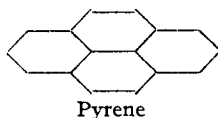
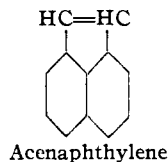


[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE THERMATOMIC CARBON CO.]

## Isolation and Identification of Acenaphthylene and Pyrene from the Products of the Pyrolysis of Natural Gas

BY ARTHUR W. CAMPBELL, NORMAN H. CROMWELL<sup>1</sup> AND JOHN J. HAGER<sup>1</sup>

In the manufacture of carbon black by the thermatomic<sup>2</sup> process, natural gas is cracked to carbon and hydrogen when passed over highly heated refractory brick. The major reaction is  $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$  but the presence in the carbon of a small amount of material extractable by acetone or benzene indicates the formation of organic compounds in very minute amounts. It has also been found that a waxy material separates from the hydrogen stream when the gas has been cooled sufficiently. This material was investigated and found to contain acenaphthylene and pyrene.



### Experimental

**Acenaphthylene.**—Separation by means of selective solvents, and of fractional crystallization, failed, so an attempt to sublime materials out of the mass was made. When some of the crude mixture was heated in a small bell jar in a water-bath at 60° for several days, a heavy crop of yellow plates collected upon the cool exposed surfaces. These melted at 89–90°, uncorr. Recrystallization from dilute alcohol gave m. p. 92–93°, corr. The odor of these yellow crystals resembled that of naphthalene.

A search of the literature for compounds falling in this group revealed that acenaphthylene answered the description as to color and melting point. As a result, the picrate and the dibromide were prepared.

	°C., corr.	Literature, °C.
Acenaphthylene	92–93	92–93 <sup>3</sup>
Acenaphthylene picrate	204–204.5	201–202 <sup>3</sup>
Acenaphthylene dibromide	124–124.5	121–123 <sup>4</sup>

The C:H ratio of our sample of acenaphthylene was determined: C, 94.53; H, 5.51. Calcd.: C, 94.65; H, 5.35.

**Acenaphthylene Polymer.**—Vacuum distillation at 20 mm. pressure was used in an attempt to separate the mixture. Two fractions were obtained, boiling range 149–200°, and 200–260°, at the indicated pressure. A small white residue remained of the first fraction when solution in ethyl

alcohol (95%) was attempted. The solution was diluted with water and a heavy, yellow precipitate came down. This precipitate was nearly pure acenaphthylene, as indicated by the melting points of the material and its picrate.

The white insoluble substance obtained from the first fraction, boiling range 149–200°, was purified by washing thoroughly with hot alcohol and acetone. It was not possible to crystallize this material, so it was further purified by precipitation with methyl alcohol from a benzene solution. This fine, white powder was dried in vacuum for several days, and found to melt at 345–350°, corr. It was thought to be the polymer of acenaphthylene, reported by Dziewonski *et al.*<sup>5</sup> They reported a polymer shown by analysis to be  $(\text{C}_{12}\text{H}_8)_n$ , giving molecular weights in bromoform and nitrobenzene ranging from 3050–3720, agreeing best with  $(\text{C}_{12}\text{H}_8)_{22}$ , molecular weight 3344, and melting at 345–350°.

Analysis of this material indicated that it was probably a polymer of acenaphthylene. Some slight oxidation may have occurred, thus causing the low C and H values. Calcd. C:H ratio: C, 94.65; H, 5.35. Obsd. C:H ratio: C, 93.86; H, 4.85.

The molecular weight was determined by the lowering of the freezing point method.

	Wt. benzene g.	Wt. subst., g.	Depression of f. p., °C.	Mol. wt.
I	15.8394	0.4983	0.105	1498
II	16.0043	.7465	.150	1555
				Average 1526

These results agree best for  $(\text{C}_{12}\text{H}_8)_{10}$ , molecular weight 1521. It is very likely that this substance is actually a mixture of polymers of acenaphthylene, and that these are only average values. It is almost impossible to obtain this substance pure, as this fine powder is highly adsorptive to impurities and solvent.

The important fact to be noted here is not the exact polymer formed, but the manner in which it was formed. Since it was not present in the original mixture, as indicated by solubilities, but was found only in the first fraction from the vacuum distillation, it was probably formed when the solid in the receiver flask was melted and poured into a flask for recrystallization. This agrees well with the observations made on acenaphthylene by Dziewonski,<sup>5</sup> to the effect that heating at or above the melting point causes polymerization. We have also observed as did Dziewonski<sup>6</sup> that acenaphthylene will polymerize slowly when the solid is exposed to diffused light.

