THE FORMATION OF AROMATIC HYDROCARBONS
AT
HIGH TEMPERATURES

A T E S I S
PRESENTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN THE
DEPARTMENT OF ORGANIC CHEMISTRY
OF THE
UNIVERSITY OF ADELAIDE

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1956.
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REFERENCES
Detailed investigation of the polycyclic aromatic hydrocarbons widely distributed in many materials in common use has gained great impetus from the highly controversial issue of the nature of the correlation between the incidence of lung cancer and the consumption of tobacco. While the carcinogenic activity of many materials produced by essentially pyrolytic methods has been known for some time, and extensive investigations of the carcinogenic activity of individual hydrocarbons have been reported, the possible harmful effects of these compounds would have been confined to small sections of the population. The impact of the present proposed correlation, which affects a high percentage of the population, can be gauged from the enormous increase in the volume of literature within the last eight years.

The most frequently reported carcinogen has been 3,4-benzopyrene, but whether this hydrocarbon is the main carcinogen remains to be decided. The presence of relatively small concentrations of 3,4-benzopyrene can be shown very easily, although not unequivocally, by the use of fluorescence spectroscopy, whereas other carcinogens do not possess a highly characteristic fluorescence spectrum and are correspondingly more difficult to identify. The constituents of cigarette smoke have been the most fully investigated to date, and the preoccupation with polycyclic aromatic hydrocarbons may be justified on the grounds that most of the carcinogenic activity is known to be confined to the neutral fraction, and that the only known carcinogens identified other than polycyclic aromatic hydrocarbons is arsenteric oxide (1).
The source of the carcinogenic hydrocarbons identified is unknown and the present investigations were designed to provide information on the mechanism of formation of 3,4-benzpyrene and other polycyclic hydrocarbons in pyrolytic reactions. Acetylene has often been suggested as the possible source of these hydrocarbons, but this hypothesis amounts to little more than a restatement of the problem, and the detailed process by which the polycyclic hydrocarbons are built up from a simple two carbon fragment is a problem unlikely to be solved without an extensive study of the pyrolytic behaviour of possible intermediates in the synthesis.

The present investigation is concerned with the compounds formed by pyrolysis of buta-1,3-diene, toluene, ethylbenzene, 2-propylbenzene, n-butylbenzene, 1-phenylbuta-1,3-diene, and a mixture of buta-1,3-diene and pyrene. The temperature of pyrolysis chosen was 700°C, which is intermediate between the combustion temperatures of cigarette and pipe tobacco (2) and approximates the decomposition point of coal, at which large amounts of hydrogen are evolved (3): the pyrolysis of shale to yield shale oil at this temperature is also known to yield a carcinogenic oil (3), and carcinogenic tars have been produced from acetylene and isoprene (4) at the same temperature.

The pyrolysis of 1-phenylbuta-1,3-diene at 550°C was also studied to determine the effect of temperature on the nature of the pyrolytic products. Toluene and n-propylbenzene are not intermediates in the synthetic scheme adopted as a working hypothesis, but were included to resolve some problems in the possible mechanism of formation of...
particular compounds and also to determine the effect of varying length of the side-chain on the nature of the products obtained. The pyrolysis of a mixture of buta-1,3-diene and pyrene was studied to test a hypothesis proposed by Weizmann (6), involving the formation of polycyclic hydrocarbons by a diene addition mechanism. New methods of analysis, involving both paper and column chromatography on partially acetylated cellulose, have resulted in more convincing demonstrations of the presence of many hydrocarbons, and also in the identification of many hydrocarbons not previously reported as pyrolytic products.

This thesis can be divided broadly into five main sections. The available evidence for the occurrence of polycyclic aromatic hydrocarbons in the human environment is summarized in Section I; Section II deals with the historical background of pyrolytic reactions and the nature of the reactions; Section III summarizes the results of the present series of investigations with particular reference to the possible mechanisms of formation of the compounds identified; Section IV deals with the analytical techniques used in the investigation, and includes the development of the methods of chromatography on partially acetylated cellulose; full details of the identification of compounds in individual pyrolyses are recorded in Section V.

It should be stressed that the mechanisms of formation proposed here are not necessarily those concerned in the formation of hydrocarbons by processes involving incomplete combustion, where intermediates containing hetero-atoms may be of importance, but
provide a background of information on which more detailed mechanisms can be based.