FUNDAMENTAL ASPECTS OF THE DIAGENESIS OF ORGANIC MATTER AND THE FORMATION OF HYDROCARBONS

Abstract

In many young sediments that have never been buried to great depths, there is a predominance of n-alkanes with an odd number of carbon atoms over those with an even number, in the range of about 27 to 37 carbon atoms. One of the things this "odd predominance" depends on is the depth of burial; with increasing depth it tends to disappear, and in petroleum accumulations the n-alkanes show a smooth distribution.

It is often suggested that the n-alkanes are derived from normal fatty acids, which in living organisms generally have an even number of carbon atoms. Since mere decarboxylation of these fatty acids would give n-alkanes with an odd-number of carbon atoms, however, this cannot be the only mechanism by which the transformation takes place. Other evidence that much more complicated processes occur is that the fatty acids present in petroleum accumulations likewise have a smooth distribution.

In order to gain a better insight into these processes, we have experimented with behenic acid, a straight-chain fatty acid with 22 carbon atoms. Mixed with clay and heated at 200°C this acid generates hydrocarbons and fatty acids. In the absence of water, the ratio of the branched-chain to straight-chain C_4 or C_5 hydrocarbons is much higher than in the presence of water. In addition to n-C_{21} and lower n-alkanes, n-alkanes with 22 to 34 carbon atoms and fatty acids with 15 to 25 carbon atoms are formed. It has been concluded that, because isomerization is strong in the experiments without water, carbonium ions act as intermediates in the generation of low-molecular-weight hydrocarbons. Since isomerization is much less pronounced in the experiment with water, radicals are likely to be the intermediates in the formation of the low-molecular-weight hydrocarbons. The formation of long-chain n-alkanes and long-chain fatty acids is assumed to take place through the intermediary of radicals both in the experiments with and in those without water.

The results of these experiments can be explained by a

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Résumé

Les sédiments jeunes qui n'ont jamais été enfouis à de grandes profondeurs, contiennent des n-alkanes caracterisés par la prédominance de molécules à nombre impair de carbone, dans la série des homologues de 27 à 37 atomes de carbone. L'un des paramètres dont dépend cette prédominance est la profondeur d'enfouissement. Quand l'enfouissement augmente, la prédominance des molécules à nombre impair de carbone tend à disparaître. Dans le brut, les n-alkanes montrent, par contre, une répartition homogène des molécules à nombre pair et impair de carbone.

Il a été souvent supposé que les n-alkanes provenaient des acides gras normaux, qui dans les organismes vivant, ont généralement un nombre pair d'atomes de carbone. Parce qu'une simple decarboxylation de ces acides gras devrait donner des n-alkanes impairs, ceci ne peut pas être le seul mécanisme assurant la transformation. Des réactions plus complexes sont probables, comme le montre aussi la distribution homogène des molécules des acides gras dans le brut.

Afin d'étudier ces réactions, des expériences ont été faites avec l'acide béhénique, un acide gras à chaîne droite à 22 atomes de carbone. Chauffé à 200° avec de l'argile, cet acide donne des hydrocarbures et des acides gras. En l'absence d'eau, le rapport: hydrocarbures C_4 ou C_5, à chaîne ramifiée sur hydrocarbures à chaîne droite est nettement plus élevé qu'en présence d'eau. En plus des n-alkanes à 21 atomes et moins, des n-alkanes ayant 22 à 24 atomes de carbone ainsi que des acides gras avec 15 à 25 atomes de carbone sont formés.

La forte isomérisation dans les expériences sans eau, permet de penser que l'ion carbonium agit comme un intermédiaire dans le processus de génération des hydrocarbures à poids moléculaire bas. Dans les expériences en présence d'eau, il y a très peu d'isomérisation et c'est pourquoi nous pensons que des radicaux jouent probablement dans ce cas un rôle d'intermédiaires. On peut supposer que la formation des n-alkanes et des acides gras à chaînes longues est produite par l'intermédiaire de radicaux dans les expériences avec aussi bien que sans eau.

Le résultat de ces expériences peut être expliqué par un mécanisme de réaction qui en partant d'un acide

reaction mechanism by which a petroleum-like mixture of n-alkanes and fatty acids can be generated from even-numbered fatty acids initially present in the living organism.

gras saturé pair peut produire un mélange de n-alkanes et d'acides gras, semblable à du pétrole brut.

INTRODUCTION

Although some investigators concerned with the formation of petroleum consider it possible that petroleum has been formed in part from inorganic substances, most of them assume that oil is derived from the remains of plants and animals deposited together with fine-grained minerals on the bottom of seas and lakes. During diagenesis this organic material is partly converted by microbial processes. With increasing overburden, the sediment is exposed to such temperatures that bacterial processes become impossible and only a chemical conversion of part of the organic matter into oil can take place. The aim of our investigation has been to obtain a better insight into these chemical processes.

Seeking a suitable system for investigation we observed that although analysis of crude oils has often shown them to contain compounds that bear no resemblance to those occurring in living organisms, it has also shown them to contain others that do resemble such compounds strikingly. For instance: pristane and phytane resemble phytol, porphyrins resemble chlorophyl or haemin, some tetracyclanes resemble steroids, and normal alkanes resemble normal fatty acids or wax alcohols. This suggests that the ones may have been formed from the others by not very complicated processes. One of these processes might well be a suitable subject for further study. The one we have chosen is the formation of n-alkanes from a straight-chain fatty acid.

It was already known in 1934 by Chibnal[1] that in plant waxes normal alkanes with an odd carbon number predominated over those with an even carbon number in a certain range. Bray and Evans[2] observed the same phenomenon with normal alkanes isolated from Recent sediments. Cooper and Bray[3] have investigated the distribution of the n-alkanes in various Recent and ancient sediments and in petroleum. Their results show that the predominance of odd-numbered n-alkanes decreases with increasing age and depth of the sediments and that in petroleum the n-alkanes are smoothly distributed. A simple decarboxylation of natural fatty acids, which have in general an even number of carbon atoms, would yield odd-numbered n-alkanes, and thus the odd-predominance of the n-alkanes would be maintained. Cooper and Bray have also investigated the distribution of fatty acids present in Recent and ancient sediments and in petroleum reservoir waters. The predominance of fatty acids with an even number

of carbon atoms decreases with increasing age and depth of the sediment and in petroleum reservoir waters the fatty acids show a smooth distribution.

The tendency of the odd-predominance of the n-alkanes and the even-predominance of the fatty acids to decrease with increasing age and depth of the sediment in which they are found and the smooth distribution of these compounds in petroleum and in petroleum reservoir waters appear consistent with the generation of a petroleum-like mixture of n-alkanes and fatty acids in the sediments.

The parallelism between the disappearance of the odd-predominance of the n-alkanes and that of the even-predominance of the fatty acids suggests that there is a relationship between the processes by which these n-alkanes and fatty acids are formed. Cooper and Bray have suggested that a petroleum-like mixture of n-alkanes and fatty acids can be formed by a stepwise degradation of the carbon chain of the even-numbered fatty acids, initially present in the living organism. This degradation is initiated by the decarboxylation of the fatty acid. The intermediate formed reacts to give two products, an n-alkane and a fatty acid. Each of these products would have one carbon atom less than the original acid. The acid produced would undergo the same reaction to form a new acid and a new n-alkane, and so on. The formation of a fatty acid from a radical infers oxidation but no experimental evidence is presented to suggest that this takes place.

