

ELECTRON-PROTON AND ELECTRON-METHYL EXCHANGES IN PYROLYSIS OF POLYACETYLENE AND POLYMETHYL ACETYLENE

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Abstract. - Pyrolysis of polyacetylene is marked by high yields of proton enriched products methane, ethane, ethylene, propane, propylene, butadiene, cyclopentadiene, cyclopentene and toluene in total amounts exceeding benzene. The activation energies for their formation are low. Polyacetylene doped with AsF_5 and iodine to conductive regime produced these pyrolyzates even in higher yields of 2 to 17 times of undoped polymers. The dominant mechanism is proposed to be random chain scission followed by electron-proton exchange reactions. Polymethylacetylene is thermally less stable than polyacetylene. Pyrolysis gave mesitylene as the expected main product. However, like in the case of polyacetylene, large amounts of proton enriched products were formed with moderate activation energies. The yields of methane, ethylene and ethane are nearly the same in the pyrolysis of polymethylacetylene as compared to that of polyacetylene at 923 K referenced to mesitylene and benzene, respectively. By analogy, mechanisms involving both electron-proton and electron-methyl exchange reactions were proposed to account for the formation of all the pyrolyzates of polymethylacetylene. These reactions, not observed in the pyrolysis of other polymers such as polypropylene and polyisoprene, are attributable to the conjugated backbone permitting facile migrations of electrons, protons and methyl groups.

INTRODUCTION

Polyacetylene, the simplest conjugated organic polymer, is a wide band direct gap semiconductor. Upon doping with oxidizing or reducing agents, its conductivity is increased more than twelve orders of magnitude comparable to mercury (1,2). Polymethylacetylene, the lowest alkyl derivative of polyacetylene, is an insulator. Doping converts polymethylacetylene to a semiconductor (3). There are overwhelming evidences that unpaired spins in polyacetylene is highly diffusive and the charged carriers have significant mobility (4). A brief study of the thermal stability of polyacetylene (5) has been reported identifying benzene as the major product and small amounts of hydrogen, ethane, ethylene, propylene, and butane as minor products at 598 K. Brown-colored high-boiling products were not characterized. Pyrolysis gas chromatography (PGC) has become a very useful tool for the elucidation of the detailed structure, thermal stability, and degradation mechanisms of polymers (6-12). In our laboratory, we have an integrated Pyrolysis Gas Chromatography Mass Spectrometry Peak Identification System (PGC-MS) (13). It has been used to study the kinetics and mechanisms of thermal and oxidative degradation of polypropylene (14,15) and polyisoprene (16,17) and their transition-metal-containing derivatives (18,19) to elucidate new flame retardation mechanisms. PGC-MS results on polyacetylene are consistent with facile electron-proton exchange processes requiring only low energies of activation. Studies on doped polyacetylenes showed the exchange reactions to be accelerated in the metallic conducting states. The products of pyrolysis of polymethylacetylene were identified and the rates of their formation obtained. The results showed that electron-methyl exchange processes also occur with relative ease. The yields of methane and ethane are nearly the same for the pyrolysis of polymethylacetylene and polyacetylene at the same temperature. The yield of benzene from pyrolysis of polymethylacetylene is less than 1% thus eliminating hydrogen abstraction by CH_3 , CH_2 , or CH fragments and their combination reactions as probable sources for the proton enriched products.

EXPERIMENTAL

Polyacetylene films were synthesized according to the method of Ito et al. (20). It has a number average molecular weight of ca. 11,000 as determined by radioquenching with tritiated methanol (21). Polymethylacetylene was synthesized by the procedure of Chien et al. (22), the polymer has \bar{M}_n ranging from 5,000 to 9,000.

