An Aromatic Hydrocarbon Isolated from Coal Bitumen

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Introduction

Many studies on the solvent extraction of bituminous coal, especially about specific extraction and extractive disintegration have been done as useful methods to study the chemical constitution of coal. However attempts to isolate a chemically pure substance from the extract and to determine its chemical structure have been scarce, so that no condensed aromatic hydrocarbon which is interesting in reference to the structure of coal has been obtained except methylanthracene isolated by F. Hofmann and P. Damm(1) from pyridine extract of Upper Silesian coal.

E. Donath(2) recognized the existence of anthracene and chrysene from color reactions of the carbon bisulfide and chloroform extracts of Rositzer coking coal, but he was not successful in isolating these substances. A. Pictet and coworkers(3) isolated two hydrogenated derivatives of fluorene from benzene extract of Saar coal.

Analytical compositions of the compounds separated by F. Hofmann and P. Damm suggested the existence of hydrogenated aromatic hydrocarbons having molecular weight of 230—330. From the measurement of molecular weight, boiling point, refractive index and H—C ratio, B. S. Biggs and J. F. Weiler(4) pointed out that the hydrogenation products of benzene extract and residue were both hydrogenated condensed ring compounds and similar in the molecular weight distribution. Therefore it seems reasonable to consider that the extract contains the materials similar to the fundamental unit of coal, in which highly condensed aromatic hydrocarbons may be included.

Furthermore it may be supposed that the crystalline substance noticed by R. V. Wheeler and C. Cockram(5) from the so-called γ_1 fraction of bitumen was a condensed aromatic hydrocarbon. The authors obtained a crystalline substance of high melting point from the benzene extract of Yūbari bituminous coal, and studied its chemical structure by means of ultraviolet absorption spectrum.

Experimental

Preparation of Bitumen—The extraction was carried out in five stages by a rotary bomb of five litres. Six hundred grams of Yūbari coal, ground through 60 Tyler mesh, were extracted once at 220°C., twice at 240°C. and finally twice at 260°C. The duration of each extraction stage was three hours. Two litres of benzene were used in each stage. The benzene solutions obtained from 3 kg. of coal were mixed and benzene was distilled off. The residual material from the extract was separated into the oily bitumen (127 g.) and the solid bitumen (195 g.) according to the ordinary method.

Isolation of Crystalline Substance—The oily bitumen was added to about twice its volume of fresh cold petroleum ether, allowed to stand, and the precipitate which appeared was filtered. The solid bitumen was extracted fifteen times with 500 cc. of petroleum ether each time. The extract was mixed with the precipitate from the oily

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(1) F. Hofmann and P. Damm, *Brenn. Chem.*, **3**, 73, 81 (1922): **4**, 65 (1923).

(2) E. Donath, *Chem. Ztg.*, **32**, 1271 (1908).

(3) A. Pictet, L Ramseyer and O. Kaiser, *Compt. rend.*, **165**, 58 (1916).

(4) B. S. Biggs and J. F. Wailer, *J. Am. Chem. Soc.*, **59**, 369 (1937).

(5) C. Cockram and R. V. Wheeler, *J. Chem. Soc.*, **1927**, 700.

bitumen and the fuller's earth. Then the mixture was repeatedly extracted with hot benzene. The benzene solution was concentrated by distillation and allowed to cool to obtain the crystalline substance. After recrystallizing from xylene it was sublimated at 280—290°C. under atmospheric pressure. The pale yellow crystal thus obtained showed the same melting point as that of the material obtained from the mother liquid of recrystallization. The yield of this material was 80 mg., 0.003% of the original coal in dry ash free basis, but the real content of the substance might be higher because of a considerable loss during isolation and purification.

m. p., 304.5—305.5°C.

Anal., Found: C, 94.01; H, 5.99.

Ultraviolet Absorption Spectrum—The ultraviolet absorption spectrum of this material was observed by photo-electric method in *n*-heptane, using Shimazu QM—60 spectrometer as a monochrometer and multiplier photo-tube 1P 28 as the detector of the incident and transmitted light. The estimation of the intensity of monochromatic ray was carried out by direct observation of micro-ammeter. The result obtained is shown in Fig. 1, where the ordinate is the absorbance and the abscissa is the wave length of light in mμ.

