

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

FORMATION OF FATTY ACIDS IN PHOTOCHEMICAL  
CONVERSIONS OF SATURATED HYDROCARBONS

T.A. Telegina, T.Ye. Pavlovskaya, and A.I. Ladyzhenskaya

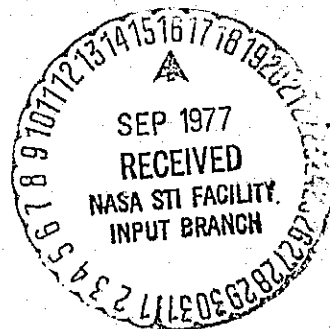
(NASA-TM-75133) FORMATION OF FATTY ACIDS IN  
PHOTOCHEMICAL CONVERSIONS OF SATURATED  
HYDROCARBONS (Kanner (Leo) Associates) 10 p  
HC A02/MF A01 CSCL 07C

N77-30173

Unclas

G3/23 42127

Translation of "Obrazovaniye zhirnykh kislot pri  
fotokhimicheskikh prevrashcheniyakh predel'nykh  
uglevodorodov," Izvestiya Akademii Nauk SSSR, Seriya  
Biologicheskaya, Vol. 9, 1974, No. 3, pp. 433-436.



1. Report No. NASA TM-75133		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle FORMATION OF FATTY ACIDS IN PHOTOCHEMICAL CONVERSIONS OF SATURATED HYDROCARBONS				5. Report Date July 1977	
				6. Performing Organization Code	
7. Author(s) T.A. Telegina, T.Ye. Pavlovskaya, and A.I. Ladyzhenskaya, Institute of Biochemistry im. A.N. Bach, Academy of Sciences USSR, Moscow				8. Performing Organization Report No.	
				10. Work Unit No.	
9. Performing Organization Name and Address Leo Kanner Associates Redwood City, California 94063				11. Contract or Grant No. NASw-2790	
				13. Type of Report and Period Covered Translation	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration, Washington, D.C. 20546				14. Sponsoring Agency Code	
15. Supplementary Notes Translation of "Obrazovaniye zhirnykh kislot pri foto-khimicheskikh prevrashcheniyakh predel'nykh uglevodorodov," Izvestiya Akademii Nauk SSSR, Seriya biologicheskaya, Vol. 9, 1974, No. 3, pp. 433-436.					
16. Abstract Abiogenic synthesis of fatty acids was studied in photochemical conversions of saturated hydrocarbons. It was shown that, in a hydrocarbon-water-CaCO <sub>3</sub> suspension, the action of 254 nm UV rays caused the formation of fatty acids with a maximum number of carbon atoms in the chain not exceeding that in the initial hydrocarbon. Synthesis of acetic, propionic, butyric, valeric, caproic, enanthic and caprylic (in the case of octane) acids occurs in heptane-water-CaCO <sub>3</sub> and octane-water-CaCO <sub>3</sub> systems.					
17. Key Words (Selected by Author(s))			18. Distribution Statement  Unclassified		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages	22. Price

FORMATION OF FATTY ACIDS IN PHOTOCHEMICAL CONVERSIONS  
OF SATURATED HYDROCARBONS

T.A. Telegina, T.Ye. Pavlovskaya, and A.I. Ladyzhenskaya  
Institute of Biochemistry im. A.N. Bach,  
Academy of Sciences, USSR, Moscow

According to the theory of A.I. Oparin [10], the /433\*  
development of life on earth was based on the formation and  
regular evolution of carbonaceous substances — hydrocarbons and  
their simplest derivatives. In the early stages of formation of  
the planet, this group of compounds could have arisen from the  
decomposition of carbides by water [2], by the conversion of the  
simplest hydrocarbon — methane, as a result of electrical dis-  
charges [12, 16] and high temperatures [11], by the radiolysis  
and by the photolysis of its molecules [14,7]. The spontaneous  
generation of hydrocarbons, from CH to C<sub>20</sub>H<sub>42</sub> in the solar neb-  
ular could have been a consequence of the catalytic reaction of  
carbon monoxide and hydrogen on dust particles of iron meteorite,  
containing the catalytically active elements Co, Fe, Ni (ac-  
cording to the well-known Fischer-Tropsch reaction) [15].

