tillation was treated as follows: the entire sample was dissolved in pure ethyl ether, using 15 ml. of solvent per gram of sample. The ethereal solution was then shaken with an excess of aqueous sodium carbonate in a separatory funnel. The saponified acid dissolved in the water and was removed. By repeating the operation several times, washing the ether solution with water and the water solution with ether, all the non-saponifiable material was concentrated in the ether solution.

After the ether was removed by gentle warming, the residual material was submitted to redistillation in the vacuum still described above. Distillates were identified from their physical properties as undecane or pentadecane which had not been completely removed in the previous distillations.

The residue from this treatment was an amber vaseline-like solid, which was found to be completely saturated, as determined by quantitative hydrogenation using Adams catalyst. Blank determinations on material which had not been bombarded failed to yield solid or liquid products.

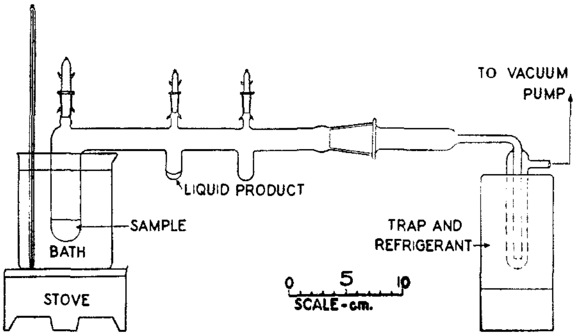

Fig. 4.—High vacuum still.

Acknowledgments.—The authors wish to thank Richard E. Honig and Earle C. Farmer for the mass spectrometric analyses. Hydrogenation apparatus was generously lent by Prof. N. A. Milas. Considerable advice and assistance was given by Prof. A. A. Morton. Many helpful suggestions were offered by Clark Goodman, W. L. Whitehead and I. A. Breger in the preparation of this manuscript.

Summary

There appear to be several processes involved in the decomposition of a fatty acid molecule under alpha-particle bombardment: (1) dehydrogenation, (2) decarboxylation, (3) formation of low molecular weight, water-soluble acids, (4) formation of methane and higher hydrocarbons, (5) production of carbon monoxide and water, either directly from the molecule or in small part from the action of alpha particles on the carbon dioxide and hydrogen already formed.

The predominant processes which have been observed are dehydrogenation and decarboxylation. There is some evidence that dehydrogenation does not occur in the same molecule as decarboxylation, since unsaturation is not found in the non-saponifiable products.

It has been shown that fatty acids can be decarboxylated by alpha-particle radiation to form hydrocarbons found in petroleum crudes.

CAMBRIDGE, MASS. RECEIVED APRIL 4, 1946

[CONTRIBUTION FROM THE DEPARTMENTS OF PHYSICS AND GEOLOGY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Effects of Radioactivity on a Naphthenic Acid[1,1a]

BY IRVING A. BREGER AND VIRGINIA L. BURTON

In a previous paper[2] initial investigations were reported regarding the possible role of radioactivity in the transformation of marine organic deposits into oil. Having shown that paraffinic components of petroleum can be produced by irradiation of fatty acids known to be present in source sediments, work has continued with an investigation as to the possibility that naphthenes can be produced similarly from naphthenic acids occurring naturally in association with petroleum crudes. The possibility of forming cycloparaffins by radioactive transformation is of particular interest to this theory of petroleum genesis, since these hydrocarbons are present to a considerable extent in all crude oils.

Naphthenic acids, similar to the one studied in this work, are known to occur in many crude oils in the range of from 0.03 to 1.6%. Although the majority of these acids contain cyclopentane rings, cyclohexane base acids have also been identified. In particular, cyclohexanecarboxylic acid was identified in Baku crudes by Tschitschibabin,[3,4] and Ney[5] reported the same acid in California petroleum. Homologs of this series have been identified in other Texas and California crudes.

The origin of these acids has been a matter of considerable discussion, but it has been well established that they exist in crude oils and are not formed by oxidation of petroleum.[6] From a consideration of facts surrounding the occurrence of the acids, it appears that they may be degradation products of sterols. It is hoped that this hypothesis can be investigated in the near future.

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(1) This paper is a contribution from American Petroleum Institute Research Project 43c. located at Massachusetts Institute of Technology: W. J. Mead. Director; Clark Goodman, Physical Director: W. L. Whitehead. Geological Director.

(1a) Presented before the Division of Organic Chemistry at the 109th meeting of the American Chemical Society. Atlantic City. New Jersey. April 9, 1946.

