

are zero, and using the value $S_{298.16}^0 = 12.4$ E.U./mole for TiO_2 (rutile),¹¹ the following values for the entropy of $\text{Na}_2\text{O}(s)$ are calculated: $S_{298.16}^0 =$ (1) 16.7, (2) 16.7 and (3) 18.7 E.U./mole, with a mean of 17.4 E.U./mole. This value may be compared with the mean value of 17.2 E.U./mole similarly obtained by Kelley from data on three sodium silicates.¹²

(11) McDonald and Seltz, *ibid.*, **61**, 2405 (1939).

(12) Kelley, *ibid.*, **61**, 471 (1939).

Summary

The heat capacities of Na_2TiO_3 , $\text{Na}_2\text{Ti}_2\text{O}_5$ and $\text{Na}_2\text{Ti}_3\text{O}_7$ were measured in the temperature range 52 to 298°K.

The following molal entropies at 298.16°K. were computed: Na_2TiO_3 , 29.1 ± 0.1 ; $\text{Na}_2\text{Ti}_2\text{O}_5$, 41.5 ± 0.2 and $\text{Na}_2\text{Ti}_3\text{O}_7$, 55.9 ± 0.3 E.U.

From these entropy values and a value for rutile reported in the literature, the entropy of $\text{Na}_2\text{O}(s)$ at 298.16°K. is estimated to be 17.4 ± 0.8 E.U./mole.

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The Effects of Radioactivity on Fatty Acids^{1,1a}

BY CHARLES W. SHEPPARD² AND VIRGINIA L. BURTON

The genesis of petroleum remains an unanswered scientific question. Pyrolysis and high pressure have been proposed as factors contributing to the reduction to petroleum fractions of the complex organic substances found in source sediments. However, there is good reason to believe that petroleum is usually formed at much lower average temperatures than are necessary for pyrolytic conversion of organic compounds. The effect of high pressures on such transformations has never been definitely established.

The suggestion that radiations from the radioactive constituents of sedimentary rocks might be a factor in the conversion of gaseous paraffins to petroleum was first made by Lind and Bardwell³ about twenty years ago. More recently, Bell, Goodman and Whitehead⁴ and Tiratsoo⁵ stated that a more likely process for the genesis of petroleum by radioactivity is the decomposition and conversion of the solid and semi-solid organic compounds in marine sediments by alpha radiation. According to Trask and Wu⁶ and Wells and Erickson⁷ from 2 to 34 parts of fatty acids per 100,000 parts of sediment have been found in various marine muds. Clarke and Mazur⁸ have recently shown that the ether-extractable lipids of diatoms contain 60 to 80% of free fatty acids.

To test the radioactivity hypothesis, certain

organic compounds likely to be found in source sediments have been bombarded by alpha particles from radon⁹ and its active deposit. Since the molecular weights of the above fatty acids are not entirely certain, four acids of varying molecular weights were bombarded in the present experiments. These acids were acetic, caprylic, lauric and palmitic. Acetic acid was bombarded in the vapor state at 130°, and the others as solids. In all four cases the gas phase was analyzed after bombardment and, in addition, the solid residues of lauric and palmitic acids were examined.

Results

Decomposition of the solid acids during bombardment yielded a complex gas-liquid-solid system. As shown in Fig. 1, the production of gas from solid acids in the initial stages was proportional to the fraction of radon decayed. As the pressure of the gas increased, however, the relationship became non-linear because of partial absorption of radiation in the gas produced.

In each experiment the gas consisted mainly of carbon dioxide and hydrogen, with small amounts of carbon monoxide, water, methane, and higher hydrocarbons as shown in Table I. The per-

TABLE I
GASEOUS PRODUCTS FROM BOMBARDMENT OF FATTY ACIDS
WITH ALPHA PARTICLES

Constituents	Volume %			
	Acetic	Caprylic	Lauric	Palmitic
H ₂	18	33	42	48
CO ₂	37	51	41	34
CO	22	10	11	6
H ₂ O ^a	..	3	4	10
CH ₄ ^a	20	0.7	0.6	0.4
C ₂ H ₆ ^a	3.7	1.0	.5	.6
C ₃ H ₈ ^a	..	0.4	.1	.1
C ₄ H ₁₀ ^a	..	0.7	.2	.8

^a Mass spectrometric analyses.

