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Gas Chromatographic Determination of C₂-C₁₀ Products from the Gamma Irradiation of Liquid Cyclopentane

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► Fourteen C₂ to C₁₀ products have been identified gas chromatographically from the gamma radiolysis of liquid cyclopentane. Direct analysis of an entire irradiation sample of less than 100 mg. allowed both a qualitative and a quantitative determination of these products over a wide range of total gamma dosage. Use of weighed encapsulated samples and internal standards allowed a high precision of all trace products observed in the presence of up to 10,000 times their weight of cyclopentane.

GAS CHROMATOGRAPHIC product analyses have been widely used in the study of radiation effects on organic materials (3, 7). Only since the advent of gas chromatography (2) has detailed evaluation of radiation processes become practicable. Despite this dependency, descriptions of this application of the technique are meager, which might be attributed to the routine nature of radiation product analyses. This work describes a modification of both radiation and analysis technique which simplifies procedures and allows precise determinations of radiation products. The direct analyses of irradiated samples were made using internal standards. The comparability and interpretation of results from micro and macro irradiations are discussed elsewhere (8).

APPARATUS

A modified version of the instrument described by Dimbat, Portor, and Stross (4) was used. The temperature range, 0° to 200° C. was obtained by placing a refrigeration radiator in the forced

air circulation oven. The refrigerant was stored in the compressor ballast tank when working above 50° C. A thermal conductivity cell, Gow Mac 9258 Pretzel, was used with a 2.5-mv. Weston recorder.

REAGENTS

Cyclopentane. Phillip's pure grade cyclopentane was purified by gas chromatography on a tritolyl phosphate column.

Reference Compounds. All but one of the required reference compounds were known. The following were obtained from Phillip's Petroleum Co. as pure grade: ethylene, propylene, *n*-butane, isobutylene, isopentane, *n*-pentane, 1-pentene, 2-pentene (*cis* and *trans*), 2,2-dimethylbutane, 2,3-dimethylbutane, methylcyclopentane, cyclohexane, *n*-heptane, and methylcyclohexane. In addition, use was made of a Phillip's gas mixture, No. 40, as a source of ethane, propane, isobutane, 1-butane, and 2-butene (*cis* and *trans*). Methyl iodide, ethyl iodide, and mesitylene were obtained from Eastman Kodak.

Cyclopentene was prepared by dehydration of cyclopentanol over 85% phosphoric acid; b.p. 43.8° C., *n*_D²⁰ 1.4203. 1,5-Hexadiene was prepared from allyl bromide and magnesium; b.p. 59.6° C., *n*_D²⁰ 1.4068. Allylcyclopentane was synthesized from cyclopentyl magnesium bromide and allyl bromide, following an existing procedure (1); b.p. 123.5-5.5° C., *n*_D²⁰ 1.4390. Vinylcyclopentane (9) was obtained on dehydration of β -cyclopentylethanol with 85% phosphoric acid; b.p. 98.5-100° C., *n*_D²⁰ 1.4356. Dicyclopentyl, from the reaction of cyclopentyl bromide and sodium (11), had a b.p. of 190° C., *n*_D²⁰ 1.4645. Ethylcyclopentane was obtained by hydrogenation of vinylcyclopentane, in propionic acid

solution, over platinum oxide; b.p. 100-5° C., *n*_D²⁰ 1.4185. Similarly, *n*-propylcyclopentane was made by hydrogenation of allylcyclopentane in ethanol solution; b.p. 130-1° C., *n*_D²⁰ 1.4258. *n*-Pentylcyclopentane was obtained in a fraction, b.p. 175-80° C., containing 10% *n*-decane, 50% *n*-pentylcyclopentane, and 40% dicyclopentyl, by gas chromatographic analysis, that resulted from the reaction of an equimolar mixture of *n*-pentyl iodide and cyclopentyl bromide with sodium in di-*n*-butyl ether.

Cyclopropylcyclopentane was prepared from the ditosylate of the known 2-cyclopentylpropane-1,3-diol (10) by treatment with a mixture of zinc, sodium iodide, and sodium carbonate in boiling acetamide following the general method of Hugh and McBee as reported by Whitmore and coworkers (13). The procedure and characterization of the compound have been described elsewhere (8).