(2) Sheppard and Burton. THIS JOURNAL, **68**, 1636 (1946).

(3) Tschitschibabin, *Chem. Zentr.*, **101**. II. 2854 (1930); **103**, II. 952 (1932); *C. A.*, **25**. 2551^{9} (1931); **26**. 3654^{8} (1932).

(4) Tschitschibabin *et al.*, *Chem. Zentr.*, **104**, I. 3389 (1933).

(5) Ney, *et al.*, THIS JOURNAL, **65**. 770 (1943).

(6) Rogers. U. S. Geological Survey. Professional Paper 117. p. 14 (1919).

The study of the effect of alpha particles and deuterons on cyclohexanecarboxylic acid was primarily undertaken to determine whether the anticipated decarboxylation would lead to the formation of ring compounds, cyclohexane in particular, or whether ring cleavage would lead to the formation of straight chain compounds.

Bombardments

Two alpha bombardments were carried out in which 10- and 13-g. quantities of the acid were exposed to the alpha particles from approximately 100 millicurie sources of radon. Following decay of the radon, analysis of the gas that was evolved (Table I) indicated decarboxylation with some dehydrogenation. A colorless, liquid conversion product (34 mg.) was separated from the irradiated acid. Physical properties indicated that this might be cyclohexane along with unsaturated C_6 hydrocarbons.

In order to obtain sufficient conversion product for a complete analysis, two deuteron bombardments were run in the M. I. T. cyclotron. In the first, a pilot run, a small quantity of the acid (8 g.) was exposed to a beam of one microampere for one hour. All the gas formed was collected and analyzed. As indicated by the gas analyses in Table I, there is little or no difference between the chemical effects of alphas and deuterons. As before, a colorless liquid conversion product (95 mg.) was separated from the bombarded residue. This material had physical properties indicating the presence of cyclohexane and cyclohexene with, perhaps, cyclohexadiene.

Improvements in the design of bombardment chambers made it possible, at this time, to expose large volumes of liquid or relatively low-melting solid material in the cyclotron. Consequently, in a second deuteron bombardment, a large quantity of the acid (85 g.) was exposed to a beam current of 13 microamperes for two hours. This beam intensity was chosen because it caused the temperature of the acid to rise to a maximum of 95°, a temperature within the limits of geological oil formation.

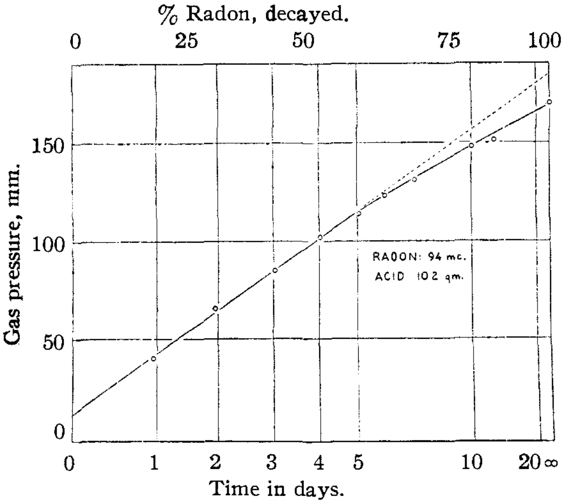

Fig. 1.—Alpha particle bombardment of cyclohexanecarboxylic acid.

A total of 3.069 g. of colorless liquid conversion product (3.5% yield) was recovered and was established as cyclohexane containing 12.5% by weight of cyclohexene. This analysis was qualitatively confirmed by infrared absorption spectra. Neither straight chain hydrocarbons nor cyclohexadienes were found present.

The acid remaining in the bombardment chamber, following removal of a small quantity of residual light conversion product, exhibited bright yellow-green fluorescence which was traced to non-saponifiable, viscous oil present in the irradiated acid to the extent of approximately 10% by weight. Data obtained indicated the greatest portion of this material probably to consist of dicyclohexyl ketone.

It has not been possible to draw up a satisfactory material balance for either the alpha or deuteron reaction. This in part is due to the fact that no accurate determination can be made of the actual number of molecules participating in the reaction, and in part to the fact that a large number of reactions appear to be taking place simultaneously.

Experimental[7]

Material.—The cyclohexanecarboxylic acid used in this work was purchased from the Eastman Kodak Company, Rochester, N. Y. It was used without further purification.