Another intriguing problem in the origin of petroleum is the occurrence of gasoline. Erdman[4] recently reported that in Recent sediments he found in the low-molecular-weight range only methane and heptane, whereas in ancient sediments he found in that range all types of hydrocarbons. The same author[5] has given a possible explanation for the appearance of the gasoline fractions of petroleum. He points out that decarboxylation and deamination of the common natural amino-acids would yield all the possible saturated hydrocarbons up to and including C_5, with the exception of neo-pentane.

In view of the foregoing, it is likely that the formation of petroleum involves the subjection of the original source material to a natural cracking process.

Seyer[6] studying the kinetic constants of "thermal cracking" concluded that even within geological time, this type of reaction could not have produced petroleum. Montgomery[7] suggested that the naturally

occurring minerals might act as catalysts and thus accelerate natural hydrocarbon production to such an extent that the reaction became geologically acceptable. The catalysing effect of fine-grained inorganic matter has been extensively discussed by Brooks[8] who concluded that the mechanism of "catalytic cracking", in which carbonium ions are the intermediates, played an important role in hydrocarbon production. Bogomolov[9] and Bedov[10] studied the influence of silica/alumina catalysts on the decomposition of unsaturated fatty acids. Klubova[11] studied the influence of clay minerals on the transformation of sedimentary organic matter into petroleum hydrocarbons and concluded that the catalytic action of the clay minerals is not due to their structure and chemical composition but to their highly dispersed state.

As the clay constituent of the mixture we selected kaolinite; this clay did not contain any detectable amounts of hydrocarbons or fatty acids. The content of organic carbon was 0·04%.

Two and a half grammes of the clay (air-dry) was thoroughly mixed with one gramme of the behenic acid; the mixture was then placed in ampoules, sealed off under vacuum and heated. Our method of isolating the reaction products is outlined in the following diagram:

(1) The ampoules were opened in an atmosphere of hydrogen. The volatile components were stripped off and frozen out in liquid nitrogen. The low-molecular-weight hydrocarbons of this fraction were analysed by gas chromatography.
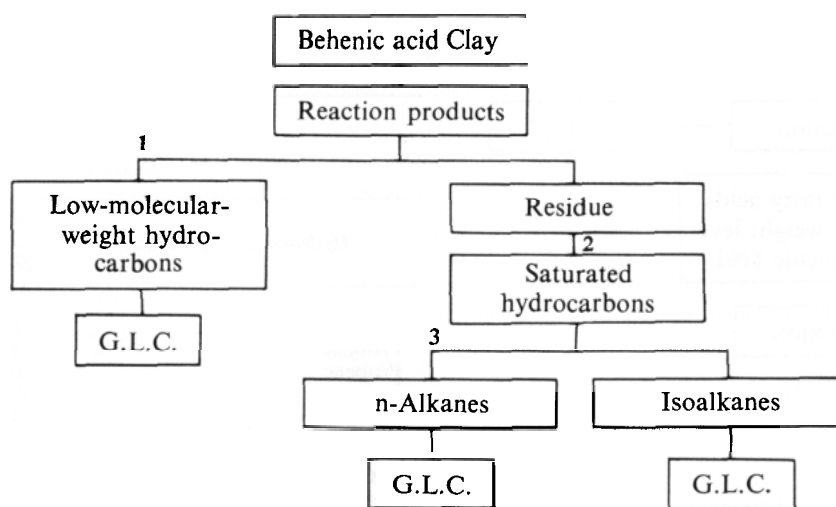
Jurg and Eisma[12] reported on the generation of low-molecular-weight hydrocarbons and long-chain n-alkanes from behenic acid which was heated in the presence of clay and water. Since that time these authors have done some complementary experiments with behenic acid. These experiments have led to the suggestion of a reaction mechanism which may be a key to the explanation of the smooth distribution of n-alkanes and fatty acids in petroleum accumulations.
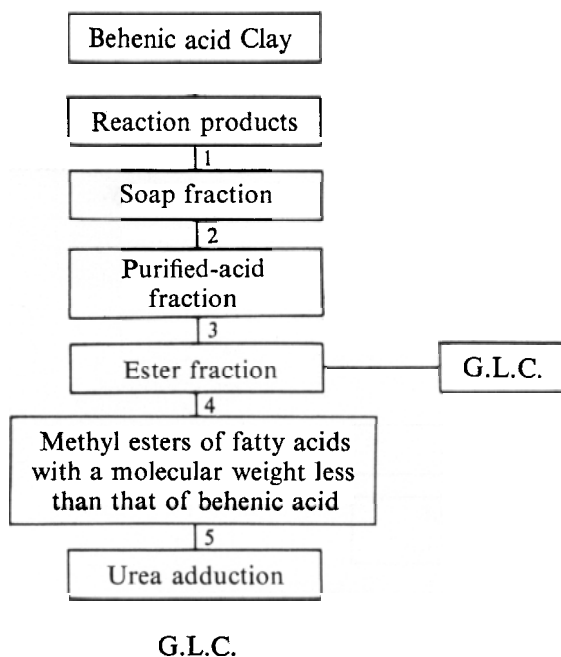
EXPERIMENTS

The behenic acid ($C_{21}H_{43}COOH$) was first purified by distillation and several recrystallizations of the methyl ester. The fatty acid recovered was recrystallized several times. Blank runs with the purified acid did not show the presence of either hydrocarbons or any other fatty acid.

(2) The residue was extracted with n-pentane. The extract was chromatographed over a column of SiO_2/Al_2O_3, in order to separate the saturated hydrocarbons from the other compounds.

(3) The saturated hydrocarbons were separated by urea-adduction into a fraction rich in n-alkanes and a fraction containing the branched-chain and the cyclic hydrocarbons. These fractions were analysed by gas chromatography.

Our method of isolating the fatty acids from the reaction mixture is outlined in the following diagram:

(1) The reaction products were treated with alcoholic KOH in order to obtain the soaps.
(2) The soaps were acidified with HCl. The fatty acids recovered were purified by chromatography.
(3) The purified acids were esterified with BF_3/CH_3OH.

(4) Because the methyl ester of behenic acid predominated very strongly we preconcentrated the methyl esters of the fatty acids with carbon chains smaller than the behenic acid by means of preparative-scale G.L.C.

(5) These preconcentrated acids were purified by urea-adduction and analysed by gas chromatography.

Behenic acid Clay

Reaction products
1

Soap fraction
2

Purified-acid fraction
3

Ester fraction	—	G.L.C.
4		

Methyl esters of fatty acids with a molecular weight less than that of behenic acid
5

Urea adduction

G.L.C.

RESULTS

Low-molecular-weight hydrocarbons

Experiments without water

In the first series of experiments we studied the influence of time on the amounts and distribution of the various low-molecular-weight hydrocarbons generated during the heating of behenic acid in the presence of clay at a temperature of 200°C. The results of these experiments are listed in Table I.

Table II gives the amounts of the various amounts of low-molecular-weight hydrocarbons generated after heating at 250°C in the presence of clay.
These results show that:

(1) The ratio of the branched-chain to the straight-chain hydrocarbons is much higher than one.
(2) Isobutane predominates over all other compounds.

