derived from methane and ethylene.

Polyynes such as diacetylene and triacetylene have not been detected in our reaction mixture since they should show respectively a characteristic maximum at 640 and 665 nm [33] which were not present in our spectra. This is in line with our thermodynamic calculations of the previous section, confirming that in our conditions acetylene shows a trend to self-condensate without liberation of free hydrogen (Scheme 1, reactions (3)–(5)) as it is required by the formation of free polyynes (Scheme 1, reactions (2) and (6)). However, this is not in contrast with other results of acetylene photolysis at 195 or 185 nm in the gas phase [18,26] where diacetylene was present together with all the other products that we observed in the present work performed using an UV radiation source with $\lambda \geqslant 200$ nm. Moreover other investigators [27] have shown that diacetylene undergoes other photolysis reactions with decomposition of the molecule.

3.3. Discussion of Fourier transform IR spectra

The yellow oily liquid obtained after having distilled off all cyclohexane from the reaction mixture obtained after ethylene or acetylene irradiation shows a turpentine fatty smell and its FTIR spectrum shows few absorption bands which indicate that the product is an aromatic–naphthenic oligomeric product probably formed by cyclization of the original intermediates that we have detected by UV spectroscopy in the previous section. Namely, both the FTIR spectrum of ethylene and acetylene oily photoproducts show a band at 3084 cm^{-1} owing to aromatic C–H stretching, two bands at 2932 and 2856 cm^{-1} which are due to aliphatic and/or naphthenic C–H stretching. These bands are shifted at 2225 and 2174 cm^{-1} in the perdeuteroacetylene oily photoproduct; the shifting is caused by the C–D stretching. Other bands observed at 1650, 1455, 1380, 1265, 1100, 1035, 806 and 680 cm^{-1} confirm the nature of the oligomeric products as aromatic–naphthenic. For reference, the most important absorption bands of benzene lie respectively at 3080, 1455, 1035 and 680 cm^{-1}. Some oxidation due to the presence of trace of oxygen cannot be excluded.

Once again these data show that the final product of acetylene and ethylene photopolymerization in cyclohexane lead to the same final mixture of products.

In previous work [28], we have shown that, when acetylene is photopolymerized in water solution, several intermediate are formed such as vinylacetylene, divinylacetylene and probably also diacetylene but the final product was a whitish solid material having the structure of an oxidized linear polyacetylene. In fact we showed that the FTIR spectrum of that photopolymer was fully comparable with that of an oxidized linear polyacetylene (with polyenic structure) obtained over Rh(I) catalyst [29,30]. In that case the early acetylene condensation products showed a tendency to form a linear polyenic polyacetylene which, by interaction with water, picked up oxygen. Elemental analysis showed that the empirical formulae assignable to acetylene photopolymer in water ranged from $(C_5H_7O)_x$ to $(C_6H_8O)_x$, indicating that approximately one water molecule is added for every two to three acetylene molecules [28]. Since no benzene formation was detected, we can hypothesize that a highly polar reaction medium (such as water) favors the formation of a linear polymer and the solvent itself reacts with the organic substrate. In the case of photopolymerization in cyclohexane (an apolar medium), apparently there is no interaction with the solvent and the formation of cyclic oligomers and benzene is favored.

In this work, as described in the experimental section we have tried to photopolymerize ethylene dissolved in water. As we show in Table 1, the photopolymer obtained from ethylene has the same FT-IR spectrum and hence seems to have the same structure of acetylene photopolymer obtained in the same conditions and hence it is an oxidized and crosslinked polyenic–polyacetylene. This point of view can be confirmed by elemental analysis which shows that the empirical formula of photopolymer obtained from ethylene is $(C_6H_{11}O)_x$. This empirical formula is in close agreement with those reported for acetylene photopolymer in water [28], but it is slightly more hydrogenated. On the basis of this formula, we may say that, on average, three molecules of acetylene, one molecule of hydrogen and one molecule of water reacted to produce the monomeric unit of the photopolymer. Also these experimental data indicate that ethylene is photolyzed to acetylene with liberation of hydrogen followed by condensation reaction of acetylene to yield the photopolymer. Experimentally we observed the liberation of hydrogen during ethylene irradiation by noticing the increase in the pressure inside the reactor (both in water and in cyclohexane medium). This was not observed during acetylene irradiation under the same conditions.

4. Conclusions

Ethylene irradiated in cyclohexane solution by a UV lamp with $\lambda \geqslant 200$ nm is decomposed to acetylene and hydrogen. This decomposition was essentially observed by the formation of divinylacetylene and benzene in the irradiated cyclohexane solution as well as the formation of an oily liquid aromatic–naphthenic hydrocarbon oligomer. We have shown that all these products are also formed when acetylene is irradiated with UV light in cyclohexane solution, confirming that ethylene is photochemically decomposed to acetylene and hydrogen.

We have proposed that benzene is formed by spontaneous isomerization of divinylacetylene since this reaction is thermodynamically favored at room temperature and at low temperatures.

Another study on ethylene photopolymerization was conducted in water solution. Also in this case ethylene gives a solid photopolymer whose FTIR spectrum and whose elemental analysis are in good agreement with the FTIR spectrum and elemental analysis of the solid photopolymer obtained by direct irradiation of acetylene in water.

Applying these conclusions to the extraterrestrial atmospheric chemistry, we could suggest that ethylene could be a source of acetylene in all giant planets of the solar system. Acetylene should be a source of benzene, vinylacetylene and divinylacetylene and the haze [2,5] observed in the atmosphere of these planets could be attributed to photopolymerization and/or photo-oligomerization of vinylacetylene and divinylacetylene with other chemical species present in the atmosphere of these planets.

A separate speech should be applied to Saturn's moon Titan. If its surface is partially covered by liquid methane–ethane oceans, acetylene and/or its precursor ethylene should be dissolved in these oceans so that we can expect that under photolysis and radiolysis there should be formation of benzene, vinylacetylene and divinylacetylene in these environments.

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