[CONTRIBUTION FROM THE DEPARTMENT OF GEOLOGY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Effects of Radioactivity on Oleic Acid[1,2]

BY VIRGINIA L. BURTON

In initial research[3,4] pertaining to the role of radioactivity in petroleum genesis, it was shown that paraffinic components of petroleum could be produced by the irradiation with alpha particles or deuterons of certain fatty acids known to occur in source sediments. Likewise, a cycloparaffin has been produced from a naphthenic acid.

In all these early bombardments hydrogen was usually the major component of the gaseous products. However, since hydrogen is found only in minute quantities in the natural gases associated with petroleum, the theory that radioactivity plays a part in petroleum genesis has been subject to some criticism. Although it had been proposed that hydrogen could disappear to the atmosphere by diffusion through the cap rock, it seemed likely that the unsaturated compounds in source sediments might be hydrogenated under the influence of radioactivity and thus absorb at least part of the hydrogen produced.

Benzoic acid was the first unsaturated compound to be bombarded with deuterons in an effort to determine if the hydrogen usually produced during a bombardment would saturate the double bonds of the ring. That is, an effort was made to determine if hydrogen produced by the decomposition of one molecule would, under the influence of radiation, enter the ring of another molecule. The volume of gas produced was very small; it consisted of 85% of carbon dioxide and only 1.8% of hydrogen. No evidence has been found for the formation of the saturated compounds, hexahydrobenzoic acid or cyclohexane, and attempts to identify the infusible reaction product have been unsuccessful.

Because considerable data were available concerning the effects of radioactivity on the fatty acids, a carefully purified sample of oleic acid was bombarded in the M. I. T. cyclotron. Bombardment techniques and equipment have been described elsewhere.[5]

Results

Gaseous products were analyzed and found to consist mainly of carbon dioxide and hydrogen. Table I shows the complete analysis. The data from a preliminary alpha bombardment are given for comparison. The columns under "deuteron" represent analyses of the gas sample collected during each thirty-minute period of the two-hour bombardment. There appears to be a consistent increase in hydrogen production and decrease in carbon dioxide formation during the irradiation.

TABLE I

GASEOUS BOMBARDMENT PRODUCTS FROM OLEIC ACID

	Volume %				
	Deuteron[a]				Alpha[b]
Component	Cut 1	Cut 2	Cut 3	Cut 4	
H_2	41.2	44.0	55.1	56.4	50.0
CO_2	41.4	42.6	32.2	28.8	41.0
CO	5.8	4.5	2.9	6.8	6.0
H_2O	3.5	2.9	4.8	0.7	..
CH_4	3.9	0.4	0.5	4.2	1.8
C_2H_6	0.4	1.2	1.0	1.1	
C_2H_4	3.9	0.4	1.1	1.9	
C_3H_8		1.5	0.5		
C_4H_{10}		1.6	.9		
C_4H_8		0.6	..		
C_5H_{12}		0.4	.2		
C_5H_{10}		0.4	.1		
C_6H_{12}			.3		
C_7H_{16}			.1		
C_7H_{14}			.1		

[a] Mass spectrometric analyses. [b] Low temperature omit combustion analysis.

The acid changed during the bombardment from a light colorless liquid to an amber, fluorescent, highly viscous material resembling heavy motor oil. Thirty-one per cent. of the original oleic acid remained after bombardment. Of the material converted, 10% was recovered as non-saponifiable material, 52.5% as polymerized acid and an estimated 1.7% as stearic acid.

Thirty per cent. of the non-saponifiable material was separated as a light colorless hydrocarbon (3% of the original oleic acid).[6]

A second product from the bombardment was a viscous material remaining in the flask following the saponification. This material, which was insoluble in the alcoholic solution and in ether, went into soapy solution in water. After hydrolysis, these polymerized acids, which were now ether-soluble, weighed 10.5 g. (52.5% of the total oleic acid bombarded). Although an infrared analysis has been run, no further data have been obtained. It appears that polymerization occurs as a result of unsaturation since no polymerized acidic material had been recovered in earlier bombardments of saturated fatty acids.