Determination of the pathways of formation of the oxygen  
containing derivatives of the hydrocarbons, first and foremost,  
of the high molecular weight fatty acids, occupies a special place  
in studies of prebiological evolution. This is connected with the  
fact that just they could have had more distinctly expressed  
surface-active properties and result in the formation of the bi-  
molecular lipid layers, which are so characteristic of the membrane  
structures of all living organisms.

---

\*Numbers in the margin indicate pagination in the foreign text.

It must be noted that the fatty acids synthesised so far in systems which simulate the original atmosphere and hydrosphere of the earth by the action on them of electrical discharges [8,1], UV rays [3,4] and heat [6] are among the lower representatives of this class of compound. The abiogenic formation of higher organic acid homologs evidently could have been connected with conversions of higher molecular weight hydrocarbons than methane. Therefore, the purpose of the present study was to study the photochemical formation of fatty acids in water emulsions of saturated hydrocarbons, with chain lengths of 7 and 8 carbon atoms.

### Materials and Methods

Commercial standard heptane (boiling point  $98.4^{\circ}$ ), commercial preparations of octane and isooctane, which were purified beforehand by the following method, were used as initial hydrocarbons. The hydrocarbon was boiled in succession (6-8 hours) with an alcoholic solution of alkali (90 g NaOH in 1200 ml of ethanol) and a 10% solution of hydroxylamine (600 ml), with an equal volume of NaOH added. After this, the hydrocarbon was shaken several times with a mixture of  $H_2SO_4 + H_2SO_4$  saturated with  $SO_3$  (oleum) (50 ml); the acid was then washed out of the hydrocarbon with water and shaken in succession with  $Na_2S_2O_5$  (2.5 g in 40 ml of water) and  $KMnO_4$  (5 g  $KMnO_4 + 9$  g NaOH + 125 ml  $H_2O$ ) solutions (15 min).

Further, the water washed hydrocarbon was shaken with sulfuric acid, it was washed with water until the disappearance of color with bromphenol blue, dried over  $CaCl_2$  and distilled in vacuum. The emulsion was prepared by mixing 25 ml of the hydrocarbon, 100 ml of water and 2.5 g of finely ground  $CaCO_3$  powder. Chalk was added to stabilize the emulsion and increase its irradiated surface. The emulsion, placed in a 200 ml quartz flask, was illuminated with UV light by a PRK-2 lamp at a distance of 30 cm from the surface, at room temperature and with continuous mixing of the test mixture by a magnetic mixer. The integral energy of

illumination of the lamp for the 250-335 nm wavelength region is  $2.27 \cdot 10^4$  erg/cm<sup>2</sup>·sec. In part of the tests, the emulsion was purged with nitrogen before and during irradiation. In tests with formaldehyde added to the hydrocarbon-water-CaCO<sub>3</sub> system, 25 ml of a 30% solution of formaldehyde in water was added. After irradiation, the test mixture was separated from the CaCO<sub>3</sub> by filtering. The water and hydrocarbon layers were analyzed separately for their fatty acid content. The water layers were analyzed by ascending paper chromatography of the hydroxamic acid derivatives of the fatty acids [13,9], in a normal butanol-acetic acid-water (40:2.5:50) system. The chromatograms were developed with an alcohol solution of iron perchlorate, which was prepared by dissolving steel wire (0.8 g) in 57% HClO<sub>4</sub> (12.3 ml) while heating, and by the subsequent addition of distilled water (7 ml) and ethanol to 100 ml. Besides, the fatty acids in the water layer were separated, in the form of their methyl esters, by gas-liquid chromatography in a KhV-1 apparatus, with a detector-katharometer in a Tween-85 phase (20%) on Chromosorb W (60-80 mesh), at 160°, in 300 x 0.6 cm columns, and a helium carrier gas flow rate ~120 ml/min. /434