TABLE I

Hydrocarbons generated	Time of heating				
	94 *h*	283 *h*	330 *h*	976 *h*	1848 *h*
Ethane + Ethene	0·03	0·07	—	0·14	0·14
Propane	0·32	0·84	1·00	1·97	2·95
Propene	0·58	0·75	0·64	0·41	0·34
Isobutane	3·04	4·28	3·94	5·94	10·14
n–Butane	0·08	0·19	0·23	0·45	0·93
Isobutene + 1–Butene	0·13	0·09	0·06	0·04	0·05
2-Butene-trans	0·08	0·12	0·11	0·09	0·10
2-Butene-cis	0·05	0·06	0·07	0·05	0·07
Isopentane	1·45	2·62	4·13	4·62	8·27
n-Pentane	0·17	0·14	0·28	0·36	0·51
1-Pentene	0·01	0·01	0·01	0·01	0·01
2 Me-1-Butene	0·03	0·06	0·03	0·02	0·01
2-Pentene-trans	0·06	0·02	0·09	0·04	0·04
2-Pentene-cis	0·02	0·11	0·03	0·02	0·01
2-Me-2-Butene	0·15	0·10	0·14	0·07	0·05
2-Me-Pentane	0·66	1·23	2·41	3·69	4·16
3-Me-Pentane	0·21	0·43	0·88	1·31	1·47
n-Hexane	0·08	0·12	0·22	0·31	0·39
Total	7·1	11·2	14·2	19·5	29·6

TABLE II

Hydrocarbons generated	Time of heating	
	283 *h*	336 *h*
Ethane + Ethene	0·26	0·46
Propane	3·08	4·13
Propene	0·70	0·35
Isobutane	10·35	12·35
n-Butane	1·19	1·88
Isobutene + 1-Butene	0·13	0·13
2-Butene-trans	0·22	9·23
2-Butene-cis	0·14	0·15
Isopentane	0·37	13·36
n-Pentane	0·70	1·04
1-Pentene	0·02	0·02
2-Me-1-Butene	0·04	0·04
2-Pentene-trans	0·09	0·10
2-Pentene-cis	0·04	0·04
2-Me-2-Butene	0·16	0·17
2-Me-Pentane	4·43	6·08
3-Me-Pentane	1·71	2·38
n-Hexane	0·54	0·77
Total	33·2	42·8

(3) The amount of unsaturated compounds is fairly constant with time; for some compounds it even decreases with increasing time.
(4) The amounts of various individual compounds generated after certain times are plotted in Fig. 1 against the total amount of low-molecular-weight hydrocarbons generated after the same times. The straight lines resulting from these plots indicate that at 200°C and 250°C the same type of reaction is taking place.
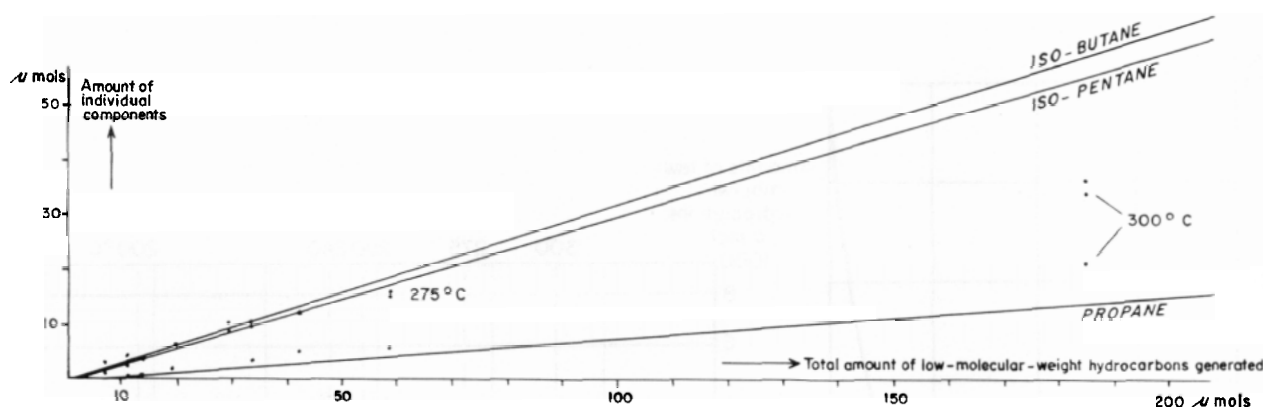
Fig. 1.—Amounts of individual components generated versus total amount of low-molecular-weight hydrocarbons generated after certain times and at various temperatures

In another series of experiments we investigated the influence of temperature on the amounts and distribution of the various low-molecular-weight hydrocarbons generated during a heating time of 283 h in the presence of clay. The results are listed in Table III.

TABLE III

	200°C	240°C	250°C	275°C	300°C
Ethane + Ethene	0.07	0·16	0·26	1·31	15·12
Propane	0·84	2·37	3·08	5·14	20·85
Propene	0·75	0·70	0·70	0·75	4·46
Isobutane	4·28	8·48	10·35	15·98	35·80
n-Butane	0·19	0·74	1·19	3·08	15·57
Isobutene + 1-Butene	0·09	0·10	0·13	0·27	2·22
2-Butene-trans	0·12	0·18	0·22	0·43	2·67
2-Butene-cis	0·06	0·12	0·14	0·27	1·80
Isopentane	2·62	6·90	9·37	15·98	36·53
n-Pentane	0·14	0·48	0·70	1·86	10·23
1-Pentene	0·01	0·01	0·02	0·04	0·45
2-Me-1-Butene	0·02	0·02	0·04	0·06	0·69
2-Pentene-trans	0·06	0·08	0·09	0·19	1·91
2-Pentene-cis	0·02	0·04	0·04	0·09	0·88
2-Me-2-Butene	0·11	0·12	0·16	0·48	2·35
2-Me-Pentane	1·23	3·33	4·43	8·04	18·24
3-Me-Pentane	0·43	1·21	1·71	3·38	8·23
n-Hexane	0·12	0·40	0·54	1·43	7·98
Cyclopentane	+	0·10	0·10	0·26	0·75
2-4-di-Me-Pentane	0·11	0·26	0·36	0·52	1·17
Me-Cyclopentane	0·07	0·28	0·44	1·17	2·81
2-Me-Hexane	0·82	2·16	2·80	5·30	10·91
2-3-di-Me-Pentane	0·14	0·37	0·45	0·74	1·88
3-Me-Hexane	0·40	1·07	1·45	2·67	7·31
Cyclohexane	0·02	0·08	0·17	0·30	0·70
3-E-Pentane	0·02	0·06	0·17	0·18	0·71
1-3-di-Me-Cyclo-pentane-trans	0·03	0·10	0·18	0·30	0·97
n-Heptane	0·13	0·39	0·48	1·27	6·92

The total amount of low-molecular-weight hydrocarbons (mg) generated and the sum of the n-alkanes and the sum of the unsaturates as percentages of the total amount of hydrocarbons generated from behenic acid after heating for 283 h at different temperatures in the presence of clay are listed in Table IV.