(9) The radon used in these experiments was kindly provided by the New England Deaconess Hospital, Brookline, Mass.

(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) Present address: Vanderbilt University, Medical School, Nashville, Tennessee.

(3) Lind and Bardwell, *THIS JOURNAL*, **48**, 1556 (1926).

(4) Bell, Goodman and Whitehead, *Bull. Am. Assoc. Petroleum Geol.*, **24**, 1529 (1940).

(5) Tiratsoo, *Petroleum*, **4**, 58 (1941).

(6) Trask and Wu, *Bull. Am. Assoc. Petroleum Geol.*, **14**, 1451 (1930).

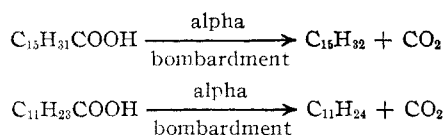
(7) Wells and Erickson, *U. S. Geol. Survey Professional Papers*, **186-D**, 69 (1940).

(8) Clarke and Mazur, *J. Biol. Chem.*, **141**, 283 (1941).

centage of hydrogen increased with the molecular weight of the fatty acid and, therefore, appears to be a function of the number of hydrogen atoms per molecule.

Small amounts of water-soluble fatty acids were found in the liquid-solid product of bombardment of lauric and palmitic acids. The lauric acid contained about 0.06 milliequivalent, and the palmitic acid 0.05 milliequivalent of acid per 100 millicuries of radon. The presence of such acids cannot be attributed to oxidation since the samples did not come in contact with air until immediately before extraction.

From lauric acid a liquid was obtained having the physical properties shown in Table II. Palmitic acid yielded a liquid having the physical properties shown in Table III. It is seen from these tables that the properties of undecane and pentadecane agree very closely with those of the respective compounds produced by alpha bombardment of lauric and palmitic acids. Thus it appears that one of the predominant reactions is decarboxylation



It is not to be assumed that simple decarboxylation is the only way in which carbon dioxide can be removed from the fatty acid molecule. In the case of palmitic acid it was observed that roughly 10^{-3} mole of carbon dioxide was produced when the acid was acted on by all of the alpha particles from the total disintegration of 100 millicuries of radon and its active deposit. If decarboxylation with the formation of a paraffin hydrocarbon is the only source of carbon dioxide, then it is to be expected that 210 milligrams of pentadecane would be produced. The optimum recovery of pentadecane per 100 millicuries was actually about 80 milligrams. It may therefore be concluded either that the recovery was incomplete or that carbon dioxide can be produced by other processes than decarboxylation, for example: bimolecular condensation to a ketone with the elimination of carbon dioxide and water.

TABLE II

LIQUID PRODUCT FROM LAURIC ACID		
Phys. properties	Liq. product	<i>n</i> -Undecane ^a
d_{20}^4	0.730	0.7402
n_{20}^D	1.4178	1.4173
$n_{20}^F - n_{20}^C$	0.0072	0.0070
%C	84.6	84.6
%H	14.9	15.4
Mol. wt.	152	156.3
B. p., °C.	195.5	195.8
M. p., °C.	-26.3	-25.6
Double bonds/molecule	0	0

^a Doss, "Physical Constants of the Principal Hydrocarbons," 4th ed., Texas Co., New York, N. Y., 1943.

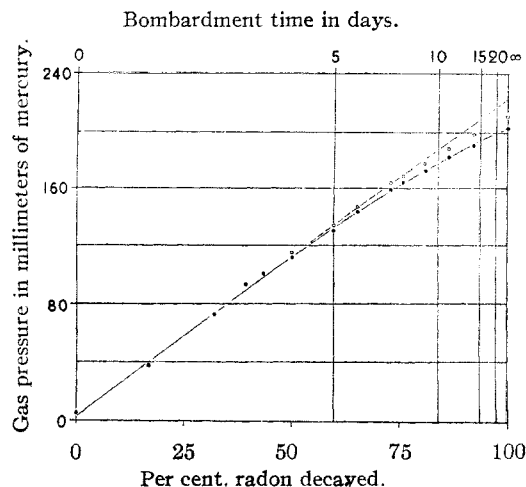


Fig. 1.—Gas production for a typical bombardment. Dots indicate recorded values; circles values corrected for absorption of energy from alpha particles by gaseous products.