Analysis of the fatty acids in the hydrocarbon layer was carried out by separation of their methylesters in a Tsvet-2 gas chromatograph, with a flame-ionization detector in a Apiezon-L liquid phase (20%), on Chromosorb W, the temperature was programmed from 50 to 240° at a rate of 6°/min, in a 100 x 0.2 cm column and a helium carrier gas flow rate ~ 120 ml/min. The fatty acid methylesters were prepared by esterification of the dry potassium salts with absolute methanol in the presence of oleum, for a period of 12-14 hours. The esters formed were extracted from the mixture with pentane. The methylesters of saturated C<sub>1</sub>-C<sub>9</sub> fatty acids were used as the standards.

## Results and Discussion

The analysis of the water and hydrocarbon phases of the irradiated hydrocarbon-water-CaCO<sub>3</sub> emulsions demonstrated the presence of aliphatic acids in both phases. The higher molecular weight acids accumulated predominantly in the hydrocarbon layer.

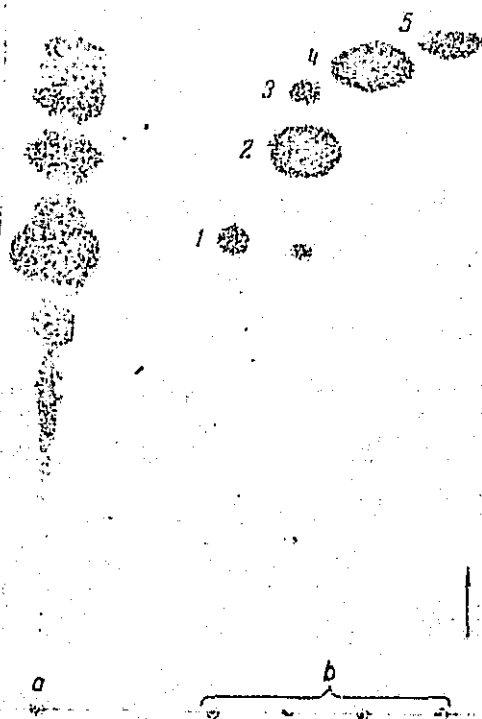


Fig. 1. Chromatogram of hydroxamic derivatives of fatty acids synthesized in UV irradiated (100 hours) heptane-water-CaCO<sub>3</sub> emulsion (a) and hydroxamic acid derivatives of the markers (b): 1. acetic, 2. propionic, 3. butyric, 4. valeric, and 5. caproic acids.

A chromatogram of the hydroxamic acid derivatives of the fatty acids accumulated in the water phase, during irradiation of the heptane-water-CaCO<sub>3</sub> system for a period of 100 hours, is presented in Fig. 1. Under these conditions, relatively large amounts of acetic, propionic, and butyric acids, as well as valeric and caproic acid and, possibly, enanthic acid in relatively smaller quantities were synthesized. Gas-liquid chromatography of the methyl esters of the water phase acids of the irradiated heptane-water-CaCO<sub>3</sub> system, with the use of an Apiezon-L liquid phase, enabled the C<sub>5</sub>-C<sub>7</sub> fatty acids to be more distinctly brought out in it. In the hydrocarbon layer of the irradiated heptane-water-CaCO<sub>3</sub> system, analyzed by the same method, C<sub>5</sub>-C<sub>7</sub> fatty acids were identified (Fig. 2). Under these conditions, synthesis of the isomers of these acids evidently is possible,

which can be decided from the presence of peaks on the chromatogram, characterized by close temperature characteristics.