COLUMNS

Preparation. All liquid phases were absorbed on 30- to 60-mesh Johns-Manville C₂₂ firebrick. The 20-foot 28% dimethylsulfolane (DMS) column contained 79 grams of packing. The TTP column held 63 grams of 28% *o*-tritolyl phosphate in 15 feet DC 550 silicone oil (20 grams of 25% liquid phase) was packed in a 6-foot column.

Operation. The DMS column was operated between -4° and 0° C. at a flow rate of 40 ml. per minute of He for the identification of C₁ through C₄ products. Low flow rates of 25 and 20 ml. per minute of He were em-

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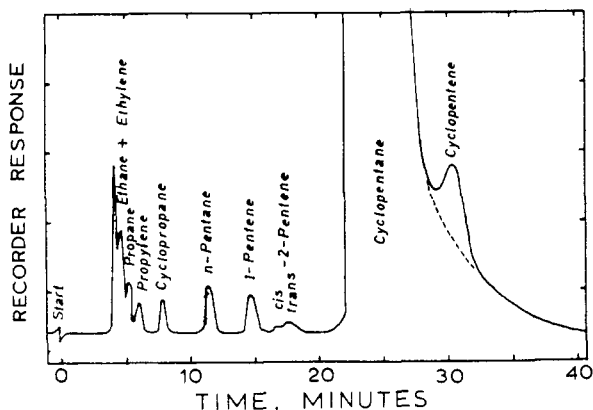


Figure 1. Gas chromatograph of irradiation mixture from cyclopentane showing the trailing edge extrapolation for starting material, DMS column at 46° C. with no internal standard

ployed, respectively, with the DMS column at 46° C. and the TTP column at 52° C., for C₅ product assignments. C₈ to C₁₀ products were determined on the TTP column at 175° C., 40 ml. per minute of He. Continuous operation of the TTP column at high temperatures for several weeks necessitated replacement of this column. The new column had identical retention ratios but a lower separation efficiency and failed to separate cyclopentane from cyclopentene at 52° C. in irradiated samples (maximum respective weight ratio <7 to 1000).

EXPERIMENTAL PROCEDURE

Chromatographically pure cyclopentane (20- to 70-mg. samples) in frangible glass capsules (0.5-ml. capacity) was subjected to gamma radiation in the High Level Gamma Irradiation Facility, Argonne National Laboratory, Lemont, Ill. An irradiated capsule was placed in the gas chromatograph inlet system, and a standard was introduced in a similar weighed ampoule or by gas expansion into the inlet system. The inlet chamber was evacuated before opening samples or introducing standard gases. The sample was opened, allowed to expand for 1 minute, and swept from the inlet system onto the column for exactly 60 seconds. The recorder inflection on initiation of inlet system flushing was used as the retention ratio reference point. Quantitative measurements were based on planimetry of the area outlined by extending peak sides, at their inflection point, to the base line. Where complete resolution was not achieved, an artificial base line was taken.

RESULTS AND DISCUSSION

The direct method of trace analyses developed required modifications of techniques for irradiation sampling and determination of the limitations in gas chromatographic analyses. The sampling technique depended on the analytical requirements for both qualitative and quantitative product de-

tection. Weighed ampoules (0.5 cc.) containing 20 to 70 mg. of cyclopentane were prepared for gamma radiolysis. Total conversion to products by irradiation never exceeded 10%, and the thermoconductivity detector response was directly equated on a weight to area basis, Table I. The sample size was increased from 20 to 70 mg. as total irradiation dose decreased. For analysis, samples were placed directly in the gas chromatograph crusher with a weighed ampoule of some standard material or a gas sample. Although no specific amount of standard was used, 0.3 to 0.7 mg. of standard was most conveniently measured with the requisite accuracy. The minimum precision in measurement on calibration materials, Table I, was 3%. A reproducibility of better than 1% was often observed.