Alpha Bombardments.—Employing the technique and apparatus described by Sheppard and Whitehead,[8] the sample to be bombarded was evenly coated on the inner surface of a 200-ml. bulb to which was attached a mercury manometer. The entire system was evacuated before introduction of the radon.[9] Rate of gas formation was recorded (Fig. 1) and, following decay of the radon (half-life 3.85 days), the evolved gas was analyzed using a 60° Nier-type mass spectrometer.

TABLE I

COMPOSITION OF GAS EVOLVED DURING ALPHA AND DEUTERON BOMBARDMENTS OF CYCLOHEXANECARBOXYLIC ACID

Bombardments	Composition. %							
	H_2O	CO	CO_2	CH_4	C_2H_6	C_3H_8	C_6H_{12}[b]	H_2
Alpha	1.7	10	66	0.3	0.3	0.2	0.5	21[a]
First deuteron	3.1	2.6	67.5	1.5	0.3	0.5	2.4	22[a]

[a] Obtained by difference. [b] Cyclohexane.

Vacuum distillation of the irradiated acid was carried out in a still constructed as follows: A 200-ml. round-bottom flask was sealed to one arm of an inverted U-tube made from 15-mm. Pyrex tubing. A receiver was attached to the other arm through a 24/40 S.T. joint. The sample was admitted through a 10/30 S.T. joint sealed to the bulb side of the U-tube, and vacuum was applied to the system through this joint and a stopcock.

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(7) All melting and boiling points are corrected.

(8) Sheppard and Whitehead, *Bull. Am. Assoc. Petroleum Geol.*, **30**, 32 (1946).

(9) The authors are indebted to the New England Deaconess Hospital for their generous gifts of radon.

Operation consisted of adding the entire sample to the bulb and closing the system with the stopcock. The bulb and sample were then immersed in a liquid air bath for fifteen minutes at the end of which period the system was evacuated with a Hyvac pump. The liquid air bath was next transferred to the receiver, and the material in the bulb was slowly warmed and maintained at 100° for two hours. After the vacuum was released, the distillate (75 mg.) was collected as two immiscible liquids of approximately equal volume. The lower phase was shown to be water by its refractive index.

The entire sample was shaken with anhydrous sodium carbonate to remove traces of acid along with most of the water, and was then distilled, under reduced pressure, through a small phosphorus pentoxide plug. An attempt to fractionate 20 mg. of this distillate[10] showed its boiling point to be 81.1–81.8°.

Upon cooling to −78° crystals separated from the liquid. Slow warming caused disappearance of the last crystal at −30°. When a synthetic mixture containing 20% by weight of cyclohexene in cyclohexane was subjected to the same procedure, the last crystal disappeared at about −35°.

First Deuteron Bombardment.—Cyclohexanecarboxylic acid (8 g.) was bombarded in the copper, water-cooled chamber described by Honig.[11] A considerable degree of interaction between the acid and copper was evident from extensive blue coloration in the chamber and acid. A small volume of liquid containing no low boiling material splashed from the target holder into the gas chamber. The material remaining in the target chamber was subjected to the same vacuum distillation as described above. The distillate consisted of two colorless, immiscible liquids similar to those from the alpha bombardment. The upper phase was removed, shaken with sodium carbonate, and distilled through phosphorus pentoxide under reduced pressure. The phosphorus pentoxide plug turned black, indicating partial polymerization of the conversion products.[12] The dried, colorless distillate (95 mg.) had n^{20}D 1.4331, d^{20}_4 0.84. Quantitative hydrogenation with Adams catalyst in glacial acetic acid indicated the presence of 50% of material having one double bond per molecule (based on an average molecular weight of 84 for the anticipated cyclohexane).

Second Deuteron Bombardment.—To prevent interaction between the acid and copper, the large bombardment chamber to be used in this work was gold-plated.[13]

During the bombardment about 5 g. of liquid distilled or splashed from the target holder into the gas chamber, n^{20}D 1.4472. Liquid remaining in the target holder had turned yellow, become very viscous, and fluoresced yellow-green under ultraviolet light, n^{20}D 1.4778. Each liquid was vacuum distilled as before, only a small amount of light conversion product being recovered from the acid which had remained in the target chamber. From target chamber, distillate n^{20}D 1.4321, residue n^{20}D 1.4808; from gas chamber, distillate n^{20}D 1.4301, residue n^{20}D 1.4778. Cyclohexanecarboxylic acid (supercooled) n^{20}D 1.4620.