TABLE IV

	200°C	240°C	250°C	275°C	300°C
Total amount of low-molecular-weight hydrocarbons (mg)	0·9	2·15	2·84	5·15	15·13
Percentage of n-alkanes	11·0	14·5	15·1	17·9	28·0
Percentage of unsaturates	9·6	4·5	3·9	3·6	7·9

The data on n-alkanes and unsaturates are also given in Fig. 2. The total amount of low-molecular-weight hydrocarbons and the percentage of n-alkanes increase as the temperature increases. The percentage of the unsaturated compounds decreases up to 275°C and increases very rapidly above that temperature.

The relative amounts (with respect to C_4) of the various groups of hydrocarbons with the same number of carbon atoms generated from behenic acid after heating for 283 hours at different temperatures in the presence of clay are given in Table V. It is clear from these data that the relative increase of (ethane + ethene) is very pronounced.

TABLE V

	200°C	240°C	250°C	275°C	300°C
$C_2 + C^{2-}$	1·6	1·7	2·3	6·8	29·0
C_3	19·0	26·0	27·0	27·0	41·0
C_4	100·0	100·0	100·0	100·0	100·0
C_5	62·0	81·0	88·0	94·0	92·0
C^6	42·0	57·0	63·0	75·0	74·0
C_7	37·0	49·0	51·0	57·0	58·0

The total amount of hydrocarbons (mg) generated from C_2 up to C_7 is plotted in Fig. 3 against $10^3/T$. The slope of the line through these points increases with
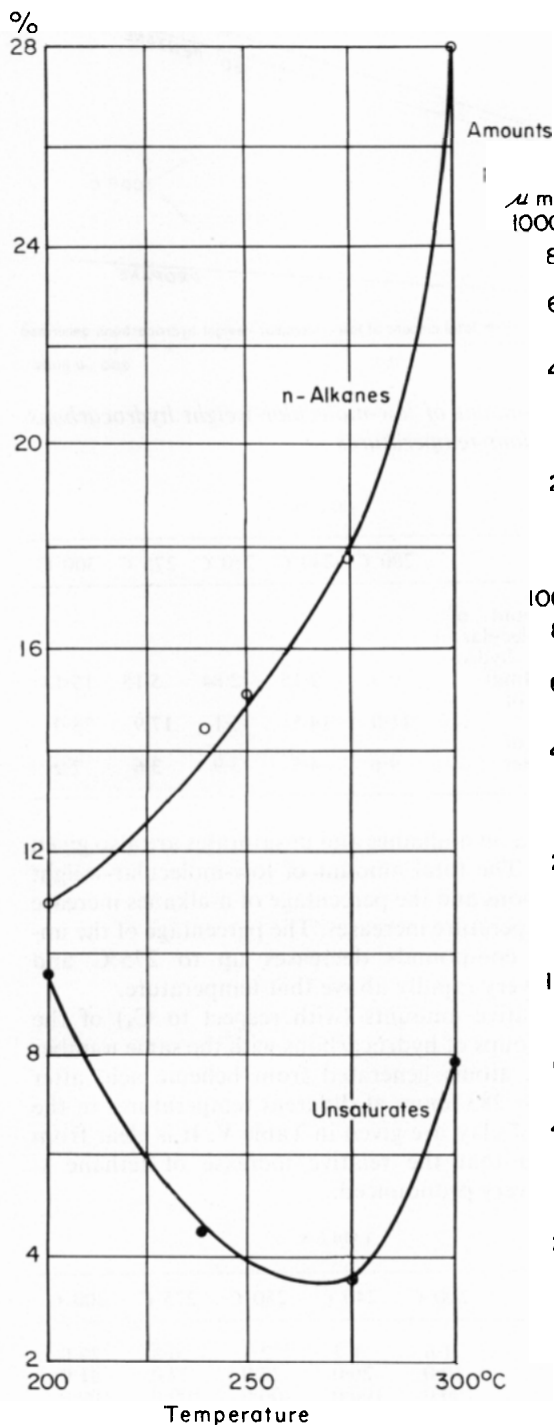
Fig. 2.—Percentages of low-molecular-weight n-alkanes and unsaturated hydrocarbons generated as a function of temperature
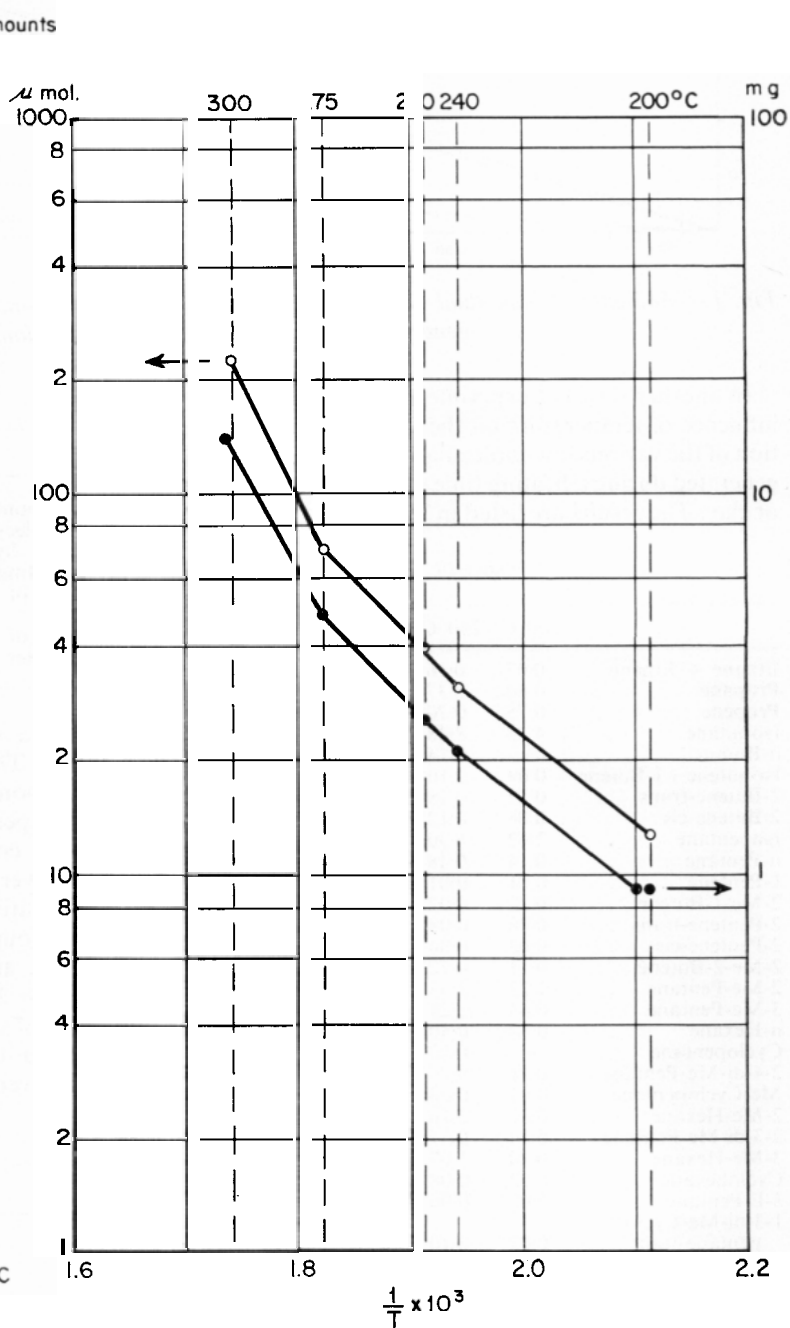
Fig. 3.—The Arrhenius plot of the amounts of low-molecular-weight hydrocarbons generated

increasing temperature. The shape of this curve suggests that a second reaction comes to the fore above 275°C. We fully realize that in an Arrhenius plot such as that in Fig. 3, the rate of the reaction should be taken into account; if this is not done, as in the present case, the indication given by the curve is valid only if the relative amounts of low-molecular-weight hydrocarbons are the same at different temperatures. Nevertheless, the shape of the curve, together with the other results, strongly indicates that above 275°C the generation of low-molecular-weight hydrocarbons is more complex than at lower temperatures.