It is to be understood that other decomposition reactions may occur in addition to those which have been observed in this research. A determination of any other decomposition products which may be present must await the development of better microtechniques or of large scale bombardments.

No attempt will be made to suggest a detailed mechanism for the chemical reactions produced by the action of alpha particles on fatty acid molecules. Current ideas concerning the role of the alpha particle energy in producing the reactions have been discussed elsewhere.^{10,11}

TABLE III
LIQUID PRODUCT FROM PALMITIC ACID

Phys. properties	Liq. product	<i>n</i> -Pentadecane ^{a,b}
d_{20}^4	0.7670	0.7689
n_{20}^D	1.4323	1.4326 ^b
$n_{20}^F - n_{20}^C$	0.0081	0.0076
%C	84.6	84.8
%H	15.4	15.2
Mol. wt.	209	212.2
B. p., °C.	273.0	272.7
M. p., °C.	7-8	10.0
Double bonds/molecule	0	0

^a Doss, "Physical Constants of the Principal Hydrocarbons," 4th ed., Texas Co., New York, N. Y., 1943.

^b Badin, THIS JOURNAL, 65, 1809 (1943).

Experimental

Bombardment Technique.—All four acids were bombarded in spherical bulbs using radon and its active deposit as the source of alpha particles. Acetic acid was bombarded in a 500-cc. bulb as a mixture of radon and acid vapor. A different method was used for the solid acids. Here the material was coated on the inner surface of the bulb, 7.5-cm. in diameter, to which was attached a manometer M and a side chamber C (Fig. 2). A stem was pro-

(10) Honig and Sheppard, *J. Phys. Chem.*, 50, 119 (1946).

(11) Sheppard and Honig, *ibid.*, 50, 144 (1946).

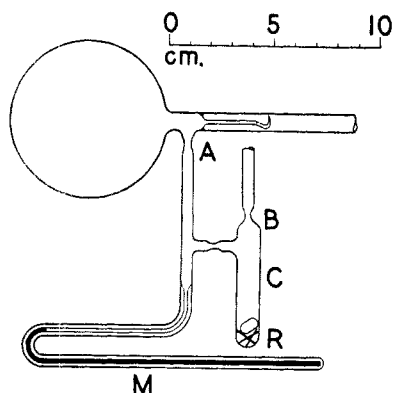


Fig. 2.—Bombardment bulb showing manometer and side chamber for introducing radon.

vided which communicated with the bulb through a thin walled hook seal A. When the radon needles, R, had been inserted into the side chamber, the system was evacuated and sealed off at B. By careful shaking, the glass needles were then broken under the impact of a glass pellet. After the side chamber was heated to facilitate the transfer of the radon into the larger volume of the main bulb, it was sealed off and removed, and the bulb was stored with the manometer upright. The technique has been described in more detail by Sheppard and Whitehead.¹² A description of the method of radon measurement is given elsewhere.¹⁰

system was evacuated, the hook seal on the bombardment bulb was broken by magnetically lifting the iron plunger and allowing it to fall. By means of a Töpler pump, gas was delivered to the apparatus as required. Only relatively small amounts of gas were available and for this reason the design of the gas analysis apparatus, shown schematically in Fig. 3, differs in scale from that commonly used in routine analyses. Carbon dioxide was absorbed with 50% potassium hydroxide, and carbon monoxide was removed with "Cosorbent." Hydrogen and methane were burned over a hot filament, and the higher hydrocarbons were frozen out with liquid air and then ignited.

The gas analysis data in Table I were supplemented by determinations made on a Nier-type 60° mass spectrometer,¹³ which is especially valuable for the identification of water vapor and small amounts of hydrocarbons.

Treatment of Acid after Bombardment.—The sour odor of the bombarded material suggested that certain water-soluble acids of low molecular weight were produced by the action of the alpha particles. For this reason, the material in the bulb was extracted several times with hot distilled water and titrated with 0.01 N sodium hydroxide. Blank extractions were made on the original lauric and palmitic acids to assure the absence of water-soluble acidic compounds in these materials before bombardment.