A large increase in the amount of introduced material occurred when irradiation samples were analyzed rather than standard compounds. To compensate for small variations in sample introduction, a known amount of the standard substance was placed in the gas chromatograph with the irradiated sample. The amount of any product was then calculated from the area under product and standard peaks, the known weight of standard, and the weight per unit area relationship. The last of these corrections was necessary only for the C₂ hydrocarbons, Table I. The lowest product yield measured in this fashion was 0.004 ± 0.001 mole % which was 2 ± 0.5 μg. in an average sample of the six samples measured. The lower limit of detectability increased with increasing time because of peak broadening. Because of the superabundance of cyclopentane, the variations of detector sensitivity in the C₅ hydrocarbon range were most important. Optimum separations were obtained by operation of the several

columns at fixed temperatures. Two columns were used in identifying each product except for permanent gases where mass spectroscopy supplemented the results on one column.

The C₅ product separation (Figure 1) was the most difficult and amply illustrates both the problems and the simplicity of a direct analysis using internal standards.

Diethyl ether was chosen as a standard for the C₅ product identification. The improbability of this material occurring as a product, the clean separation of ether from other materials which might appear in this products group over a wide temperature range (Figure 2), and the sharpness of the standard peak were used as criteria for selection of the standard. Diethyl ether always preceded cyclopentane in elution from a polar liquid phase. Qualitative analyses using internal standards were based on the retention ratio, the retention ratio being defined as the ratio of retention times for a given component to that of the standard. The moment of sample introduction was taken as zero, and the peak maxima as the time of elution. A similar ratio can be obtained for symmetrical peaks using one half the sum of the leading and trailing edge ratios, where leading or trailing edge emergence times were divided by the standard peak maximum elution time. This edge ratio showed an appreciable increase in cyclopentane retention times particularly after column flooding, a good indication that slight dissymmetries in the cyclopentane peak at low concentrations were amplified for larger samples. Whether the flatness of large peaks was due to column flooding or to exceeding the detector sensitivity limits was not determined. The leading edge for any peak was relatively sharp, while the trailing edge was diffuse. Since an internal standard method was employed for both qualita-

Table I. Relative Weight to Area Ratios for Detector Response^a

Compound	Weight/Unit Area
Hydrogen ^b	66 ± 2
Methane ^b	17.3 ± 0.4
Ethylene ^b	24.2 ± 0.5
Propylene ^b	32.9 ± 1
n-Butane ^b	34.5 ± 1
Cyclopropane ^b	33.3 ± 1
Isopentane ^c	33.8 ± 0.1
n-Pentane ^c	33.4 ± 0.7
2,3-Dimethylbutane ^c	33.5 ± 1
Diethyl ether ^c	33.8 ± 0.4
Cyclopentane ^c	33.7 ± 0.5
Cyclopentene ^c	34.0 ± 0.3

^a Lower limit of quantitative determinations 1 to 5 μg. depending on retention time.

^b Measured at -4° to 0° C.

^c Measured at 52° C.

tive and quantitative analysis, the diffuse trailing edge caused by a corrugated bellows sample introduction chamber was reduced by allowing only a 60-second sweep of this chamber. More than 75% of the sample was swept into the column during 60 seconds at 52° C.

It was evident that *n*-pentane, 1-pentene, and 2-pentene, all of which precede the cyclopentane peak, would be determined in very small amounts since it was only necessary to increase the initial cyclopentane sample size. This is not the case for cyclopentene. In fact, when 100 mg. of Phillip's Petroleum research grade cyclopentane was used (0.02% cyclopentene), the quantitative gas chromatographic results for cyclopentene were only 50% of Phillip's mass spectroscopic analysis. In this case, the cyclopentane trailing

edge had been displaced so far that the cyclopentene appeared only as a shoulder and not as a distinct peak. Although the base line was displaced in all cyclopentene determinations, the extrapolation of the cyclopentane curve, Figure 1, gave reproducible results when a distinct cyclopentene peak appeared. Distinct peaks were observed for low irradiation doses in samples up to 75 mg. The prolonged sample sweep, 60 seconds, through a Sylphon bellows crusher chamber, 56.74 cc., caused a slight trailing even on small peaks but did not decrease reproducibility in quantitative determinations by peak triangulation and planimeter measurements. Standard samples showed the long slope on cyclopentane peaks to be a real trailing edge and not slow detector recovery after flooding.