Experiments with water

In Table VI we list the amounts of low-molecular-weight hydrocarbons generated from behenic acid that were heated in the presence of clay and water. Above 250°C the glass ampoules lost their transparency, indicating that devitrification of the glass had taken place.

TABLE VI

Heating-temperature	200°C	250°C	265°C	265°C	275°C
Heating-time ..	75 h	275 h	625 h	1300 h	330 h
Ethane + Ethene	0·06	0·04	0·21	0·26	0·24
Propane	0·01	0·03	0·08	0·12	0·14
Propene	0·07	0·08	—	0·25	0·16
Isobutane ..	—	0·02	0·03	0·04	0·03
n-Butane ..	0·01	0·02	0·07	0·09	0·13
Isobutene + 1-Butene	0·01	0·03	0·06	0·08	0·06
2-Butene-trans ..	—	0·02	0·07	0·10	0·08
2-Butene-cis ..	—	0·01	0·05	0·06	0·06
Isopentane ..	—	0·01	0·01	0·03	0·02
n-Pentane.. ..	0·02	0·05	0·06	0·09	0·13
1-Pentene ..	—	0·01	0·01	0·09	—

The experiments in which we added water revealed some marked differences from those in which the behenic acid was heated only in the presence of clay, viz:

(1) The total amount of low-molecular-weight hydrocarbons generated during the heating is much less than in the experiments without water.

(2) The amount of (ethane + ethene) generated during the heating predominates over all other compounds, whereas in the experiments without water the hydrocarbons with 3, 4 or 5 carbon atoms predominate.

(3) In the experiments with water the ratios of isobutane to n-butane and of isopentane to n-pentane are much less than 1, while in the experiments without water these ratios were greater than 1. Table VII gives the ranges of the ratios of iso-C_4/n-C_4, and iso -C_5/n-C_5, for the 200°C experiments

in the absence of water and the corresponding ratios for the various experiments in the presence of water.

TABLE VII

	Experiments without H_2O	Experiments with H_2O
iso-C_4/n-C_4 ..	11–38	0·25–1·00
iso-C_5/n-C_5	9–16	0·17–0·33

The amounts of low-molecular-weight hydrocarbons generated from behenic acid heated for 330 hours at 275°C in the presence of clay and water, are compared in Table VIII with those generated in an experiment in which we omitted the clay.

TABLE VIII

	Experiment without clay	Experiment with clay
Ethane + Ethene	0·05	0·24
Propane	0·03	0·14
Propene	0·06	0·16
Isobutane	—	0·03
n-Butane	0·02	0·13
Isobutene + 1-Butene ..	0·07	0·06
2-Butane-trans	0·02	0·08
2-Butene-cis	0·02	0·06
Isopentane	—	0·02
n-Pentane	0·03	0·13
1-Pentene	—	—

These experiments clearly show that the clay influences the reaction, even when a large amount of water is present.

High-molecular-weight hydrocarbons

The quantity of high-molecular-weight hydrocarbons generated as a result of the heating of behenic acid in the presence of clay, with or without water, amounted to only a few milligrammes. To concentrate the n-alkanes by urea adduction we need at least 4 mg of the saturated-hydrocarbon fraction. When this quantity was not available we used the saturated hydrocarbon fraction itself for the gas-chromatographic analyses. Both in the experiments with water and in those without, we found that n-alkanes with longer and with shorter carbon chains than the behenic acid were formed during the heating. There was always a strong predominance of the C_{21} n-alkane, which can be attributed to the decarboxylation of the behenic acid.

In Table IX we give the experimental conditions and the amounts of high-molecular-weight hydrocarbons generated.

TABLE IX

Behenic acid	Clay	Water	Heating time	Heating temp.	Mg sat. hydrocarbons	Mg non adduct	Mg adduct
A	1 g	2·5 g	7·5 g	330 h	250°C	1	—	—
B	1 g	2·5 g	—	400 h	200°C	2	—	—
C	1 g	2·5 g	—	500 h	250°C	8	6	2

More detailed results of these experiments are given in Fig. 4 which shows the amounts of n-alkanes formed during the reaction relative to the C_{21} n-alkane of that experiment.

By means of gas chromatography we identified, in the various experiments in which the behenic acid was heated in the presence of clay, with or without water, fatty acids with carbon numbers ranging from 15 to 24.

From an experiment in which the behenic acid was heated for 600 hours at 300°C in the presence of clay, we calculated the amounts of fatty acids generated relative to the amount of behenic acid. These data are given in Table X.

Fig. 5 shows a gas chromatogram of the preconcentrated methyl esters from an experiment in which the behenic acid was heated for 120 hours at 300°C in the presence of clay.
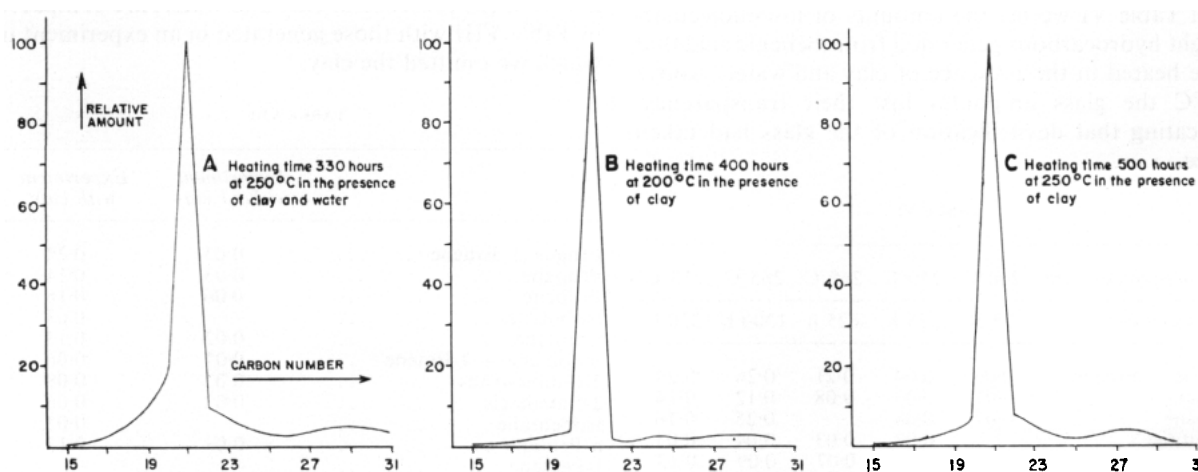

Fig. 4.—*Relative amounts of the high-molecular-weight n-alkanes generated from behenic acid*

No information could be obtained from the gas chromatogram of the urea-non-adduct since this was too complex to be unravelled.