Thermogravimetric analysis (TGA) at a helium flow rate of 40 mL/min and a heating rate of 3°C/min was performed with a duPont 900 thermal analyzer. This experiment provided informa-

tion on the temperature range over which degradation occurred. The pyrolysis experiments were carried out using a Chemical Data Systems Pyroprobe 100 instrument. A weighed solid polymer sample was placed in a quartz tube (25 mm x 2 mm i.d.) which was then inserted into a heated interface connected to a gas chromatograph. The sample was heated to a final temperature limit preset at a value up to 1000°C. The probe heating rate and the duration of pyrolysis were preset and were highly reproducible. Since the pyroprobe was interfaced directly to the chromatograph, trapping of the pyrolyzates and reinjection was not needed. The gas chromatograph was a Varian Instruments model 3700 with an injection needle insert adapted for the pyrolysis unit. Two columns were used to separate the pyrolyzates. A Chromosorb 102 porous polymer column (60/80 mesh, 6 ft x 1/8 in. o.d.) was used to separate low-boiling compounds. The column temperature was programmed from 40 to 230°C at 10°C/min; the flow rate of the helium carrier gas was 40 mL/min. For higher-boiling products an SE-30 silicone gum-fused silica capillary column (13 m x 0.32 mm i.d.) was employed, programmed from 40 to 225°C at 5°C/min. Helium flow rate was 2 mL/min and the inlet splitting ratio was 30:1. The flow rate of helium makeup gas was 30 mL/min. Pyrolysis products were detected by flame ionization.

About 100 µg of polyacetylene was weighed into the quartz tube of the pyrolyzer and purged with helium for 10 min; the temperature of pyrolysis interface was kept at ca. 230°C to avoid the condensation of pyrolyzates. Tenax GC (60/80 mesh) was packed in the glass sleeve inside the injector to keep any very high-molecular-weight products from the column. The eluted pyrolysis peaks were identified by a Hewlett-Packard model 5985A mass spectrometer coupled with a 5840A gas chromatograph by a jet separator for the packed column or by a platinum-iridium transfer line for the capillary column. For this part of the study, only total ion chromatograms were collected using the mass spectrometer as the sole detector. This insured optimal transfer of pyrolyzates to the ion source of the mass spectrometer. The electron impact ionization source operated at an ionizing voltage of 70 eV, the ion source temperature being 200°C. A Hewlett-Packard model 2648A data system was used to aid in interpretation of mass spectra.

RESULTS AND DISCUSSION

Pyrolysis Products and Distributions

TGA curve of polyacetylene at a heating rate of 3 K min⁻¹ and or He flow rate of 40 mL min⁻¹ showed initial rapid weight loss to commence at 573 K. Between 703 K and 793 K the pyrolysis was slow, followed by accelerated weight loss at higher temperatures. At ca. 943 K the processes are complete leaving about 25% of the polymer in the form of carbonaceous char. The pyrograms of polyacetylene at 923 K are shown in Figure 1.

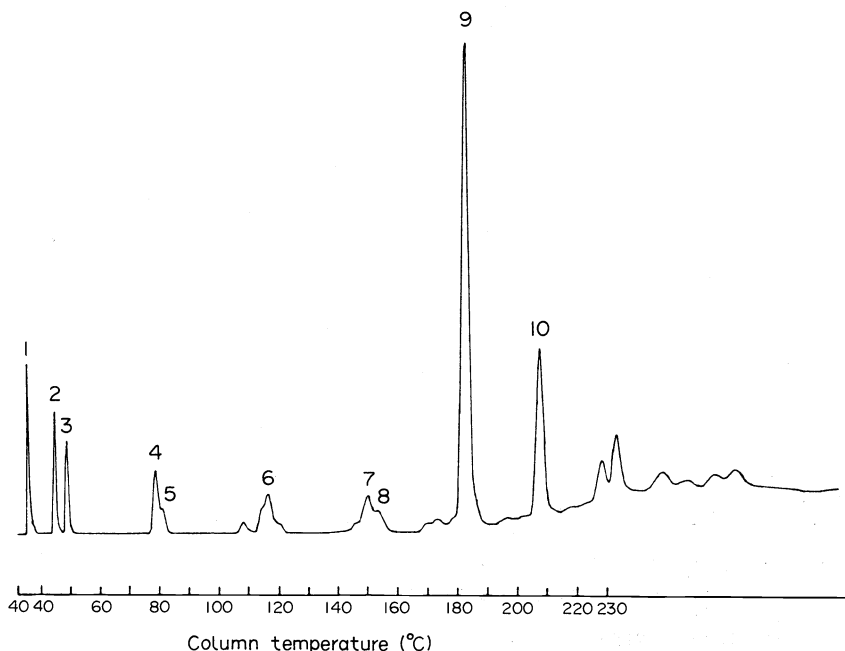


Figure 1a. Low temperature pyrogram of polyacetylene.