After the stearic acid was isolated, it was purified and mixed with an authentic sample of the compound. The stearic acid recovered from the bombarded oleic acid had a melting point of 69.5° and the mixed melting point was 70°. No stearic

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

(2) Presented before the Division of Organic Chemistry at the 112th meeting of the American Chemical Society, New York, N. Y., Sept. 18, 1947.

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

(4) Breger and Burton, *ibid.*, **68**, 1639 (1946).

(5) Honig, *Rev. Sci. Instruments*, **18**, 389 (1947).

(6) Burton and Breger, submitted for publication.

acid could be detected in the original unbombarded oleic acid proving that hydrogenation had taken place under the influence of the deuteron beam.

The following material balance was drawn up for the bombardment:

Reactant	Mole
Oleic acid	0.201
Products	
(Total moles liberated during bombardment)	
Oleic acid (recovered after bombardment)	0.063
Carbon dioxide	0,043
Hydrogen	0.066
Other gaseous products	0.019
Heptadecene	0.007
Stearic acid	0.003
Polymeric acids (52.5%) and uninvestigated non-saponifiables (7%)	...
Total	0.201

The moles of polymeric acids formed could not be calculated because of the difficulty in determining the molecular weight of the material. These acids were insoluble in the solvents commonly used for this purpose and a high molecular weight is therefore inferred.

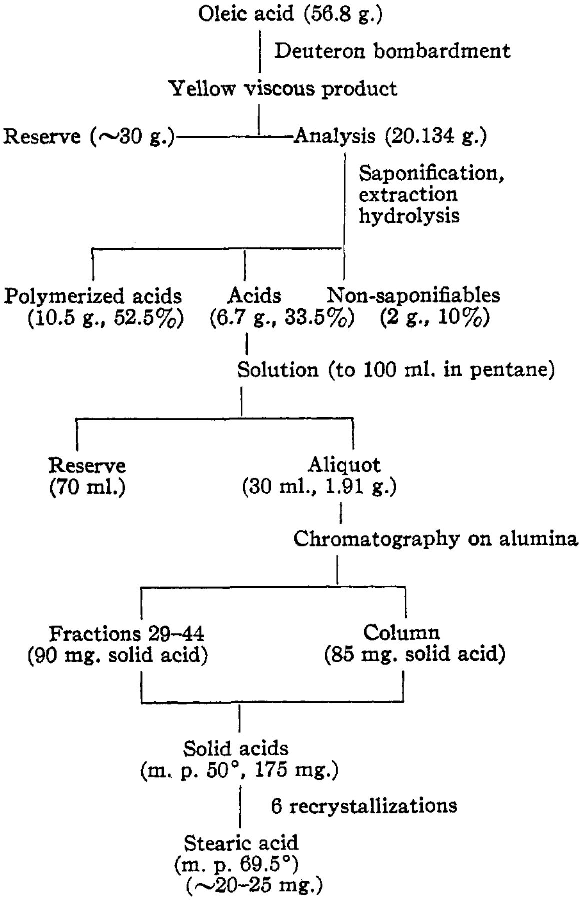

Fig. 1.—Analytical scheme used in separating stearic acid.

The number of molecules of oleic acid converted per one hundred electron volts of energy input was 2.16. Likewise, the number of molecules of stearic acid formed was 0.047. This indicates that approximately 2.5 molecules of stearic acid were formed for every one hundred molecules of oleic acid that were converted.

Experimental

Several methods for the purification of oleic acid were attempted, but a modification of the procedure of Wheeler and Riemenschneider[7] was used. This method consisted of the fractional distillation and crystallization of the methyl esters followed by hydrolysis and distillation of the acid.