After water extraction, the sample was distilled in a small specially designed high vacuum still (Fig. 4). In each experiment a liquid distillate (approx. 80 mg./100 mc. radon) collected in the small depression in the side arm, and was identified from its physical properties as undecane (from lauric acid) or pentadecane (from palmitic acid).

Anal. Calcd. for $C_{11}H_{24}$: C, 84.6; H, 15.4. Found: (liq. distillate from lauric acid): C, 84.6; H, 14.9.

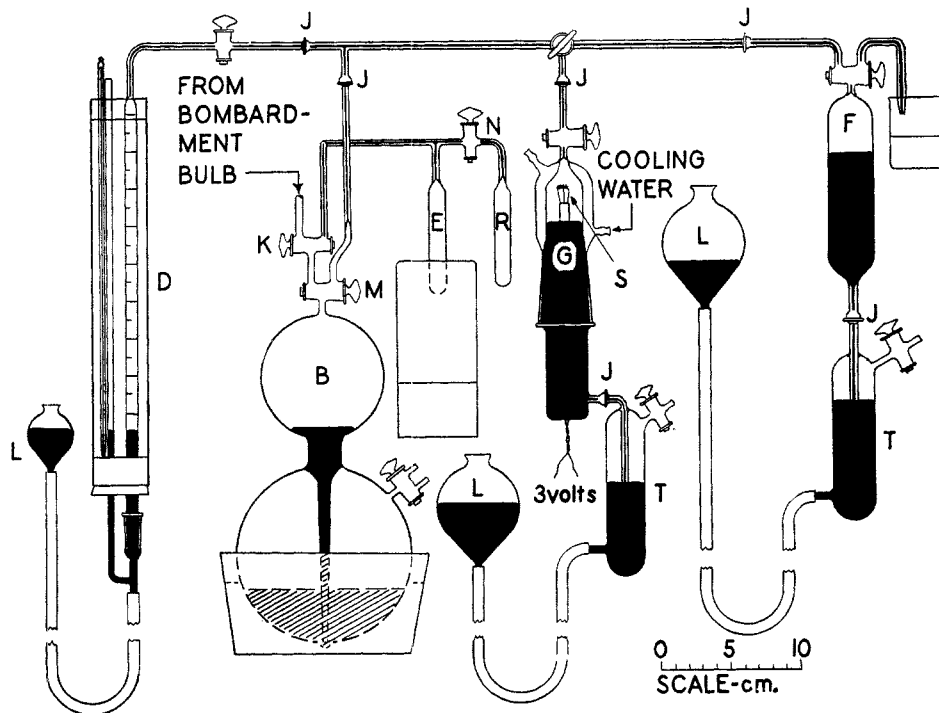


Fig. 3.—Gas analysis apparatus.

Gas Analyses.—The manometer was removed following decay of the radon to a negligible activity (6 weeks or more). An iron plunger was inserted in the stem of the bombardment vessel which was then attached to the analytical apparatus with a ground-glass joint. After the

Anal. Calcd. for $C_{15}H_{32}$: C, 84.8; H, 15.2. Found: (liq. distillate from palmitic acid) C, 84.6; H, 15.4.

In order to establish the presence or absence of higher boiling conversion products, the residue from each dis-

(12) Sheppard and Whitehead, *Bull. Am. Assoc. Petroleum Geol.*, **20**, 32 (1946).

(13) Constructed by R. E. Honig in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Massachusetts Institute of Technology, 1944.

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.

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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

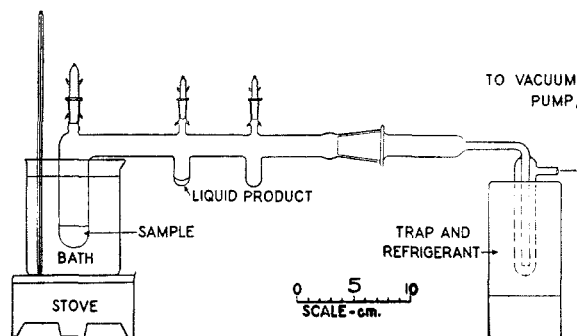


Fig. 4.—High vacuum still.

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.

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The Effects of Radioactivity on a Naphthenic Acid^{1,1a}

BY IRVING A. BREGER AND VIRGINIA L. BURTON

In a previous paper² 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

(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).

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 Ney⁵ 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.

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