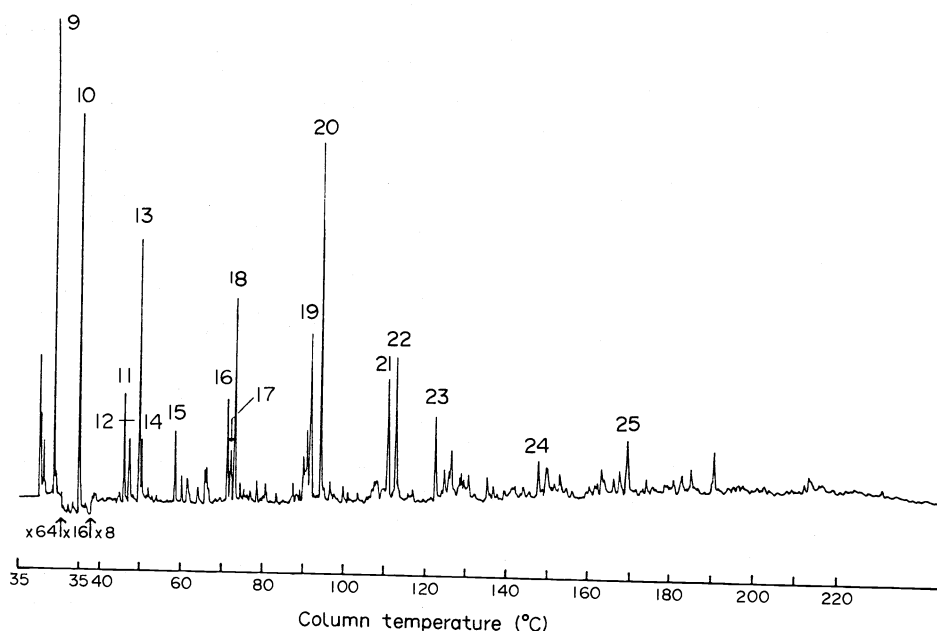


Figure 1b. High-boiling pyrogram of polyacetylene.

Polymethylacetylene is thermally less stable than polyacetylene; TGA weight loss begins at about 423 K reaching completion at about 700 K and leaves 7% of the polymer as char. At least two factors probably contributed toward the greater thermal stability of polyacetylene. Polyacetylene is a more conjugated molecule than the methyl derivative, the former has identical backbone carbon atoms but they are different in polymethylacetylene by virtue of the substituent. The non-bonded repulsion between the pendant methyl groups may cause deviation of the backbone from planarity. Secondly, the cooperative π interaction between polyacetylene molecules is strong as evidenced by its insolubility and infusibility. This interaction is small in polymethylacetylene and the polymer is readily dissolved in common solvents. Figure 2 shows typical low boiling and high boiling pyrograms of polymethylacetylene.

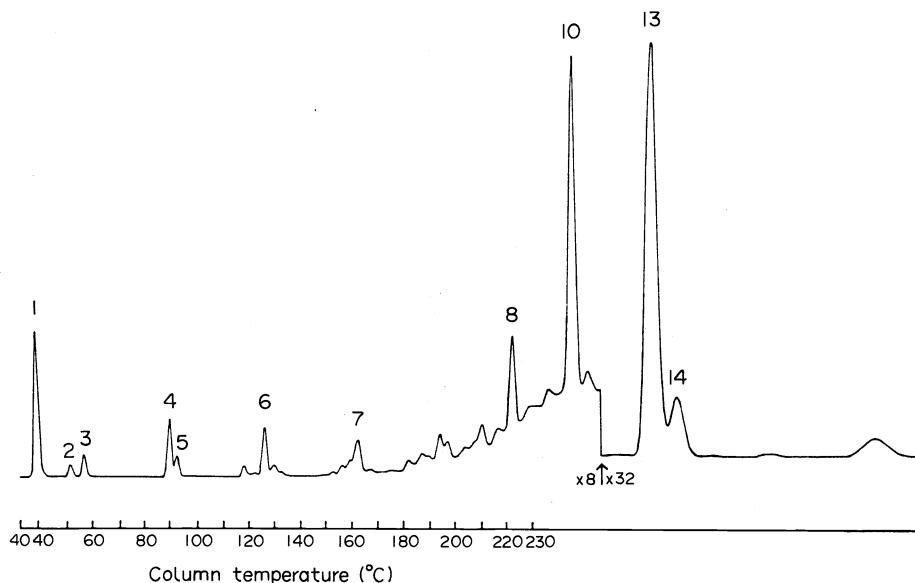


Figure 2a. Low-boiling pyrogram of polymethylacetylene.