The sharp leading edge and spreading

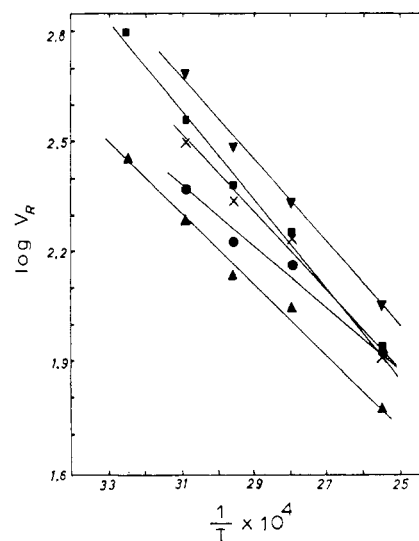


Figure 2. Effect of absolute temperature of chromatography on retention volume for four materials boiling between 34° and 39° C. and one higher boiling hydrocarbon, TTP column

Table II. Retention Ratios of Hydrocarbons and Selected Internal Standards

Column ^a	DMS		TTP		DC 550
	-4 to 0 <i>n</i> -Butane	46 <i>n</i> -Hexane ^b	52 Diethyl ether	175 Mesity- lene	173 <i>n</i> -Decane
Compound					
Air	0.347		0.176	0.109	
Hydrogen	0.351				
Methane	0.373				
Ethane	0.411				
Ethylene	0.428				
Propane	0.535				
Propylene	0.712				
Isobutane	0.748				
<i>n</i> -Butane	1.000				
Cyclopropane	1.16				
Acetylene	1.31				
1-Butene	1.50				
Isobutene	1.61				
<i>trans</i> -2-Butene	1.94				
<i>cis</i> -2-Butene	2.25				
Isopentane		0.460	0.476		
<i>n</i> -Pentane			0.575		
1-Pentene			0.664		
2,2-Dimethylbutane			0.681		
2-Pentene			0.790		
2,3-Dimethylbutane			0.899		
Diethyl ether			1.000		
<i>n</i> -Hexane		1.000			
Cyclopentane		1.12		0.164	
Cyclopentene		1.42	1.205		
Biallyl		1.89		0.198	
Methylcyclopentane		1.572		0.214	
Cyclohexane		1.936		0.224	
<i>n</i> -Heptane		2.058			
Ethylcyclopentane				0.250	0.401
Methylcyclohexane				0.302	
Vinylcyclopentane				0.351	
Methyl iodide		3.10			
<i>n</i> -Propylcyclopentane				0.374	
Allylcyclopentane		6.28		0.401	
Cyclopropylcyclopentane				0.457	
<i>n</i> -Decane				0.517	1.000
1-Decene				0.572	
Ethyl iodide		6.38			
<i>n</i> -Pentylcyclopentane				0.737	1.37
Mesitylene				1.000	
Dicyclopentyl				1.165	1.86

^a Column liquid phases are: DMS—dimethylsulfolane; TTP—*o*-tritolyl phosphate; and DC 550—Dow Corning 550 silicone oil.

^b Values measured in this work. Retention ratios for C₅ and some lower hydrocarbons were extrapolated, using 1-pentene as a standard, from the data of references (5) and (6).

trailing edge were useful in the gas chromatographic purification of cyclopentane. Although Phillip's research grade cyclopentane contains only traces of cyclopentene as an impurity, their pure grade contained traces of isopentane, *n*-pentane, and 2,2-dimethylbutane, but no cyclopentene. Since the impurities in the pure grade material all precede cyclopentane off the column (Table II), it was possible to purify 0.25 cc. of cyclopentane at a single pass. The small amounts of material necessary for a sample in this irradiation and analysis procedure made such a purification technique practical.

