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THE ANALYSIS OF PILE IRRADIATED HYDROCARBONS WITH THE INFRARED SPECTROMETER

Progress Report I

By
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Hanford Works
Richland, Washington

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Progress Report I

INTRODUCTION

Samples of condensed ring hydrocarbons ranging in size from benzene to dinapthocoronene are being analysed after irradiation in the pile. The determination of primary importance is that for the amount of unchanged material, and this is being done by direct infrared analysis. In addition, the identification and analysis of the irradiation products are being attempted, using chromatographic techniques to isolate these products prior to identification by infrared analysis.

Direct infrared analysis of irradiated samples of benzene, naphthalene, anthracene, phenanthrene, 1,2-benzanthracene, pyrene, and 1,2,5,6-dibenzanthracene has been completed and some work has been done to determine the identity of the compounds produced from them by the irradiation process. When the materials are available, it is planned to irradiate and analyse samples of chrysene, perylene, triphenylene, coronene, dibenzocoronene, and dinaphthocoronene.

This work is being done in the hope that the results will shed light on the nature of the changes which occur in graphite upon irradiation in the pile. These compounds become increasingly graphite-like in structure with increasing molecular weight, and since their structures are known, the nature of changes which may occur upon irradiation may be deduced more readily after analysis of the resulting products than is true in the case of graphite, whose structure is incompletely known. These results may be of assistance in determining the cause of graphite expansion.

Work on this problem has been delayed for a considerable period because of difficulties in procurement of the more complex compounds in the series to be irradiated; however, there are a number of analogous studies in progress at various sites, so it is felt that the analytical techniques and results should be described in a progress report because of the general applicability of the methods employed.

SUMMARY

(1) Infrared analysis of irradiated samples of benzene, naphthalene, anthracene, phenanthrene, 1,2-benzanthracene, pyrene, and 1,2,5,6-dibenzanthracene has been completed.

(2) A sample of irradiated anthracene has been analysed chromatographically with results in excellent agreement with the infrared analysis.

(3) Combined chromatographic and infrared analysis show the presence of phenyl derivatives in the irradiation products from naphthalene, anthracene, and pehnanthrene. The latter two are also found to contain naphthyl derivatives.

INFRARED ANALYSIS

The instrument used in this work was the Perkin-Elmer, Model 12-C Infrared Spectrometer. Samples were dissolved in carbon disulfide prior to analysis so that fixed type liquid sample cells could be used, thus avoiding difficulties involving analyses with solid films or Nujol suspensions. Sodium chloride windows were used in the cells.

In general, the procedure followed in the analysis of these materials was much the same for each sample. The spectrum of each pure material at some suitable concentration in carbon disulfide was obtained and the absorption bands suitable for analysis selected by inspection of the absorption curves. A series of standard solutions of each compound was then prepared, using carbon disulfide as the solvent, and the absorption of each of these solutions measured by permitting the instrument to scan through the region of the absorption band, or bands, previously selected. In this way, a family of peaks (absorption bands) is obtained, the height of each being a function of the concentration of the solute plus the general absorption of the solvent. When the absorption of the solvent is subtracted at the wave length of maximum absorption due to the solute, the optical density of the solute at each concentration is obtained. These values are plotted against concentration on linear paper to obtain a calibration curve from which concentrations of unknowns can be determined after a measurement of their optical densities.

The absorption bands selected for purposes of quantitative analysis for the various compounds submitted as samples are shown in Table I. Where possible, more than one band is used to minimize the effect of interferences. The calibration data are not included here because of the number of measurements (approximately 240) involved, but from the total spread of points about the curves, a precision of ±2.5% is indicated.

TABLE I

LOCATION OF ABSORPTION BANDS FOR QUANTITATIVE ANALYSES OF CONDENSED RING HYDROCARBONS

Compound	Position of Absorption Band, cm^{-1}			
Benzene	1036	*	*	*
Naphthalene	955	784	*	*
Anthracene	727	*	*	*
Phenanthrene	810	734	*	*
1,2-Benzanthracene	883	799	781	748
Pyrene	846	745	710	*
1,2,5,6-Dibenzanthracene	803	748	*	*

*No other selection made.

Two groups of irradiated samples have been submitted and the determination made of the amount of material remaining unchanged after irradiation. The results are shown below in Table II. Calculations of percent loss assume 100% purity of materials before irradiation. As had been anticipated, the extent of destruction diminishes with increasing size of the molecule, an effect which favors the validity of extrapolating results to the graphite case.

TABLE II

RESULTS OF ANALYSES OF IRRADIATED HYDROCARBONS

A. Samples Submitted January 1, 1949

Sample	% Found		% Loss	
Benzene	55.0		45.0	
Naphthalene	69.0		31.0	
Anthracene	58.0)	58.5	42.0)	41.5
"	59.0)		41.0)	
1,2-Benzanthracene	77.0		23.0	

B. Samples Submitted January 25, 1949

Sample	% Found		% Loss	
Naphthalene	66.0)	65.5	34.0)	35.5
"	65.0)		35.0)	
Anthracene	55.6)	55.9	44.4)	44.1
"	56.2)		43.8)	
Phenanthrene	69.8)	68.1	30.2)	31.9
"	69.4)		33.6)	
1,2-Benzanthracene	69.9)	70.3	30.1)	29.7
	70.7)		29.3)	
Pyrene	71.2)	71.2	28.8)	28.8
"	71.2)		28.8)	
1,2,5,6-Dibenzanthracene	77.5)	77.9	22.5)	22.1
	78.3)		21.7)	

Questions may arise as to the validity of treating these samples as two component systems, i.e., compound plus solvent, for after irradiation numerous reaction products are present in addition to the parent compound. Actually the complexity of the reaction products makes this procedure feasible, for the reaction products are so numerous in kind that they contribute only a non-resolvable absorption, a sort of enhanced background, upon which the normal spectrum of the parent compound is superimposed. Thus, it is possible to balance out the non-selective absorption due to the irradiation products with the amplifier controls and then proceed with the measurement of the absorption due to the parent compound. While it is true that the complexity of the irradiation products presents a condition favorable to the determination of the unchanged parent compound, it was soon evident that direct infrared analysis would not serve to identify any of the products. This led to attempts to effect separations.