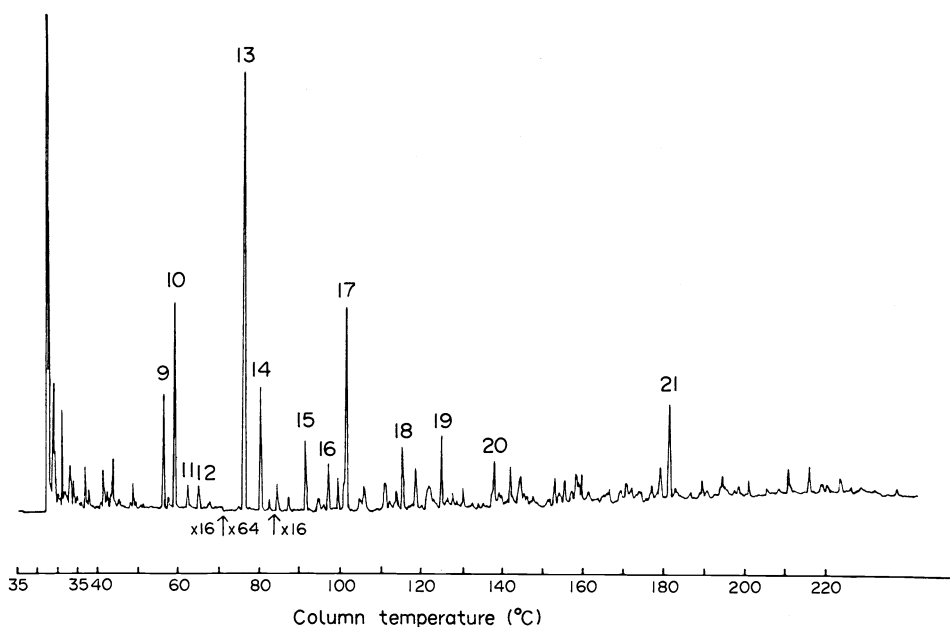


Figure 2b. High-boiling pyrogram of polymethylacetylene.

The pyrolysates of polyacetylene obtained at 1023 K and their relative molar amounts are summarized in Table I; the peak numbers correspond to the ones in Figure 1. The results for polymethylacetylene are also contained in the Table.

Table I. Products of Pyrolysis at 1023 K

Polyacetylene				Polymethylacetylene			
Peak #	Product	Rel. mole	ΔE kcal mole ⁻¹	Peak #	Product	Rel. mole	ΔE kcal mole ⁻¹
1	methane	0.85	11.0	1	methane	0.8	11.6
2	ethylene	0.45	10.4	2	ethylene	0.14	22.3
3	ethane	0.28	5.3	3	ethane	0.13	18.9
4	propylene	0.24	7.8	4	propylene	0.17	14.7
5	propane	0.06	0.6	5	propane	0.06	16.4
6	butadiene	0.23	3.1	6	butadiene	0.06	
7	cyclopentadiene	0.11	4.9	7	pentadiene-1,2	0.06	10.9
8	pentadiene-1,3	0.08	1.9	8	toluene	0.08	
9	benzene	1.0	3.1	9	2,3,5-trimethyl-cyclopentadiene	0.05	
10	toluene	0.14	3.7	10	p-xylene	0.31	5.2
11	ethylbenzene	0.02	3.1	11	o-xylene	0.07	9.0
12	p-xylene	0.01	7.2	12	1,3,3,4-tetramethyl-cyclopentadiene	0.02	
13	styrene	0.05	2.5	13	mesitylene	1.0	0.8
14	o-xylene	0.01	1.9	14	1,2,4-trimethyl benzene	0.28	1.4
15	o-methylstyrene	0.01	1.8	15	1-ethyl-3,5-dimethyl benzene	0.08	6.8
16	α -methylstyrene	0.02	0	16	3,5-dimethylstyrene	0.05	8.2
17	indane	0.01	0.3	17	1,3,4,5-tetramethyl benzene	0.10	0
18	indene	0.04	5.1	18	1-i-propenyl-2,4,6-trimethyl benzene	0.02	
19	methyl-indene	0.03	3.1	19	1,5,7-trimethyl indane	0.03	
20	naphthalene	0.05	3.1	20	1,5,7-trimethyl indene	0.03	
21	2-methylnaphthalene	0.02	2.3				
22	1-methylnaphthalene	0.02	0.2				
23	biphenyl	0.01	3.1				