Although quantitative measurements were necessary to determine product *G* values, the qualitative identification of products has been the key to paths for irradiation decomposition. As shown in Figure 2, the separation between various types of organic matter was not invariant with temperature on a single column. Likewise, the order of elution and time required for appearance depended on the column liquid phase and carrier gas flow rate. No rigorous attempt was made to optimize all these conditions although a number of other columns, temperatures, and flow rates were tried. Those columns and conditions chosen were based on empirical separations of the expected irradiation products and literature reports (5, 6).

Identifications were made by determining the retention ratios of a pure compound relative to the inter-

nal standard. Thus, sample introduction point and the internal standard maxima were used as reference points. Those retention ratios measured are given in Table II. The selections for compound measurement were based on possible reaction mechanisms and reported products from analogous reactions (3, 7). The alkyl iodides were included for identification of halide products in iodine scavenger experiments. In employing the two-column method for identification, it was assumed that no two materials would have identical retention ratios on both columns. This assumption was valid for all the materials tested. The retention ratios for the radiation products were measured under the same conditions. The product assignments, Table III, were made by comparing retention ratios with those in Table II. In all cases, the retention ratio observed was within the limits of reproducibility for only one of the measured pure materials. In addition to the 14 C₂ to C₁₀ hydrocarbon products observed, hydrogen and methane were identified as products of cyclopentane gamma radiolysis.

The polar liquid phases employed had the same order of retention ratios for basic types of structural products eluted. The structural order was branched chain < straight chain < olefins < cyclic < cyclic olefins. Although all these peaks were identified, tracer experiments using the tritium radiation-exchange technique of Riesz

Table III. Identified Irradiation Products and Mole Per Cent Yields^a for C₂-C₁₀ Hydrocarbon Products at 10⁸ Rep.

Product	Mole % Yield ^b × 10 ²
Hydrogen	
Methane	
Ethane	
Ethylene	27 ± 1
Propane	14 ± 0.5
Propylene	13 ± 1
Cyclopropane	11 ± 3
n-Pentane	12 ± 1
1-Pentene	19 ± 1
2-Pentene	7 ± 1
Cyclopentene	52 ± 1
Methylcyclopentane	<1
Ethylcyclopentane	14 ± 1
Vinylcyclopentane	4.1 ± 0.2
Methyl iodide	
n-Propylcyclopentane	2.6 ± 0.3
Ethyl iodide	
n-Pentylcyclopentane	12.5 ± 0.5
Dicyclopentyl ¹	51 ± 1

$$\frac{\text{Moles Product}}{\text{Moles Starting Material}} \times 100 = \text{Mole \% Yield.}$$

^b Average values for three to six samples.

and Wilzbach (12) show a large number of radioactive peaks which may lie below the thermoconductivity detector noise level. Methylcyclopentane was identified in tritium radiation experiments.

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A Study of Trailing in the Paper Chromatography of Sugars

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► Some sugars and sugar acids were chromatographed to determine quantitatively the amount of material trailing behind the spot on the paper and the cause of this trailing. The approximate percentages of trailing material were 0.1% for maltose, 0.2% for glucose, arabinose, and sodium glucuronate, and 2% for sodium gluconate. Some of this material was the same as that in the spot. A number of variables were investigated for their effect on the amount of trailing material. The results support the explanation that adsorption is the cause of the trailing material.

THE prevailing opinion concerning filter paper chromatography is that it is a combination of liquid-liquid distribution, adsorption, and (where applicable) ion exchange (7). Little, however, has been done experimentally to determine what part each process plays. Theoretical treatments of liquid-liquid distribution (8), adsorption (4, 11), and ion exchange columns (9) generally assume linear adsorption isotherms and predict a Gaussian distribution of the solute for a large number of theoretical plates. These treatments seem applicable also to filter paper chromatography.

That is:

$$\frac{Q}{Q_{\max}} = e^{-1/2t^2} \text{ or } \ln Q - \ln Q_{\max} = -1/2t^2$$

where in this application,

Q_{\max} = the concentration of the solute at the center of the spot, or in the theoretical plate with maximum concentration

Q = the concentration of solute in a plate at a distance t from the plate of maximum concentration

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