The gas chromatograms for the determination of the n-alkanes in the urea-adduct or in saturated hydrocarbon fraction itself, showed a strong background indicating that other compounds were also present. In any case, in addition to the higher n-alkanes a great number of other hydrocarbons were generated. It is likely that small amounts of aromatics (such as isopropylbenzene and tertiary butylbenzene) were also present.

Fatty acids

Since in the fraction separated from the reaction mixture with KOH and containing the fatty acids, the behenic acid predominated strongly over all other compounds, we can only give qualitative results on the generation of fatty acids other than behenic acid.

TABLE X

Fatty acid	Relative amount
C-15	+
C-16	+
C-17	0·1
C-18	0·1
C-19	0·1
C-20	0·2
C-21	0·3
C-22	100·0
C-23	1·0
C-24	0·5

DISCUSSION OF THE RESULTS AND CONCLUSIONS

From the foregoing it is clear that the distribution of the various hydrocarbons generated depends on the experimental conditions. A similar phenomenon has been observed in cracking reactions.

The cracking of pure hydrocarbons has been studied in terms of carbon-number distributions and structures of the fragments. On the basis of this work cracking

systems are assigned to two fundamental classes, each of which is described by a set of characteristic reactions. Correspondingly, two types of reaction mechanisms are proposed.

> *A radical mechanism* (thermal cracking) based on the work of Rice-Kossiakoff.[13] The major reaction products of an n-paraffin subjected to thermal cracking are, n-paraffins, (α-β) olefins and ethylene.

The experiments without water

The composition of the low-molecular-weight hydrocarbons indicates that isomerization is strongly favoured in these experiments. We therefore conclude that carbonium ions are the intermediates in the formation of the low-molecular-weight hydrocarbons.

From the Arrhenius plot of the amounts of low-molecular-weight hydrocarbons generated at various
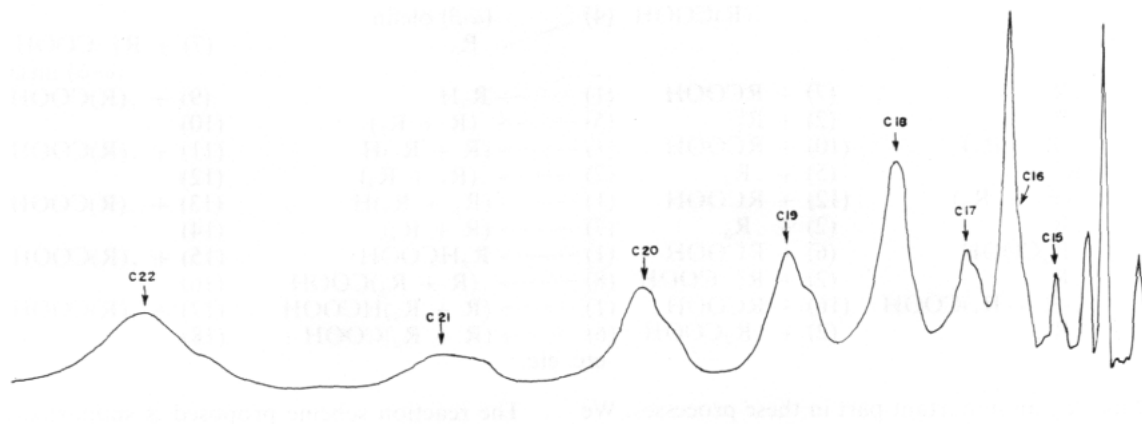

Fig. 5.—Gas chromatogram of the preconcentrated methyl esters of the fatty acids generated as a result of the heating of behenic acid in the presence of clay for 120 hrs at 300°C

> *A carbonium-ion mechanism* (catalytic cracking) based on the theory of cracking according to Greensfelder, Voge and Good.[14] The major products of an n-paraffin subjected to catalytic cracking are branched-chain hydrocarbons, the hydrocarbons with 3 or 4 carbon atoms being predominantly formed.

The thermal cracking takes place at a relatively high temperature as a homogeneous process. Its rate may be increased, however, by the presence of dispersed materials such as pure alumina. It is somewhat uncertain whether this reaction is to be considered as a heterogenerous catalytic process. Greensfelder et al. and Tung[15] have discussed this phenomenon. Where in the following discussion reference is made to the radical type of reaction it must be understood that this belongs to the above class of cracking reactions. It should be stressed that one characteristic they have in common with the genuine radical reaction is the absence of skeletal isomerization.

The results of the above-described experiments on the heating of behenic acid in the presence of clay, with or without water, will now be discussed in the light of these considerations concerning the various cracking mechanisms.

temperatures it follows that above 275°C a second reaction comes to the fore. The experimental results which lead us to the conclusion that in the second reaction radicals acted as intermediates are:
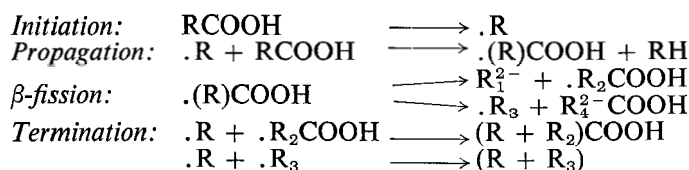
(1) The percentage of n-alkanes in the low-molecular-weight range increases with increasing temperature.

(2) The relative amount of (ethane + ethene) increases very strongly above 275°C.

(3) The amount of unsaturated hydrocarbons decreases with increasing temperature up to about 275°C and increases very strongly above that temperature.

The experiments with water

The pronounced formation of (ethane + ethene) n-alkanes and (α-β) olefins indicates that when behenic acid is heated in the presence of clay and water radicals are likely to be the intermediates in the formation of the low-molecular-weight hydrocarbons.

The most remarkable observation from both series of experiments is the generation of n-alkanes and fatty acids with a carbon chain longer than that of the behenic acid.