The pyrolysis of polyacetylene described above, as expected, gives benzene as the major product. The surprising result is the formation of large amounts of C_1 , C_2 alkanes; C_2 , C_3 alkenes, and butadiene, as well as alkyl-substituted aromatic compounds such as toluene and xylenes. Therefore, there is a qualitative difference between the pyrolysis of conjugated polyacetylene and polyolefin or diene polymers. It can be shown readily that methane and ethane cannot be derived from end groups. Even though 20-30% of the polyacetylene chains has an ethyl group derived from the initiator, it amounted to less than 0.1% of the polymer with a number-average molecular weight of about 11,000 (21). It is also unlikely that the products are formed by hydrogen abstraction of fragmented intermediates which are diradicals or carbenes. The large amounts of C_1 , C_2 alkanes, C_2 , C_3 alkenes and butadiene, which totaled in number of moles 1.34 times that of benzene at 873 K and the ratio is 2.4 at 1073 K. Acetylene was not detected as a product. In addition there was produced significant quantities of alkyl substituted aromatic compounds such as toluene and xylenes. These proton-enriched products must gain the hydrogens from the proton-depleted products chief among these is the carbonaceous char which amounted to about 25 wt. %. About one-third of polyacetylene pyrolyzed as multiples of CH units, i.e. benzene, styrene and methyl indenenes. There is relatively good material balance. For instance at 1073 K Table I showed that the proton enriched products gained a total 9.7 μmole of hydrogen atoms whereas the proton depleted products and char lost a total of 7.8 μmole of hydrogen atoms. Therefore, there is no formation of H_2 during pyrolysis. At lower temperature of 873 K the hydrogen atoms gained is about 5.9 μmole by the proton enriched products and the loss is about 6.9 μmole for the char and proton depleted products. Therefore, the material balance is within 20% at low temperatures. Some of the high molecular weight proton depleted products may not be eluted in the gas chromatography or not swept out of the pyroprobe at low pyrolysis temperatures.

In the case of polymethylacetylene there was also the formation of proton enriched and proton depleted products. At 1023 K pyrolysis of 11.8 μmole of $(CH_{1.33})_x$ there was a gain of 3.9 μmole of hydrogen atoms and a loss of 2.4 μmoles of hydrogen atoms which includes the 7 wt. % of carbonaceous char. The material balance on hydrogen is about 12%. Thus, the same conclusions apply to polyacetylene and polymethylacetylene.

Kinetics

Pyrolysis of polyacetylene was performed from 873 K to 1073 K. The rate of formation of benzene at 925 K is about 5×10^{-5} mole per mole of monomer per sec with an activation energy of 3.1 kcal mole⁻¹. From the yields of the products determined over this 200 K temperature range, the activation energies for this formation were obtained and listed in Table I. The proton rich products have activation energies of formation larger than that for benzene; the value is higher the greater is the proton enrichment. Methane has the highest ΔE of ~ 11 kcal mole⁻¹. Most products with molecular weight greater than benzene have activation energies comparable to or less than that for benzene. Only *p*-xylene and indene seem to be somewhat out-of-line.

The rate constant of formation of benzene at 573 K was obtained by indirect measurements. This temperature was selected because it is the lowest temperature for measurable reaction. Polyacetylene was heated at this temperature in vacuum from a few min to two hrs. The samples were subsequently pyrolyzed for 20 sec at 923 K in He and the products analyzed by GC-MS. In the case of benzene the amount liberated at 923 K decreases with the increase of time of preheating at 573 K. In other words a portion of the benzene was produced during the preheating so that lesser amounts can be formed by the subsequent pyrolysis. The results gave a value of 1.8×10^{-4} sec⁻¹ for the rate constant for the formation of benzene at 573 K.

