NOTES

SOME KINETICS OF THE CARBONIZATION OF BENZENE, ACETYLENE AND DIACETYLENE AT 1200°

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When benzene is heated to 1200° in a helium stream at a concentration of 0.1 mole % and at residence times of 4 milliseconds, the primary products of decomposition are mainly a molecule each of acetylene, diacetylene and hydrogen,¹ reaction 1.

$C_6H_6 \longrightarrow HC \equiv CH + HC \equiv C - C \equiv CH + H_2$ (1)

The kinetics of this reaction are complicated by the fact that about 12% of biphenyl is also produced. No doubt dissociation of a hydrogen atom from benzene is a primary reaction and it is probable that the phenyl radical produced undergoes further decomposition which results in acetylene and diacetylene. Because no proof of the reaction mechanism was obtained, no mechanism will be suggested. However, the fact that no six-carbon, open-chain product was observed by gas chromatography may be of significance. Both acetylene and diacetylene decompose at 1200°; this is of interest in connection with the decomposition of benzene. Consequently, kinetic data for these hydrocarbons also are included.

Experimental

The kinetics of the pyrolysis of benzene, acetylene and diacetylene were studied in apparatus described previously.¹ Essentially the procedure was to pass the hydrocarbon in a helium stream through a porcelain tube 20 cm. by 5 mm. inside diameter. The tube was heated by a platinum resistance furnace which was regulated by a recording temperature controller to within $\pm 1^{\circ}$. The temperature of the gas stream rose to the temperature of the furnace on travelling about 5 cm. through the tube. It then remained constant within about 5° for a distance of 5 cm., and then fell very rapidly owing to a water-cooled coil of copper tubing wound around the exit. The furnace temperature was regulated so that the calculated temperature of pure helium passing through the tube was between 1200 and 1205°, based on measured temperatures obtained from a calibrated platinum-platinum 10% rhodium thermocouple inserted in the gas stream. This thermocouple was with drawn during runs with hydrocarbons.

The product gases were passed through a Dry Ice-acetone cooled trap and then through two traps cooled with liquid nitrogen. Uncondensed gases, mainly methane and hydrogen, were oxidized to carbon dioxide and water and the amounts of these gases calculated from these data. The gases condensed at liquid nitrogen temperatures included acetylene, ethylene, methylacetylene, allene, diacetylene and vinylacetylene. The amounts were determined by a Perkin-Elmer 154C Vapor Fractometer.

Discussion

The rate of disappearance of benzene at 1200° , at a concentration of 0.1 mole % and at residence times of 4 to 112 milliseconds is exponential with time as shown in Fig. 1. Plotted semilogarith-

(1) C. R. Kinney and R. S. Slysh, "Proceedings of the Fourth Conference on Carbon," Pergamon Press, London, 1960, p. 199. mically, a straight line can be drawn through the points implying disappearance by first-order kinetics and giving a rate constant of 20.6 sec.⁻¹. This first-order behavior was tested further by increasing the initial contraction of benzene by five and ten times. In each case the percentage benzene decomposed remained constant to within an experimental error of about 5%, confirming first-order behavior. This conclusion agrees with previous work² and the work of Tesner and co-authors³ who developed quite a different technique.

developed quite a different technique. The percentage of benzene decomposed rises from about 10 to 90% with contact times of 4 to 112 milliseconds, respectively, Table I, and therefore covers a wide range of the decomposition of benzene at the temperature and concentration used. The decomposition products at 4 milliseconds are characterized by large amounts of acetylene and diacetylene, but considerable quantities of carbon, polymer or tar, and biphenyl also are produced, Table I. At longer contact times the proportion of these products decreases and carbon is produced instead. Smaller amounts of methane, ethylene, methylacetylene, allene and vinylacetylene which appear are undoubtedly secondary products.

LABLE I

YIELD OF PRODUCTS, WEIGHT % OF BENZENE DECOMPOSED Initial concn. of benzene, 0.1 mole %: 1200°

Contact time, millisec.	4	8	56	112
% of feed decomposed	9.8	22.4	68.0	90.0
Carbon	12.8	16.7	62.0	76.4
Polymer or tar	16.4	10.2	4.9	2.3
Biphenyl	12.2	10.9	a	a
Acetylene	26.4	25.0	17.5	12.1
Diacetylene	28.0	22.1	4.6	2.7
Methane	3.3	3.7	2.0	2.5
Ethylene	2.0	1.4	0.1	a
Methylacetylene + allene	1.9^b	1.5	a	a
Vinylacetylene	0.8	0.5	с	c
Hydrogen	2.0	2.0	6.0	6.2
Total products, %	105.8	94.0	97.1	102.2
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 a Trace. b Methylacetylene 1.4%; allene 0.5%. c None detected.