All these phenomena lead us to the conclusion that

Initiation: $\quad$ RCOOH $\quad\longrightarrow$ .R
Propagation: $\quad$ .R + RCOOH $\quad\longrightarrow$.(R)COOH + RH
β-fission: $\quad$.(R)COOH $\quad\longrightarrow R_1^{2-}$ + .R₂COOH
$\qquad\qquad\qquad\qquad\qquad\longrightarrow$ .R₃ + R_4^{2-}COOH
Termination: $\quad$ .R + .R₂COOH $\quad\longrightarrow$ (R + R₂)COOH
$\qquad\qquad\qquad$ .R + .R₃ $\qquad\longrightarrow$ (R + R₃)

This reaction scheme can be developed as follows:

A. $\qquad\qquad$ RCOOH $\quad$ (1) ——→ .R $\qquad\qquad$ (2) + CO₂ + .H
B. $\quad$ .R $\qquad$ (2) + RCOOH $\quad$ (1) ——→ RH $\qquad$ (3) + .(R)COOH $\quad$ (4)
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad R_1^{2-}$ $\qquad$ (5) + .R₂COOH $\quad$ (6)
C. $\qquad\qquad$.(R)COOH $\quad$ (4) $<$ (α-β) olefin
$\qquad\qquad\qquad\qquad\qquad\qquad$ .R₃ $\qquad$ (7) + R_4^{2-}COOH $\quad$ (8)
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (ω-ψ) unsat. acid

D. $\quad$ .R₃ $\qquad$ (7) + RCOOH $\quad$ (1) ——→ R₃H $\qquad$ (9) + .(R)COOH $\quad$ (4)
E. $\quad$ .R $\qquad$ (2) + R_1^{2-} $\qquad$ (5) ——→ .(R + R₁) $\quad$ (10)
$\quad$.(R + R₁) $\quad$ (10) + RCOOH $\quad$ (1) ——→ (R + R₁)H $\quad$ (11) + .(R)COOH $\quad$ (4)
F. $\quad$ R²⁻ $\qquad$ (5) + .R₃ $\qquad$ (7) ——→ .(R₁ + R₃) $\quad$ (12)
$\quad$.(R₁ + R₃) $\quad$ (12) + RCOOH $\quad$ (1) ——→ (R₁ + R₃)H $\quad$ (13) + .(R)COOH $\quad$ (4)
G. $\quad$ .R $\qquad$ (2) + .R₃ $\qquad$ (7) ——→ (R + R₃) $\quad$ (14)
H. $\quad$ .R₂COOH $\quad$ (6) + RCOOH $\quad$ (1) ——→ R₂HCOOH $\quad$ (15) + .(R)COOH $\quad$ (4)
I. $\quad$ .R $\qquad$ (2) + R_4^{2-}COOH $\quad$ (8) ——→ .(R + R₄)COOH $\quad$ (16)
$\quad$.(R + R₄)COOH $\quad$ (16) + RCOOH $\quad$ (1) ——→ (R + R₄)HCOOH $\quad$ (17) + .(R)COOH $\quad$ (4)
J. $\quad$ .R $\qquad$ (2) + .R₂COOH $\quad$ (6) ——→ (R + R₂)COOH $\quad$ (18)

etc. etc.
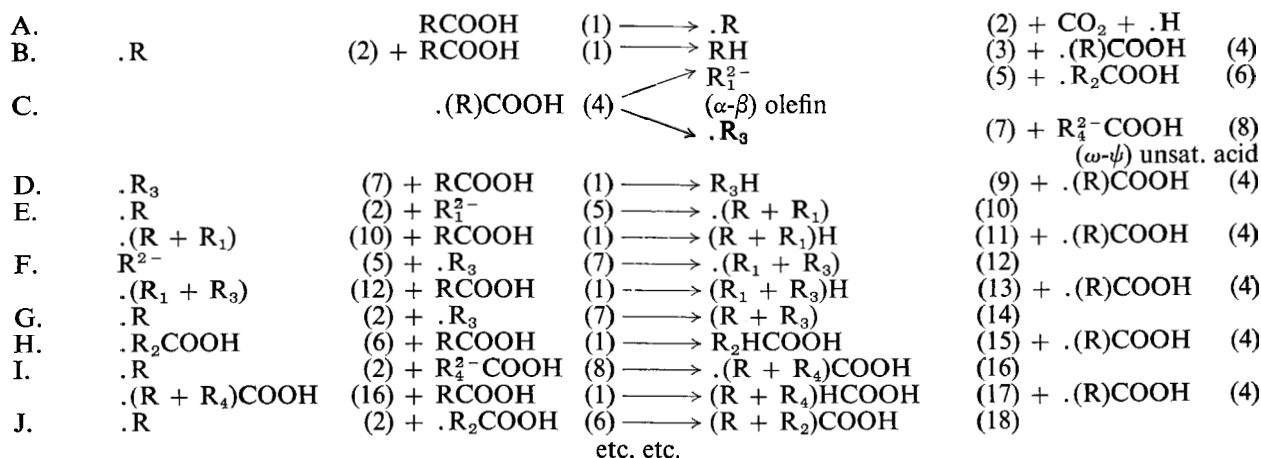
radicals play an important part in these processes. We therefore suggest the following reaction scheme for the generation of n-alkanes and fatty acids with carbon chains longer and shorter than that of the original behenic acid.

The initiation step of this mechanism is given by the decarboxylation of the fatty acid (1) resulting in an alkyl radical (2). This intermediate will react with the original fatty acid, which is present in the relatively highest concentration, to give the n-alkane (3) and the secondary radical of the fatty acid (4). This secondary radical can split up by β-fission into four products:

A. an (α-β) olefin (5) and a primary radical of a fatty acid (6) or,
B. a primary alkyl radical (7) and an (ω-ψ) unsaturated fatty acid (8).

The possible reactions by which the various compounds can be formed from these intermediates are shown in Table XI.

TABLE XI

	Reaction	Products
n-alkanes with a carbon chain shorter than the decarboxylated fatty acid	D	9
	F	9
n-alkanes with a carbon chain longer than the decarboxylated fatty acid	E	11
	F	13*
	G	14
Fatty acids with a carbon chain shorter than the original fatty acid	H	15
Fatty acids with a carbon chain longer than the original fatty acid	I	17
	J	18

* Depending on the values of R_1 and R_3.

The reaction scheme proposed is supported by the following arguments:

(1) The C_{21} n-alkane (corresponding to product (3) of reaction B) is always the predominating n-alkane formed during the reaction. This indicates that decarboxylation is an important step in this reaction. That decarboxylation is essential for the generation of the n-alkanes with a carbon chain longer than the original acid follows from an experiment in which we used n-hexadecane instead of behenic acid. After heating n-hexadecane in the presence of clay we were not able to find hydro-carbons with a carbon chain longer than n-C_{16}.

(2) In general the absolute amount of unsaturated low-molecular-weight hydrocarbons decreases with increasing heating time.

(3) In general a radical reaction can be controlled by adding either an initiator or an inhibitor to the reaction mixture. We have chosen the initiator, and have used as such 2-2' azopropane ($(CH_3)_2CH—N=N—CH—(CH_3)_2$).

In Table XII are listed the relative amounts of the various n-alkanes generated as a result of heating one gram of behenic acid for 300 hours at 200°C:

(a) In the presence of clay and water.
(b) In the presence of 25 mg 2-2' azopropane.

The gas chromatograms pertaining to these experiments are shown in Figs. 6 and 7. In the experiment in which we used the 2-2' azopropane, the C_{24} n-alkane predominates. This can be attributed to the combination

of the C_{21} radical from the behenic acid and the C_3 radical from the 2-2' azopropane.