The product yields from polymethylacetylene was measured from 773 K to 1023 K. The rate of production of mesitylene is 8×10^{-5} mole per mole monomer per sec at 925 K. The corresponding rate for the formation of benzene from polyacetylene at this temperature is 5×10^{-5} . However, the activation energy for the former process is only 0.8 kcal mole⁻¹ as compared to 3 kcal mole⁻¹ for the latter. The temperature dependence of pyrolysate yields showed two types of behaviors. The first is a linear Arrhenius plot, and some of the products belong to this class. The activation energies for the formation of these products are given in Table I. It is interesting to compare these values with those for polyacetylene pyrolysis. For the two polymers the values of ΔE for methane formation are nearly identical. On the other hand, the activation energies of formation for the other low boiling products are anywhere from 5 kcal mole⁻¹ to 10 kcal mole⁻¹ higher from polymethylacetylene than those for polyacetylene. The results indicate that methyl group migration requires more activation energy than proton migration which occurs with greater ease.

Effect of dopant

Pyrolysis of polyacetylene doped to conducting states with AsF_5 and iodine were investigated from 923 K to 1123 K. The pyrograms of $[CH(AsF_5)_{0.14}]_x$ showed nearly identical peaks as the

undoped moles. In the case of $[\text{CHI}_{0.06}]_x$, additional products were observed such as CH_3I , $\text{C}_4\text{H}_4\text{I}$ and others not identified. Doping greatly enhanced the formation of proton enriched products as can be seen by the comparison of 1023 K pyrolysis yields in Table II. The

Table II. Comparison of Pyrolysate Yields of Undoped and Doped Polyacetylene at 1023 K Under Identical Conditions

Products	$[\text{CH}]_x : [\text{CH}(\text{AsF}_5)_{0.14}]_x$: $[\text{CHI}_{0.066}]_x$	Products	$[\text{CH}]_x : [\text{CH}(\text{AsF}_5)_{0.14}]_x$: $[\text{CHI}_{0.066}]_x$
Methane	1:7.3:13.6	Styrene	1:1:1.5
Ethylene	1:1.7:4.3	o-Xylene	1:2.8:8.1
Ethane	1:3.0:11.7	Methylstyrene	1:1.6:3.8
Propylene	1:1.5:5.5	Indane	1:1.4:4.8
Propane	1:2.3:17	Indene	1:1.1:1.4
Butadiene	1:0.8:6.4	Naphthalene	1:0.9:1.1
Pentadiene	1:0.8:1.5	2-Methylnaphthalene	1:1.2:1.9
Toluene	1:1.9:3.3	1-Methylnaphthalene	1:1.4:1.3
Ethylbenzene	1:1.9:6.6	Biphenyl	1:1.3:2.4
p-Xylene	1:2.1:4.1		

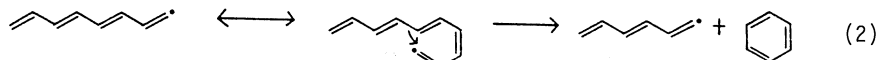
effect is greater for iodine doping than it is for AsF_5 doped polymers. In contrast, products which are multiples of CH units or which are proton depleted are not significantly affected by doping. For instance, compare methylstyrene with styrene and indane with indene. Furthermore, the yield enhancement is greater for the more saturated hydrocarbons, i.e., methane, ethane and propane as compared to ethylene and propylene, and xylene and ethylbenzene over toluene and styrene. Doping also affects the yield of carbonaceous char. The average char yields from $[\text{CH}]_x : [\text{CH}(\text{AsF}_5)_{0.14}]_x : [\text{CHI}_{0.06}]_x = 1:2.1:1.5$.