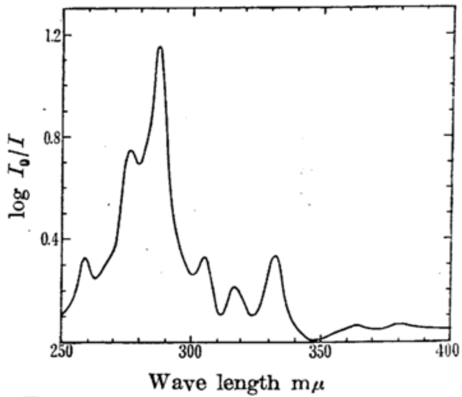
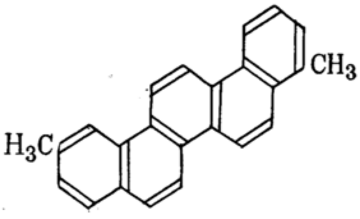


Fig. 1.—Ultraviolet absorption spectrum.

Result

Comparison of the wave numbers calculated from this spectrum with those of many condensed aromatic hydrocarbons having 4 or 5 rings which were reported by H. B. Klevens and J. R. Platt⁽⁶⁾ suggests that this material has a skeletal structure of either 1.2-benzanthracene, 3.4-benzophenanthrene or picene. If it is one of the 1.2-benzanthracene or 3.4-benzophenanthrene derivatives, it is considered as one of their methyl derivatives from its analytical composition. But their melting points are so much lower that the material can not be one of them. For instance the highest melting points of their isomers are as follows; 1.2-(3′-methylbenz) anthracence: 194—195°C., 3.4-benzo-6-methylphenanthrene: 80—81°C.⁽⁷⁾ If it is a picene derivative, its analytical composition shows very good coincidence with dimethylpicene. Three isomers of dimethylpicene have been synthesized by L. Ruzicka and coworkers, namely 2.11-dimethylpicene,⁽⁸⁾ m. p. 293—294°C., 4.9-dimethylpicene,⁽⁹⁾ m. p. 380—381°C., and 4.11-dimethylpicene,⁽¹⁰⁾ m. p. 305—306°C. Moreover L. Ruzicka reported that 4.11-dimethylpicene could be sublimated at 260°C. in a high vacuum. Therefore it appears certain that the material is 4.11 (?)-dimethylpicene.



Anal., Calc. for $C_{24}H_{18}$: C, 94.12; H, 5.88.

Discussion

The fact that the Yūbari coal bitumen contains 4.11 (?)-dimethylpicene may suggest that it is one of the hydrocarbon skeletons of fundamental unit of coal and comes in free state by chance. Though definite discussion is impossible owing to our poor knowledge of coal structure, the following facts can be pointed out as the foundation of this opinion;

1. H. C. Howard⁽¹¹⁾ described that coal had a polymeric character, and that cryoscopic measurement in catechol of the degradation products of Pittsburg seam coal always gave molecular weight of 250—350 due to the dissociating or depolymerizing action of strongly polar solvent catechol, which was considered as the molecular weight of the fundamental unit of coal. The authors found that molecular weight of the fractions of bitumen and pseudobitumen from Yūbari coal were approximately 280—360 when measured by the same

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(6) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949).

(7) G. Egloff, "Physical Constants of Hydrocarbon IV", Reinhold Publishing Corporation, New York (1947).

(8) L. Ruzicka and E. Mörgeli, *Helv. Chim. Acta*, **19**, 377 (1936).

(9) L. Ruzicka and K. Hofmann, *Helv. Chim. Acta*, **22**, 126 (1939).

(10) L. Ruzicka and K, Hofmann, *Helv. Chim. Acta*, **20**, 1155 (1937).

(11) H. C. Howard, *J. Phys. Chem.*, **40**, 1103 (1936).

method. The molecular weight of dimethylpicene is 306.

2. The coal is considered to be constructed from the crystallite having graphitic hexagonal structure from the viewpoint of X-ray diffraction. The breadths of network along "a" axis of regenerated humic acids from typical Japanese coals were measured by K. Inouye;(12) Yūbetsu coal: 12.4 A., Takamatsu coal: 9.6 A., Takashima coal: 14.3 A., and Shishimachi coal: 7.8 A. It seems to be same order of Yūbari coal. Assuming that the distance between carbon atoms in picene is nearly equal to graphite, the molecular dimension of picene is 11.3 A.

3. By the study about the hydrogenation products of benzene extract and residue from Edenborn coal, B. S. Biggs and J. F. Weiler(4) found that the ratios of the compounds having 5—7 condensed rings in the hydrocarbon skeletons of extract and residue were 23% and 15% respectively.

4. Picene(13) was included in condensed aromatic hydrocarbons obtained from hydrogenation product of coal which were described in the patents of I. G. Farbenindustrie.

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(12) K. Inouye, This Bulletin, **23**, 132 (1950).

(13) I. G. Farbenind., Brit. Pat. 470,338 (1936).