The distillate obtained from that material which had distilled into the gas chamber was shaken with anhydrous sodium carbonate and calcium sulfate: 3.069 g., n^{20}D 1.4285, d^{20}_4 0.78, b. p. 81.1–82.1°, specific dispersion 104. Hydrogenation indicated 17 ± 5% of material containing one double bond per molecule.

(a) To establish the nature of the unsaturated material in the above mixture, it (351 mg.) was ozonized in ethyl acetate at −30°. The solvent was removed under vacuum and upon addition of water, white crystals appeared. Analysis of this mixture showed the absence of acetic, oxalic, malonic, and succinic acids. The crystals were identified as adipic acid by their melting point. These results showed the absence of hexenes, hexadienes, and cyclohexadienes in the distillate, and identified the unsaturated component of the conversion products as cyclohexene.

(b) The absence of hexanes was shown by hydrogenating the distillate (241 mg.) in the absence of solvent using Adams catalyst. Following removal of the catalyst by centrifugation, the liquid had n^{20}D 1.4262, m. p. −1.5 to −0.5°; cyclohexane[14] n^{20}D 1.4263, m. p. 6.47°. Since this melting point depression could be attributed either to the presence of *n*-hexane originally present in the sample as a conversion product or to hydrogenation by-products, this liquid was further investigated.

The entire sample was fractionated in a column constructed of 8 mm. Pyrex tubing (10 cm. long) in which a Nichrome wire (32 gage) spiral had been wound. Using an air jet to condense the reflux, and an electrically controlled jacket around the column to maintain fractionating conditions, two fractions were obtained. Fraction I, m. p. 5.2–6.0°, n^{20}D 1.4262; Fraction II, m. p. 5.4–6.2°, n^{20}D 1.4262; residue, m. p. −10.0 to −5.5°, n^{20}D 1.4263. Hexanes, if present, would have shown up by depression of the melting point of Fraction I.

Since the refractive index *vs.* composition curve for mixtures of cyclohexane and cyclohexene was found to be a straight line, it was possible, from the value for the distillate, n^{20}D 1.4285, to establish the composition of the mixture as cyclohexane containing 12.5% by weight of cyclohexene. To confirm the analysis, infrared spectra were taken of the original conversion mixture and of a standard sample containing 14.0% of cyclohexene in cyclohexane. The spectra were identical in absorption peaks, nearly identical in intensity, and showed no indication of dienes.

The irradiated acid from the target chamber, following removal of low-boiling components by vacuum distillation as described above, was dissolved in *n*-hexane and saponified with an excess of aqueous sodium carbonate. After the hexane solution was dried over anhydrous calcium sulfate, the solvent was evaporated and a viscous, yellow-green, fluorescent oil was recovered in yield approximating 10% based on the quantity of acid bombarded: n^{20}D 1.4985, d^{20}_4 0.980.

TABLE II

PHYSICAL PROPERTIES OF FRACTIONS OBTAINED BY MOLECULAR DISTILLATION OF OIL FROM DEUTERON BOMBARDMENT OF CYCLOHEXANECARBOXYLIC ACID

	n^{20}D	d^{20}_4	Distil. temp., °C.
Original oil	1.4955	0.980	
Cut 1	1.4771	.935	(25)
Cut 2	1.4822	.943	25
Cut 3	1.4875	.987	50
Residue	1.5078		
Dicyclohexyl ketone[a]	1.4851/14°	.986	

[a] Anderson and Gooding, THIS JOURNAL, **57**, 999 (1935).

A 4-g. charge of the oil was subjected to molecular distillation in a specially designed semi-micro molecular still.[15] Physical properties of two of the fractions so obtained (Table II) suggested the presence of ketones, dicyclohexyl ketone in particular. Since the quantities of these fractions were very small, analysis by means of infrared absorption was undertaken. The spectra obtained showed absorption indicative of the carboxyl group and of cyclohexyl rings, adding further evidence for the presence of dicyclohexyl ketone.

Since the sodium carbonate solution from the above acid treatment was somewhat yellow even after further hexane extraction, it was shaken with several portions of ethyl ether. On evaporation of the ether a very small amount of very viscous, waxy, yellow substance was recovered, n^{20}D 1.5095.

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[10] Morton and Mahoney, *Ind. Eng. Chem., Anal. Ed.*, **13**, 494 (1941).

[11] Honig, submitted to *J. Applied Phys.*, Figs. 7 and 8.

[12] This was later traced to polymerization of cyclohexene; Truffault, *Bull. soc. chim.*, [5] **3**, 442 (1936).