Mechanism

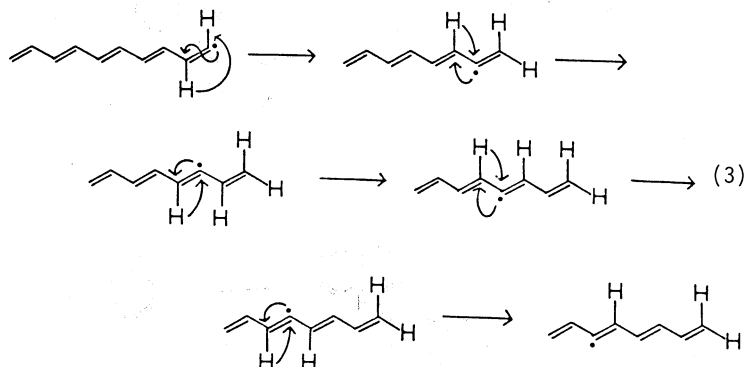
The activation energies obtained above were for the formation of each individual product which does not include the initial chain scission activation energy. In other words, once the initiation occurred it required very little more energy to form the products. Even so the additional energies required were remarkably small. The fact that the yields of CH_4 were greater from the pyrolysis of polyacetylene than from polymethylacetylene, this and other low molecular weight proton enriched products cannot be formed by hydrogen abstraction and combination reaction of CH_3 , CH_2 , CH fragments. We proposed facile electron-proton exchanges as the dominant mechanism for the pyrolysis of polyacetylene. The initiation process is probably the thermal excitation of bonding π electrons to the antibonding state across the band gap (23) of ca. 36 kcal mole⁻¹ resulting in bond dissociation.



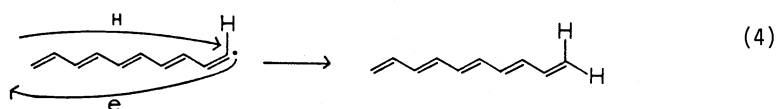
Intramolecular electron migration and ring closure leads immediately to benzene:



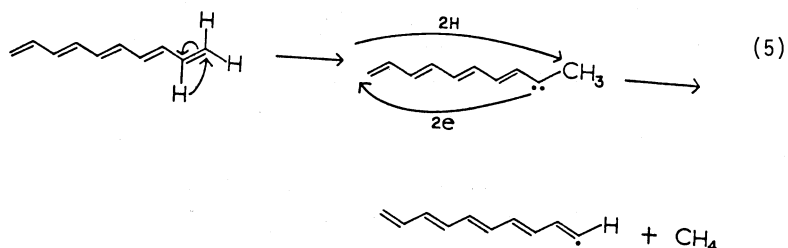
To account for the other products we postulate a series of proton migration, electron migration, and shifting of the alternating short and long carbon-carbon bonds. As π bonds are broken and the π electrons move to another part of the chain to reform π bonds, the protons released migrate in the opposite direction. Although the electron-proton exchange is probably nonclassical, it can be depicted, albeit clumsily, by a series of classical chemical events. Consider the radical produced in the chain scission [eq. (1)], the terminus gains a proton from somewhere down the polymer chain in exchange for its π electron as follows:



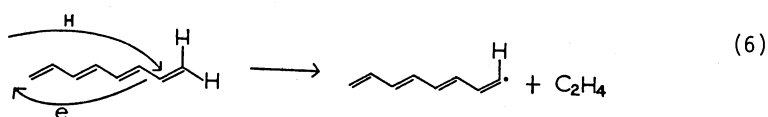
Therefore, we can write an abbreviated representation for the above process as



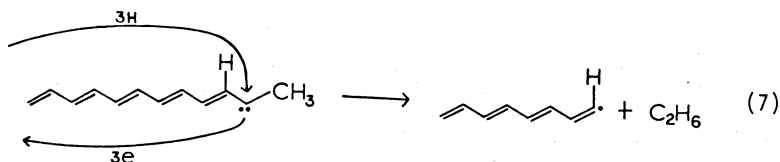
To produce methane, the events are



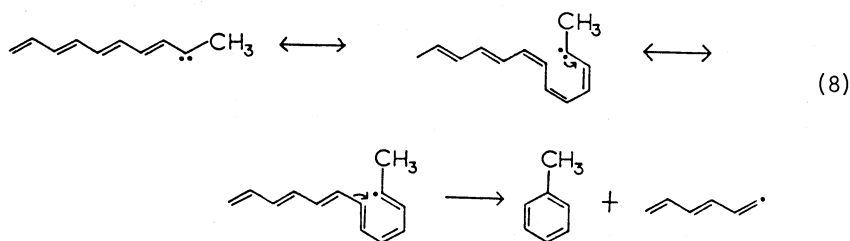
An alternative process is the formation of ethylene