Technical oleic acid (2 l.) obtained from the Eastman Kodak Company, Rochester, New York, was converted to the methyl ester by refluxing with 2 l. of methanol and 75 ml. of sulfuric acid for three hours. The methyl ester was then fractionated under 1–2 mm. of mercury in a two-foot jacketed Vigreux column to give 1765 ml. of product.

To simplify handling, all crystallizations were carried out batchwise. The ester (1320 ml.) was dissolved in 16.8 l. of acetone and cooled to −60° with stirring to remove the linoleic and linolenic acids. The heavy white precipitate of methyl oleate was rapidly filtered on a Büchner funnel maintained at the crystallization temperature by a Dry Ice–acetone jacket.

The crystals were allowed to melt, and the material was then dissolved in acetone (10 ml. per g.) and crystallized at −37° to remove palmitic and stearic acids. The precipitate was filtered on a Büchner funnel as before. This procedure was repeated twice and was then followed by another −60° crystallization; yield, 480 ml. Unlike the method of Wheeler and Riemenschneider, which included a second distillation of the methyl esters followed by two crystallizations at −65°, the methyl oleate was next hydrolyzed with alcoholic potassium hydroxide. The soap formed was carefully neutralized with hydrochloric acid to remove the pure acid and this was then fractionated under 1 mm. of mercury to yield 75 ml. of oleic acid, b. p. 220–221° (1.5 mm.), $n^{20}D$ 1.4592, freezing point (from curve) 5.74°–8.92°. Small percentages of linoleic and linolenic acids were probably still present in the final product. These compounds were of little importance to the object of this work.

The purified oleic acid (56.8 g.) was bombarded for two hours with an average beam intensity of 9 microamperes using the gold plated chamber described by Honig.[5] After the bombardment, 20 g. of the thick viscous product was saponified by refluxing for three hours with 50 ml. of 10% sodium hydroxide and 100 ml. of alcohol. The amber-colored solution was decanted from the insoluble polymerized acids and was then extracted with ether, enough water being added to yield two phases. A small amount of hexane was added to cut down the solubility of the water in ether.

The sodium hydroxide solution was acidified with excess hydrochloric acid and was extracted with ether which was then dried over sodium sulfate and evaporated on a steam-bath. The residue was made up to 100 ml. with pentane in a volumetric flask (6.7 g., 33.5% of the oleic acid bombarded). To a 30-ml. aliquot was added 70 ml. of pentane, 15 ml. of ether, and 2 ml. of benzene to obtain a clear solution which was then passed through a 12 × 800 mm. column packed with a mixture of five parts of J. T. Baker alumina to one part of Celite 545. The filtrate was collected in 10-ml. portions in a running chromatogram and the column was washed with 175 ml. of the pentane–ether–benzene solution, 50 ml. of pentane containing 10% methanol, and 120 ml. of pentane containing 20% methanol. A total of 44 cuts was collected.

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(7) Wheeler and Riemenschneider, *Oil and Soap*, **16**, 207 (1939).

Fractions 29–44 contained an infusible solid in each flask after the solvent was evaporated. When ether was added the precipitate swelled and became very gelatinous. Following hydrolysis of several of the above cuts with hydrochloric acid, extraction with ether, and evaporation of the solvent, an oily residue remained indicating that the acids had come through the column as aluminum salts. Since a solid residue was recovered from cut 44 after hydrolysis, cuts 29–44 inclusive were combined, hydrolyzed, extracted with ether and dried over sodium sulfate. After the ether was evaporated on a steam-bath, 90 mg. of solid material was separated from the above cuts by crystallization from acetone at −20°.

The chromatographic column was next cut into four sections each of which was eluted with methanol. The three lower sections contained gelatinous precipitates which, after hydrolysis, yielded solid residues. One hundred and seventy-five milligrams of solid material (m. p. 50°) was separated from the column and the filtrates. By means of six crystallizations from acetone at −20° in a centrifuge tube, the melting point of this solid was raised from 50 to 69.5°. A mixed melting point with authentic stearic acid was 70° (stearic acid, m. p. 70°). All melting points were taken on a microscope hot stage. The analytical scheme to this point is shown in Fig. 1.