TABLE XII

	(a)	(b)
n-C_{17}	2·7	1·9
n-C_{18}	3·4	2·4
n-C_{19}	3·6	3·2
n-C_{20}	3·2	5·8
n-C_{21}	100·0	100·0
n-C_{22}	5·2	6·2
n-C_{23}	4·3	4·9
n-C_{24}	4·1	37·6
n-C_{25}	2·8	2·6
n-C_{26}	2·1	2·0
n-C_{27}	1·7	2·0
n-C_{28}	1·7	2·1
n-C_{29}	1·1	2·1

of water normal alkanes with chains shorter and longer than that of the fatty acid can be formed, without any preference for the odd-numbered normal alkanes, with the exception of the normal C_{21}, however, which is present in a very high concentration. Here it should be kept in mind that the starting material in the experiments is a free fatty acid and that with decarboxylation a free hydrogen atom is also formed. An explanation for the high n-C_{21} concentration may be that there is a strong chance that the alkyl radical and the hydrogen atom will combine to form the n-C_{21}. From the sedimentary organic matter only traces of fatty acid can be extracted, or none at all, and it must therefore be assumed that the fatty matter is bound on one or another way to the bulk organic matter. This may mean
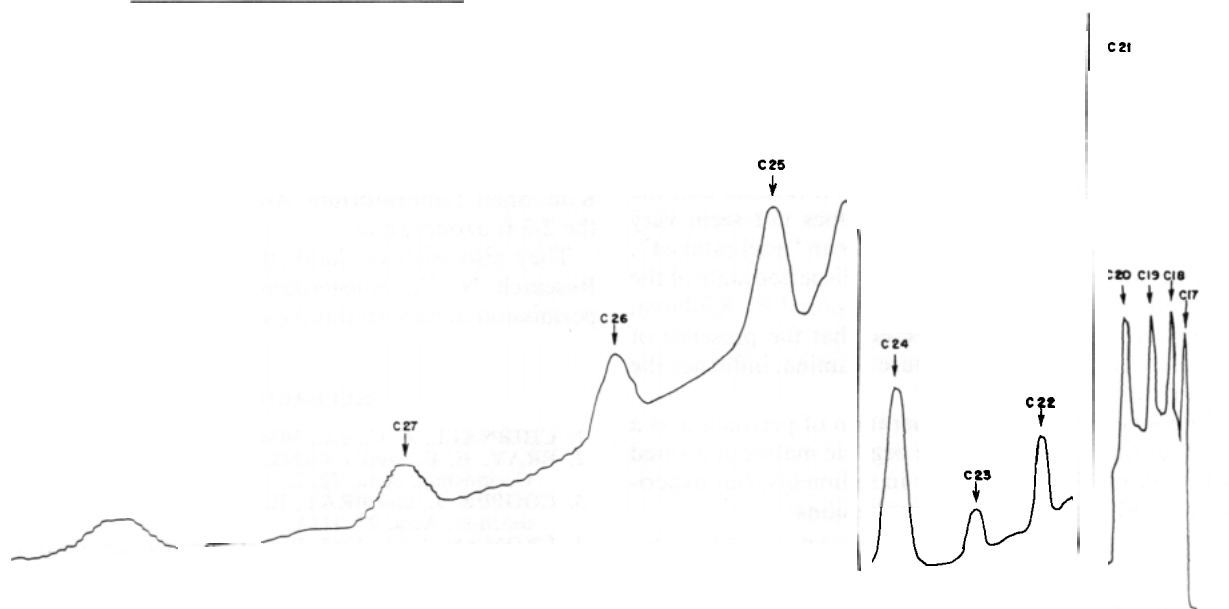

Fig. 6.—Gas chromatogram of the n-alkanes generated during the heating of behenic acid in the presence of 2–2' azopropane for 300 hrs at 200°C

The analogy between the results of the experiments on behenic acid, clay and water and the experiments on behenic acid and 2-2' azopropane indicates that radicals are indeed intermediates in the formation of the long chain n-alkanes and the fatty acids.

DISCUSSION OF SOME ASPECTS OF OIL GENESIS

This investigation was initiated in order to obtain a better insight into the chemical conversion of organic matter into oil. Several aspects will now be considered.

In the first place, can the disappearance of odd predominance of normal alkanes in deep sediments be explained? It has been established that in the presence

6—II

that, as the process takes place in nature, no hydrogen atom becomes available in the first decarboxylation step. This, however, is a point for further investigation. At present the decarboxylation and the subsequent radical reaction may be considered as the key to the solution of the problem of the disappearance of odd predominance.

In the second place, low-molecular-weight hydrocarbons are formed together with high-molecular weight hydrocarbons from long-chain fatty acids. This suggests another path for the generation of low-molecular-weight hydrocarbons besides the one suggested by Erdman, i.e. from amino acids. At present we have no means of deciding whether one path is more important than the other.
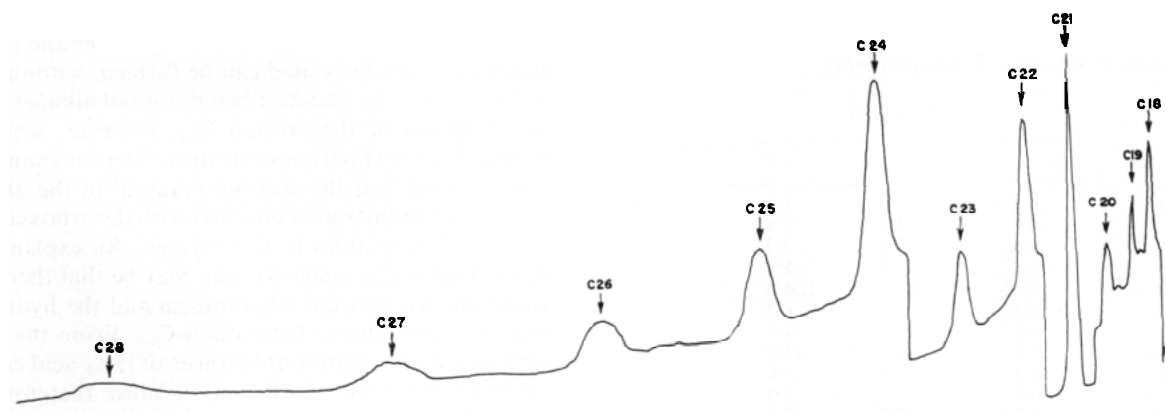
Fig. 7.—Gas chromatogram of the n-alkanes generated during the heating of behenic acid in the presence of clay and water for 300 hrs at 200°C

In the third place, the problem should be considered whether clay influences the conversion of organic matter into hydrocarbons. From the previously described experiments it is clear that water largely prevents carbonium-ion reactions. From this it follows that the mechanism suggested by Brooks does not seem very likely, and that the clay cannot act as an "acid catalyst". It seems more likely that the highly dispersed state of the clay influences the reaction, as proposed by Klubova. In any case it has been observed that the presence of dispersed materials, such as pure alumina, influence the rate of radical reactions.[14, 15]

In connection with the generation of petroleum as a result of the diagenesis of the organic matter deposited with clay minerals and water in sediments, our experiments lead to the following conclusions:

(1) The formation of n-alkanes and fatty acids with a carbon chain longer than that of the behenic acid suggests that n-alkanes and fatty acids present in oil accumulations are not necessarily derived from fatty acids with a longer chain. The homologous series of n-alkanes and fatty acids can be formed from one fatty acid. Although the n-alkane directly resulting from the fatty acid by decarboxylation is still predominant, the generation of such a mixture in the sediment may explain the smooth distribution of n-alkanes and fatty acids in petroleum and petroleum-reservoir waters respectively.

(2) The low-molecular-weight hydrocarbons generated during the transformation of the fatty acid may contribute to the gasoline fraction of the petroleum.

Acknowledgements

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