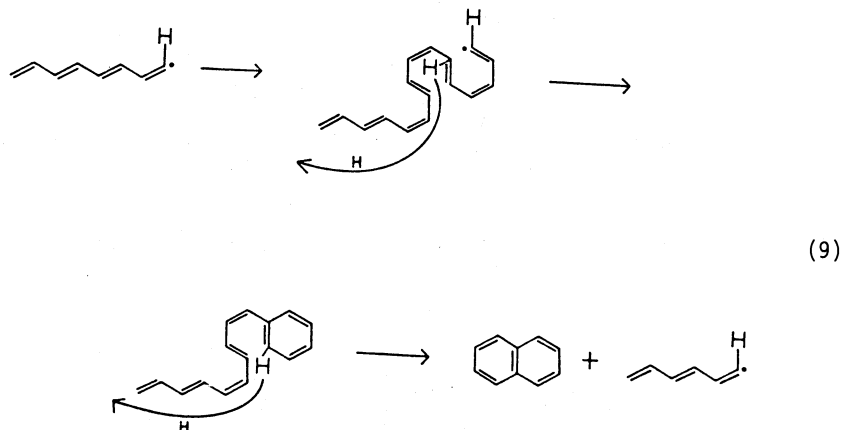
Ethane is obtained in a similar manner:

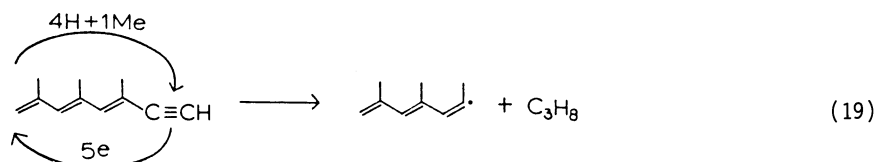
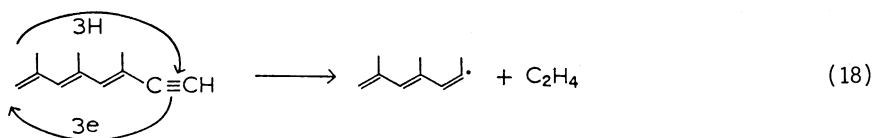
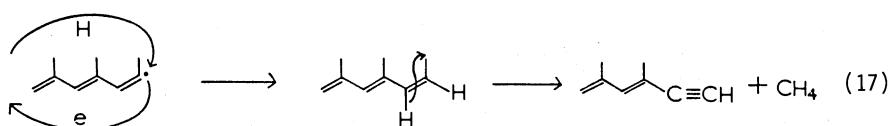


To depict the formation of toluene, we arrange the chain end to resemble the product before proton-electron exchange for illustrative purposes:

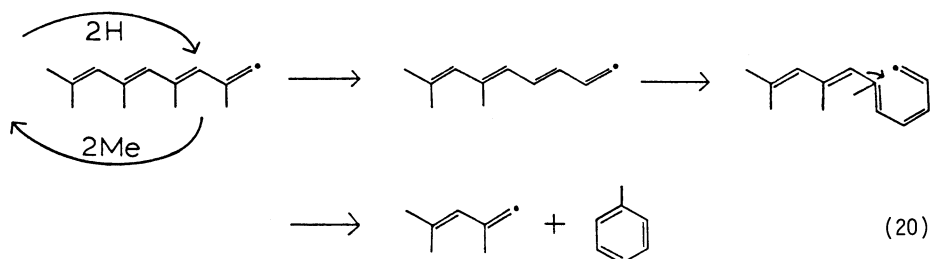


Finally, for naphthalene, which was produced in low yield, we write:





The following pathway to form toluene can be extended to account for all the other aromatic products:



In conclusion, by virtue of the conjugated backbones, the pyrolysis of polyacetylene and polymethylacetylene proceed apparently by very facile electron-proton and electron methyl exchanges requiring very little activation energies. The processes are helped by the presence of dopants. There could be some correlation between these chemical exchange reactions and carrier transport properties.

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