Because the loss of stearic acid during recrystallization was so great, it was necessary to use an indirect method to estimate the amount present. A blank chromatogram containing 3% of stearic acid (42 mg.) in the purified oleic acid was next run. Seventy-four milligrams of solid acid (m. p. 50°) was separated as above. From melting point curves for mixtures of oleic and stearic acids,[8,9] it was established that the isolated material contained 25% of stearic acid, a recovery of 18.5 mg. or 44%.

The solid separated from the bombarded oleic acid (175 mg.) also contained 25% stearic acid (43.8 mg.) as indicated by its melting point of 50°. After correcting for the 44% recovery by chromatography, as indicated above, it was found that the stearic acid isolated (100 mg.) amounted to 5.3% of the non-polymerized saponifiable material. On the basis of the original acid bombarded this figure becomes 1.7%.

Since the stearic acid isolated had been concentrated by a factor of nearly three upon the removal of the polymeric acids and the non-saponifiable material (62.5%), it was necessary to determine if the acid (1.7%) represented original impurity which was below the limit of chromatographic detection using the unbombarded acid. A sample of the purified oleic acid to which was added 1% of stearic acid was, therefore, chromatographed by the above procedure and the stearic acid was easily detectable. No stearic acid could be isolated when the oleic acid itself was chromatographed.

This work indicated that the original oleic acid contained less than 1% of stearic acid and the bombarded oleic acid contained approximately 1.7%, both values being determined by the same analytical technique. It was thus shown that oleic acid was hydrogenated to stearic acid.

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Summary

Purified oleic acid has been bombarded with deuterons in the M. I. T. cyclotron. Analysis of the irradiated material has revealed the formation of stearic acid, heptadecene, and polymerized acids.

It has been shown that the hydrogen produced by decomposition of an organic molecule under the influence of radioactivity can enter the double bond of a neighboring molecule. It has thus been demonstrated that hydrogen which may be produced by the effects of radioactivity on the organic constituents of a petroleum source sediment could, in part, be removed from the gas phase by reaction with unsaturated components of the sediments.

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[8] Smith, *J. Chem. Soc.*, 974 (1939).

[9] Markley, "Fatty Acids," Interscience Publishers, New York, N. Y., 1947, p. 124.

[10] Original manuscript received January 28, 1948.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Metal–Salt Interactions at High Temperatures: the Cerium–Cerium Chloride System[1]

BY DANIEL CUBICCIOTTI[2]

The properties of alkali halide crystals containing excess metal have been the subject of extensive investigation by Pohl and co-workers.[3] Their study has led to an explanation of the ability of an alkali halide to dissolve excess metal and to the development of the theory of lattice defect points in crystals.[4] For divalent halides, studies of the miscibility of metal and salt have been made[5]; however, few other data have been accumulated on such systems. Only one report of metal–salt equilibria for trihalide salts is known to this author. The bismuth–bismuth trichloride and bismuth–bismuth tribromide phase diagrams are reported by Eggink.[6] These systems appear to be similar to those recently reported for divalent halides.[5]

To extend the data in the field of metal–salt equilibria the present study on a trivalent halide was made. The system cerium–cerium chloride was chosen because the melting point of cerium

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[1] This work was conducted under the direction of the late Professor E. D. Eastman and sponsored by the Manhattan Project.

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[3] Pohl, *Proc. Physical Soc.* (*London*), **49**, extra part, p. 3 (1937).

[4] For a discussion see: Mott and Gurney "Electronic Processes in Ionic Crystals," The Oxford Press, London, 1940.

[5] Cubicciotti and Thurmond, THIS JOURNAL, **71**, 2149 (1949).

[6] Eggink, *Z. physik. Chem.*, **64**, 493 (1908).