Because acetylene and diacetylene appear to be primary products in the decomposition of benzene, the kinetic behavior of these hydrocarbons under similar conditions also has been studied. Their rates of disappearance with residence time are shown in Fig. 1. Acetylene, in contrast with both benzene and diacetylene, is more stable thermally and it was necessary to increase its concentration to

(2) D. B. Murphy, H. B. Palmer, C. R. Kinney, "Conference on Industrial Carbon and Graphite," Society of Chemical Industry, London, 1958, p. 77.
(3) P. A. Tesner and A. I. Yecheistova, Dokl. Acad. Nauk.,

(3) P. A. Tesner and A. I. Yecheistova, Dokl. Acad. Nauk., S.S.S.R., 87, No. 6, 1029 (1952); P. A. Tesner and I. S. Rafalkes, *ibid.*, 87, 821 (1952). 0.5 mole % to get sufficient decomposition to measure the products satisfactorily at contact times as low as 8 milliseconds. At this concentration, about 1% is decomposed at 8 milliseconds and 23% at 112. The shape of the disappearance curve in Fig. 1 shows that the rate of decomposition accelerates, at least to 112 milliseconds. Possibly this is due to the deposition of carbon which acts as a catalyst.

The yields of decomposition products from acetylene vary from those obtained from benzene in several respects. The percentage converted to carbon at a short residence time is larger and there is less tar or polymer, Table II. The most important product after carbon is diacetylene. Since such a large amount of diacetylene is produced in spite of its higher rate of decomposition, Fig. 1, and since diacetylene yields acetylene on pyrolysis, Table III, it seems likely that these reversible reactions occur

$$2HC \equiv CH \rightleftharpoons 2HC \equiv C - + 2H - (2)$$
$$2HC \equiv C - \swarrow HC \equiv C - C \equiv CH (3)$$

Acetylene also produces rather large quantities of methylacetylene, allene and methane, Table II. The mechanism by which these odd-numbered carbon derivatives is formed has not been proven, but their appearance in the decomposition products of benzene should be noted because they may be

characteristic of acetylene decomposition rather than benzene.

The rate of disappearance of diacetylene when

TABLE II

YIELD OF PRODUCTS, WEIGHT % OF ACETYLENE DECOMPOSED

Initial concn. of benzene, 0.1 mole %; 1200°

Contact time, millisec.	8	56	112
% of feed decomposed	1.2	6.9	22.8
Carbon	36.4	48.3	50.6
Polymer or tar	4.5	7.0	7.5
Diacetylene	32.0	19.6	20.0
Methane	4.5	8.4	13.0
Ethylene	ь	5.6	1.5
Methylacetylene	18.2	2.1	1.1
Hydrogen	4.5	3.5	2.9

Total products, % 100.1 94.5 96.6 ^a A trace of vinylacetylene was detected at 8 milliseconds but none at longer contacts. ^b Trace.

TABLE III

Yield of Products, Weight % of Diacetylene Decomposed

Initial concn. of acety	lene 0.5 m	ole %; 12	200°
Contact time, millisec.	8	56	112
% of feed decomposed	21.0	69.1	92.2
Carbon	44.5	63.6	70.6
Polymer or tar	12.0	2.9	ь
Acetylene	37.2	21.8	19.2
Methane	1.6	4.4	4.2
Ethylene	0.8	0.3	0.2
Hydrogen	0.4	1.5	1.5
Total products %	96.5	94 5	95.7

^a Traces of methylacetylene, allene and vinylacetylene were detected at all contact times. ^b Trace.



Fig. 1.—Effect of contact time on the rate of pyrolysis of benzene, diacetylene and acetylene.

heated to 1200° at a concentration of 0.1 mole % is shown in Fig. 1. The rate constant calculated from the data is $22.4 \text{ seconds}^{-1}$. No doubt the mechanism of decomposition is complex because of the variety of products obtained, Table III. However, the diacetylene molecules that are decomposed are converted to carbon more completely than either benzene or acetylene. The next largest product is acetylene, which probably involves the dissociation of diacetylene to acetylenyl radicals which then capture hydrogen atoms by collision with diacetylene molecules, as indicated by the reverse of reactions 3 and 2. In this connection, the production of diacetylenyl radicals may account for the larger conversion of diacetylene to carbon than that of acetylene. The other decomposition products observed are similar to those obtained from benzene and acetylene.

The results of the investigation show that benzene decomposition is first order at 1200°. Of the products diacetylene also decomposes by first-order kinetics, but acetylene decomposes at an accelerating rate suggesting that a decomposition product, possibly carbon, affects the rate in a marked manner.

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STEPWISE ADSORPTION OF KRYPTON ON NICKEL

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The adsorption of krypton on nickel powders, sintered at temperatures between 200-600°, has