

A NEW MECHANISM FOR ACETYLENE PYROLYSIS TO AROMATIC HYDROCARBONS

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Pyrolysis of acetylene to a mixture of aromatic hydrocarbons has been the subject of many studies, commencing with the work of Berthelot in 1866.(1) The proposed mechanisms have ranged from formation of CH fragments by fission of acetylene (2) to free-radical chain reactions initiated by excitation of acetylene to its lowest-lying triplet state (3) and polymerization of monomeric or dimeric acetylene bi-radicals.(4) Photosensitized polymerization of acetylene and acetylene-d<sub>2</sub> and isotopic analysis of the benzene produced indicated involvement of both free-radical and excited state mechanisms.(5)

In a study of the formation and reactions of arynes at high temperatures (6) we pyrolyzed tenth molar quantities of phthalic anhydride and acetylene, separately and in admixture, at 690° in a Vycor tube filled with Vycor beads in a stream of dry nitrogen for contact times of 4-5 seconds. The major products boiling above 150° are shown in Table I.

TABLE I

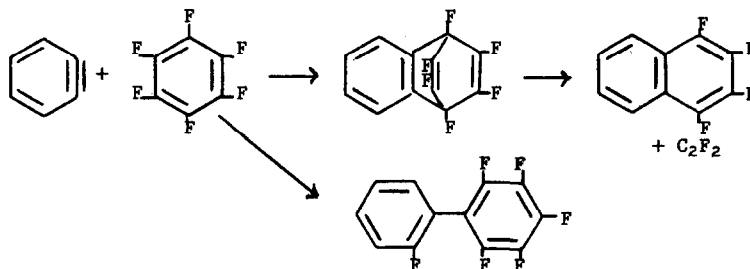
Compound Pyrolyzed	Acetylene	Phthalic Anhydride	Phthalic Anhydride and Acetylene
Total weight of high-boiling products, g.	0.35	1.5	1.8
Product	Relative Intensity <sup>a, b</sup>		
Naphthalene	100	100	100
Biphenylene	5	7	6
Biphenyl	16	80	16
Anthracene and Phenanthrene	49	227	68
Phenylnaphthalene	12	43	16
Triphenylene	20	61	22
Binaphthylene	27	30	17

(a) Relative intensities of parent peaks in the low-voltage (7.5 ionizing volts, uncorrected) mass spectrum, normalized to naphthalene = 100.

(b) Analyses were performed with a Consolidated model 21-103c mass spectrometer with the inlet system at 250°; with a directly-coupled gas chromatograph-mass spectrometer also employing a 21-103c instrument with an electron multiplier in place of the Faraday-cup detector; and with gas chromatography on a column of polyethylene glycol sebacate on Chromosorb W. Mass spectra were measured at the conventional 70 ionizing volts and at low voltage--7.5 volts, uncorrected. For the low-voltage measurements, the repellers were maintained at an average potential of 3 volts, the exact values being selected to give maximum sensitivity.

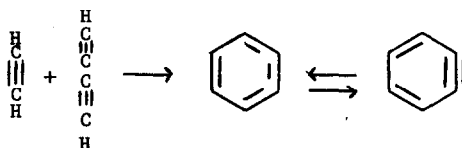
The striking similarity in the nature and some of the relative concentrations of the products in the three reactions strongly suggests common mechanisms and intermediates for their formation. Phthalic anhydride gives benzyne upon pyrolysis (7); the parallel behavior of acetylene suggests that it also forms benzyne at high temperatures.

To test this hypothesis, phthalic anhydride, acetylene, and acetylene- $d_2$  were separately reacted with hexafluorobenzene at 690° under the same conditions as those used with acetylene alone. Phthalic anhydride gave tetrafluoronaphthalene, by 1,4-addition, (8) and hexafluorobiphenyl, by insertion of benzyne, in a 1:5 ratio as estimated from the low-voltage mass spectrum and combined gas chromatography-mass spectrometry:

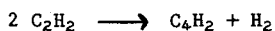


Acetylene with hexafluorobenzene also gave tetrafluoronaphthalene and hexafluorobiphenyl, though in a 4:1 ratio, and also tetrafluoroanthracene. Acetylene- $d_2$  under the same conditions gave tetrafluoronaphthalene- $d_4$  and hexafluorobiphenyl- $d_4$  in a 9:1 ratio, as well as tetrafluoroanthracene- $d_6$ .

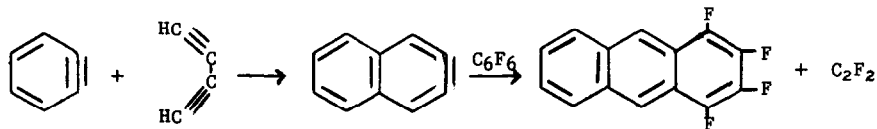
Benzyne probably forms from acetylene by cycloaddition reaction of acetylene and diacetylene, concerted or stepwise<sup>9</sup>:



Diacetylene is a known pyrolysis product of acetylene, (9) and from shock-wave pyrolysis studies has been postulated as the first product formed from acetylene. (10) Thermochemical data (11) show that the reaction is exothermic to the extent of about 13 kcal./mole. Benzyne



may react further with diacetylene to form naphthalene, which in turn would be expected to react with hexafluorobenzene to give tetrafluoroanthracene (12):



Our evidence that benzyne is at least one of the intermediates in acetylene pyrolysis has many mechanistic implications. The reactions of acetylene with aromatic compounds at high temperatures is being investigated further in this light.

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13. Alternatively, tetrafluoroanthracene could form by the reaction of benzyne with tetrafluoronaphthalene. In that case however, some difluoroanthracene should also form by 1,4-addition of benzyne to the fluorinated ring. No difluoroanthracene or difluoroanthracene-d<sub>8</sub> was found in the products from the reactions of hexafluorobenzene with acetylene and acetylene-d<sub>2</sub>, respectively.