This polymer was obtained in another form. By addition of petroleum ether, boiling point 28–38°, to its benzene solution, a transparent gum settled out, which, on evaporation of the solvent, formed a hard, clear, glass-

(1) Submitted by Messrs. Cromwell and Hager to the faculty of the Rose Polytechnic Institute in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemical Engineering. Investigation directed by A. W. Campbell of the Thermatomic Carbon Company.

(2) U. S. Patent 1,478,730; Moore, *Ind. Eng. Chem.*, **24**, 21 (1932).

(3) Mulliken, "Identification of Pure Organic Compounds," Vol. 1, p. 177; Behr and van Dorp, *Ber.*, **6**, 753 (1873).

(4) Blumenthal, *ibid.*, **7**, 1093 (1874).

(5) K. Dziewonski and Z. Leyko, *ibid.*, **47**, 1679–90 (1914), *C. A.*, **8**, 2729 (1914).

(6) Dziewonski and Paschalski, *Ber.*, **46**, 1986 (1913).

like substance. This form is believed to be less pure, for solvent or impurities are very likely entrained.

**Pyrene.**—On recrystallization of the 200–260° fraction from 95% ethanol, a crop of tan crystals, m. p. 142–143°, came down on cooling. A crop of acenaphthylene was obtained from the filtrate on dilution with water. The first crop of crystals was recrystallized from 95% ethanol, and then 100–105° petroleum ether, reaching a constant m. p. 148.5° corr. The picrate was prepared in alcohol, from which long silky, deep red needles separated on cooling.

Compound	M. p., °C.	M. p. picrate, °C.
Compound	148.5 corr.	224 corr.
Pyrene <sup>7</sup>	149	222

(7) Freund, *Ber.*, **30**, 1383 (1897).

Mixed melting points with a sample of pure pyrene did not show any depression, nor did mixed melting points run with the respective picrates.

### Summary

1. Acenaphthylene and pyrene were identified in organic matter formed by the pyrolysis of natural gas.

2. Polymers of acenaphthylene differing in molecular weight from those previously described in the literature were found.

TERRE HAUTE, INDIANA

RECEIVED APRIL 23, 1936

## NOTES

### The Thermal Decomposition of Acetone

BY A. O. ALLEN<sup>1</sup>

The mechanism of the thermal decomposition of acetone to methane and ketene is at present unsettled, Winkler and Hinshelwood<sup>2</sup> assuming it to be unimolecular, while Rice and Herzfeld<sup>3</sup> have proposed a chain mechanism. In this note evidence is presented which favors strongly the latter view.

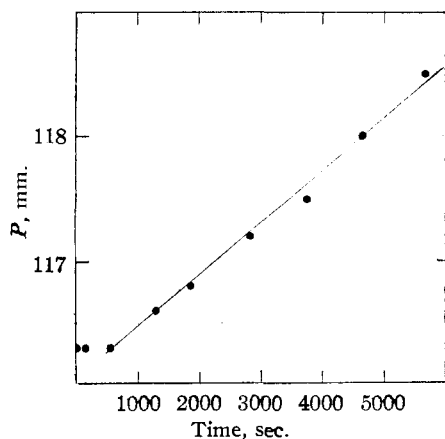


Fig. 1.—Pressure vs. time in the decomposition of acetone at 462°.

The reaction was studied by the usual static method, being followed by pressure change. With

(1) Sheldon Traveling Fellow, 1936. Present address, Department of Chemistry, Victoria University, Manchester, England.

(2) Winkler and Hinshelwood, *Proc. Roy. Soc. (London)*, **A149**, 340 (1935).

(3) F. O. Rice and Herzfeld, *THIS JOURNAL*, **56**, 284 (1934).

the object of getting rid of complications due to the decomposition of ketene, the reaction was run at temperatures where it proceeds slowly, and was carried to only about 5% decomposition. A constant-volume manometer with mirror scale was used which could be read to 0.1 mm. This method allows an accurate evaluation of the initial slope of the pressure–time curve, which, assuming two molecules are formed from each molecule of acetone decomposed, will give the true rate of acetone decomposition, uncomplicated by the slow decomposition of the ketene produced.

At the highest temperature used (529°) the reaction proceeded perfectly smoothly. At somewhat lower temperatures it was always found that the measured initial pressure was higher than would be obtained by extrapolation of the pressure–time curve to zero time. This suggested a short induction period, but was at first thought to be due to an incomplete establishment of pressure equilibrium. However, on going to a still lower temperature, it was found that the induction period, though corresponding to only about 0.3% decomposition, was undoubtedly real, lasting some ten minutes at 462° (Fig. 1).

The experiments were then repeated, with the 1-liter reaction vessel packed with short pieces of 10-mm. glass tubing. It was found that packing had three effects: (1) the shape of the rate–pressure curve was entirely changed, the curve of  $\log k$  (unimolecular) vs.  $\log p$  at any temperature being concave upward, instead of convex as usual;