CHROMATOGRAPHIC ANALYSIS

Chromatographic techniques have been used with pronounced success in purifying compounds of this type (1), so it was reasoned that it might be possible to separate the unchanged parent compound from its irradiation products and thus obtain a check on the infrared analysis for the unchanged parent compound, and at the same time, improve upon the chances of identifying components of the irradiation products. Unfortunately, each sample presented a special problem because of the widely varying adsorption coefficients, and it soon became evident that the quantity of irradiated material (50 to 200 milligrams of each sample) at hand would be insufficient to complete development of chromatographic techniques. Accordingly, plans were made to irradiate 6-10 g. samples of at least the simpler compounds in order to provide sufficient material to effect accurate separations of the unchanged compound from its irradiation products and also to allow experimentation with the possibility of effecting further separations within the irradiation products themselves. At this writing the larger supply of irradiated samples has not been received.

Working with limited amounts of materials, it proved possible to separate anthracene completely and naphthalene and phenanthrene almost completely from their irradiation products by passing a carbon disulfide, or preferably, carbon tetrachloride solution of the sample through a column containing Al_2O_3 activated with lime water. Only the irradiation products are adsorbed. These may be eluted with acetone or methyl alcohol. Repeated treatment is required to effect complete removal of irradiation products. The separation may be considered complete when the weight of parent compound recovered from the column washings by evaporation to dryness becomes constant.

The results of analysis by this method applied to an irradiated anthracene sample are:

% Anthracene, Chromatographed from CS_2	53.3%
% Anthracene, Chromatographed from CCl_4	54.4%
% Anthracene, By Infrared Analysis	55.9%

Difficulty was experienced in effecting complete removal of naphthalene and phenanthrene from the column, although it was felt that this difficulty could be surmounted by varying the adsorbing power of the adsorbent or by more careful control of the washing. The method fails completely when applied to irradiated naphthacene samples, for this material adsorbs as strongly as its irradiation products.

The irradiation products were eluted from the column, evaporated to dryness, and redissolved in carbon disulfide. The absorption spectra of these solutions were then obtained on the infrared spectrometer. For the irradiated anthracene sample, the spectrum of its irradiation products show bands indicative of the presence of both naphthyl and phenyl derivatives. A similar result is obtained in the case of the irradiated phenanthrene sample. The irradiation products of naphthalene appear to contain only phenyl derivatives. With the limited amount of sample available further identification could not be effected.

ABSORPTION SPECTRA AT 400-700 mμ

The irradiated compounds all show pronounced changes in color and yield reddish amber solutions in carbon disulfide or other solvents. The absorption spectra of dilute solutions (0.03-0.06%) of irradiated naphthalene, anthracene, phenanthrene, 1,2-benzanthracene, pyrene, and 1,2,5,6-dibenzanthracene in carbon disulfide and in benzene were measured on the General Electric Recording Spectrophotometer. The results are the same in each solvent. No absorption bands occur, merely a sloping line showing increasing transmission with increase in wave length. Surprisingly enough, however, the curves for all samples may be almost exactly superimposed to give a single curve, a fact which indicates that the color producing compound to be found in the irradiation products from each sample is the same despite the dissimilarity of its various sources.

The absorption spectrum of naphthacene is a special case. This very insoluble compound gives a yellow solution in carbon tetrachloride, showing two distinct absorption maxima at 446 and 475 mμ. Since this material proved to be so insoluble that no satisfactory absorption spectrum could be obtained on its solutions using the infrared spectrometer, an attempt was made to develop a method for its determination using its absorption bands at 446 and 475 mu. Preliminary experiments showed, however, that the color exhibited by solutions of this compound is light-sensitive and fades rapidly on standing.

MISCELLANEOUS ANALYSES

Benzene is a somewhat special case inasmuch as it is the only liquid of all the compounds irradiated. Molecular fragments produced by irradiation have greater mobility in this case than is true of the other cases, and the results may be expected to differ appreciably.

Irradiation of benzene in the pile produced am amber colored resin of apparently very high molecular weight. The yield of resin was 36%. The resin proved to be totally insoluble in all solvents available for trial. It is insoluble in cold concentrated sulfuric acid and chars slowly. It melts with decomposition at a temperature in excess of 360°C. It can be ignited and will burn quietly in air with a yellow smoky flame. Attempts to test for the degree of unsaturation with bromine in carbon tetrachloride and with potassium permanganate in acetone failed as a result of the insolubility of the resin. A carbon-hydrogen analysis yielded the result:

$$\% \text{ C} = 89.48$$

$$\% \text{ H} = 7.31$$

The ratio of carbon to hydrogen is 12.2:1, indicating about the same degree of unsaturation as for benzene.

ACKNOWLEDGMENTS

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REFERENCE

(1) Zechmeister, L., and Cholnoky, L., "Principles and Practises of Chromatography," John Wiley & Sons, New York (1944), pp. 209-219.