[13] Honig, ref. 11, Figs. 4, 5 and 6.

[14] Huntress and Mulliken, "Identification of Pure Organic Compounds—Order I," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 587.

[15] Design to be published.

Acknowledgment.—The authors are grateful to R. E. Honig and E. C. Farmer for their help in the physical aspects of the problem, and for the mass spectrometric gas analyses; to T. A. Merritt and P. R. Walke of the Polaroid Corporation for their assistance in obtaining the infrared spectra; and to N. A. Milas and A. A. Morton for their helpful suggestions.

Summary

It has been proposed that naturally occurring naphthenic acids may be degradation products of sterols.

Irradiation of a naphthenic acid by alpha particles and deuterons has led to its transformation into a naphthenic constituent of crude oils.

It has been demonstrated that cyclohexane rings, and presumably the more stable cyclopentane rings, are not opened as a result of alpha or deuteron bombardment.

The mechanism by which cyclohexanecarboxylic acid was transformed into cyclohexane and cyclohexene is as yet unknown. The transformation may have taken place through any one of a number of processes as (1) simultaneous decarboxylation and dehydrogenation to cyclohexene, with subsequent hydrogenation of part of this compound to form the saturated hydrocarbon; (2) decarboxylation to cyclohexane followed by partial dehydrogenation to cyclohexene; (3) preliminary bimolecular reduction to intermediate dicyclohexyl ketone with subsequent conversion of this compound into hydrocarbons.

Work now in progress on the bombardment of benzoic acid and proposed for the bombardment of oleic acid may clarify the question of reaction mechanism depending upon whether or not hydrogenation of double bonds can be shown to take place.

CAMBRIDGE, MASS. RECEIVED APRIL 25, 1946

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS COMPANY]

Isomerization of Alkanes. III.[1] The Water–Aluminum Halide Reaction and Isomerization of *n*-Butane with the Reaction Product

BY R. C. WACKHER AND HERMAN PINES

In preceding papers of this series [1,2] it was shown that the isomerization of alkanes in the presence of aluminum bromide or aluminum chloride an be greatly influenced by "impurities" which might be present in the reagents as such or introduced through an improper experimental technique. Thus, it was found that under certain conditions, aluminum bromide–hydrogen bromide or aluminum chloride–hydrogen chloride does not cause the isomerization of *n*-butane to isobutane unless traces of olefins are present. Similarly, it was found that aluminum bromide or aluminum chloride can catalyze isomerization of *n*-butane even in the absence of olefins and hydrogen bromide if the reaction is carried out in the presence of traces of oxygen; the amount of oxygen in the form of air necessary to promote the isomerization being less than one mole per ten thousand moles of hydrocarbon present.

The present paper reports results on the effect of a third possible impurity, water, on the isomerization of *n*-butane, using aluminum chloride and aluminum bromide. We have found, in this investigation, some evidence of a new series of compounds formed by the reaction of aluminum chloride or aluminum bromide and water, and have produced in this reaction an isomerization catalyst for *n*-butane which does not require added hydrogen halide promoter and which produces only very small amounts of hydrogen halide during the isomerization reaction.

In order to investigate the role of water upon isomerization, it was necessary first to determine the effect of water upon the aluminum halides and then to investigate the effect of the compounds resulting from such an action upon the isomerization of *n*-butane.

The effect of water upon the isomerization of *n*-butane, using aluminum bromide or aluminum chloride catalyst, was studied by two methods. 1. Aluminum bromide or aluminum chloride was treated with various amounts of water, the mixture was heated, and any liberated hydrogen chloride or hydrogen bromide was pumped off. The resulting product, freed of non-combined hydrogen halide, was then used as a catalyst for isomerization of *n*-butane. 2. Aluminum halide, *n*-butane and water were mixed.

Aluminum Bromide–Water.—Preliminary exploratory experiments gave indications that possibly the aluminum bromide–water reaction, under certain conditions at least, was not the simple production of aluminum hydroxide and hydrogen bromide generally indicated. For example, when water was added to aluminum bromide at liquid nitrogen temperature and warmed slowly to room temperature, very little hydrogen bromide was generated. Upon further heating in a water-bath, the evolution of hydrogen bromide was still slow up to 75°, at which point the reaction was very rapid, with melting of the aluminum

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[1] For Paper II of this series see H. Pines and R. C. Wackher. THIS JOURNAL, 68, 595 (1946).

[2] H. Pines and R. C. Wackher, *ibid.*, 68, 599 (1946).