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.

	M. p., °C.	M. p. picrate, °C.
Compound	148.5 corr.	224 corr.
Pyrene[7]	149	222

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

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

NOTES

The Thermal Decomposition of Acetone

BY A. O. ALLEN[1]

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

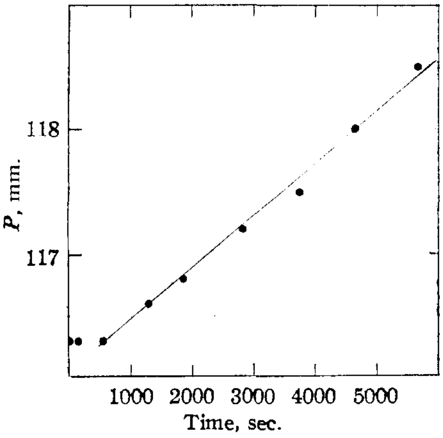

Fig. 1.—Pressure *vs.* time in the decomposition of acetone at 462°.

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

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[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).

(2) the apparent rate at high pressures, practically unchanged at 529°, was decreased at lower temperatures, being only about half the normal value at 465°; (3) the induction period was no longer apparent at any temperature.

These effects are practically sufficient to prove the reaction a chain. On the chain hypothesis, the short induction period appears naturally as the time necessary for the chain-carrying radicals to attain their steady-state concentrations; packing shortens the chains, rendering the induction period inappreciable and reducing the rate most at the lower temperatures, where chains of this type are longest.[3] The change of shape of the rate–pressure curve by packing also shows the great complexity of the reaction.

Though packing may lower the apparent rate by promoting condensation reactions, it seems very unlikely that a 50% reduction could be caused in this way. An induction period might conceivably occur if the reaction proceeded through some active form of acetone, in equilibrium with the ordinary form, the active form decomposing unimolecularly; but in this case, if increased surface shortened the induction period it must increase, rather than decrease, the observed rate.[4] Hence the reaction must be a chain.

The most likely mechanism for the reaction is the Rice–Herzfeld one

$$\begin{array}{rcll} CH_3COCH_3 & = & 2CH_3 + CO & (1) \\ CH_3 + CH_3COCH_3 & = & CH_4 + CH_2COCH_3 & (2) \\ CH_2COCH_3 & = & CH_3 + CH_2CO & (3) \\ 2CH_3 & = & C_2H_6 & (4) \\ CH_3 + CH_2COCH_3 & = & C_2H_5COCH_3 & (5) \end{array}$$

The combination of two acetonyl radicals is not included, as the diacetonyl formed would decompose rapidly at the temperatures used;[3] a steady-state concentration of diacetonyl must exist, however, and it is probably the building-up of this compound that causes the induction period. Rice and Herzfeld have attempted to obtain, from this type of mechanism, expressions for the pressure and temperature dependence of the reaction rate. This procedure assumes that the reactions involved have a simple order of one or two; this cannot be the case, unfortunately, for in the range of pressures used, reactions (1), (3), (5) and possibly (4) will have "fallen off" from their high-pressure rates by the well-known theory of unimolecular reactions, and will thus possess no definite order. This effect introduces so many unknown variables into the picture that it seems impossible to make any real progress by further study of the thermal reaction alone.

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[4] The argument is as follows: Let the reaction scheme be

$$\begin{array}{lr} X = Y \text{ (active)} & (1) \\ Y = X & (2) \\ Y = \text{products} & (3) \end{array}$$

Then $dY/dt = k_1X - k_2Y - k_3Y$. At the steady state, this equals zero, whence $Y = k_1X/(k_2 + k_3)$; observed rate $= k_3Y = k_3k_1X/(k_2 + k_3)$. Then increasing k_3, the only way in which increased surface could decrease Y and hence lower the induction period, will increase the observed rate.

Pumice as a Support for Copper–Chromium Oxide Catalysts in Dehydrogenations[1]

BY RALPH E. DUNBAR, DONALD COOPER AND ROBERT COOPER

Investigations involving the dehydrogenation of various alcohols to the corresponding aldehydes have been reported from time to time.[2] Oxide catalysts, pressed into pellets of approximately 0.15 g. each, have frequently been used.[3] Since the formation of the catalyst into pellets is extremely laborious and time consuming, it seemed advisable to find a suitable support so that the catalyst could be prepared directly for immediate use.

Experimental Part

The best results in the preparation of this catalyst were achieved by precipitating and decomposing with heat the catalyst in the presence of finely divided pumice. Two solutions were prepared as follows: (A) 300 ml. of a solution containing 87 g. of cupric nitrate hexahydrate and 10.4 g. of barium nitrate. The barium nitrate was first dissolved in the least amount of water possible at a temperature near the boiling point of water. The cupric nitrate hexahydrate was then added and the solution diluted to the 300 ml. required. Solution (B) was prepared from 300 ml. of a solution containing 50.4 g. of ammonium dichromate and 75 ml. of a 28% solution of ammonium hydroxide. Solution (B) was added to 177 g. of Italian, acid washed, pumice of size 20. This was allowed to digest for one hour on a steam-bath with frequent stirring. Solution (A) was then heated to 80° and added to solution (B) with thorough stirring. The treatment from this point was identical with that of Connor, Folkers and Adkins[4] except that the final decomposition was carried

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[1] Original manuscript received April 22, 1935.

[2] Bouveault, *Bull. soc. chim.*, [4] 3, 119 (1908); Conant, Webb and Mendum, THIS JOURNAL, **51**, 1250 (1929); Adkins, Folkers and Kinsey, *ibid.*, **53**, 2714 (1931); Weston and Adkins, *ibid.*, **50**, 1930 (1928).

[3] Adkins, Kommes, Struss and Dazler, *ibid.*, **55**, 2992 (1933).

[4] Connor, Folkers and Adkins, *ibid.*, **54**, 1138 (1932).