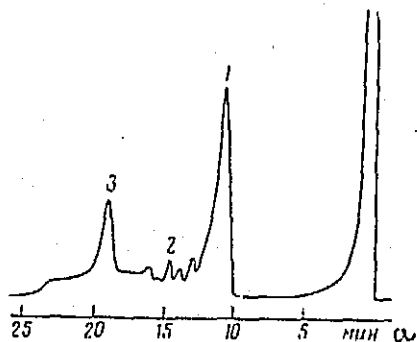


Fig. 2. Chromatogram of methyl esters of fatty acids synthesized in UV irradiated (100 hours) heptane-water-CaCO<sub>3</sub> emulsions; hydrocarbon layer: 1. methyl ester of valeric acid; 2. methyl ester of caproic acid; 3. methyl ester of enanthic acid.  
Key: a. min

Photochemical synthesis of aliphatic acids also occurs in an octane-water-CaCO<sub>3</sub> emulsion. Data from the analysis of the water phase of this system, irradiated by UV 435 rays for a period of 100 hours, are presented in Fig. 3. They indicate the presence of C<sub>2</sub>-C<sub>6</sub> fatty acids in the reaction products, with quantitative predominance of the low molecular weight acids. Similar results were obtained for the water phase of the isooctane-water-CaCO<sub>3</sub> system irradiated with UV rays for the same period of time. The hydrocarbon (octane) layer contains organic acids with C<sub>4</sub>, C<sub>6</sub>, C<sub>8</sub>, identified by gas-liquid chromatography.

In order to remove dissolved oxygen from the emulsion, the octane-water-CaCO<sub>3</sub> system was purged with nitrogen before the start and during irradiation. In this case, exposure for a period of 100 hours led to the same results as without bubbling nitrogen, namely, changes in the quantitative composition of the fatty acids formed, which also were represented by C<sub>2</sub>-C<sub>8</sub> acids, were not observed.

It should be noted that, in the emulsions containing heptane or octane, fatty acids form photochemically, with a maximum number of carbon atoms in the chain not exceeding that in the initial hydrocarbon. The amounts of them vary from 10<sup>-4</sup> to 10<sup>-3</sup> M.

We anticipated that the introduction of formaldehyde into the carbohydrate-water-CaCO<sub>3</sub> system would promote the lengthening of the carbon chain of the fatty acids synthesized. Upon introduction



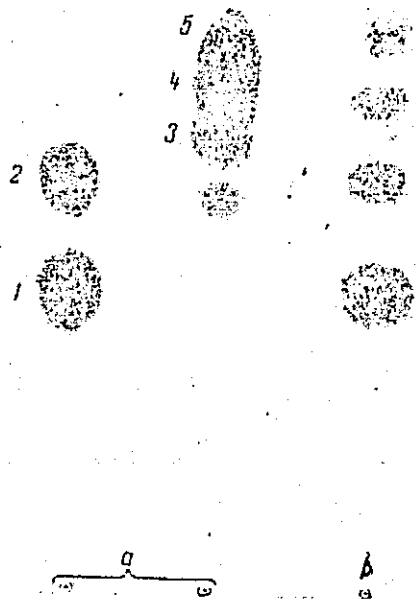


Fig. 3. Chromatogram of hydroxamic acid derivatives of fatty acids synthesized in UV irradiated (100 hours) octane-water-CaCO<sub>3</sub> emulsion (b) and hydroxamic acid derivatives of markers (a); 1. acetic, 2. propionic, 3. butyric, 4. valeric, 5. caproic acids.

of CH<sub>2</sub>O into an octane-water-CaCO<sub>3</sub> system, irradiated with UV rays for a period of 20 hours, we observed no changes in the qualitative composition of the fatty acids synthesized. In this case, acids with C<sub>1</sub>-C<sub>8</sub> also were identified and an increase was noted in only some of the low molecular weight acids, formic acid in particular. An increase in irradiation time of the octane-water-CaCO<sub>3</sub> system with CH<sub>2</sub>O added from 20 to 100 hours favors the accumulation of acids in both phases, but it does not change their qualitative composition.

The mechanism of the photochemical synthesis of fatty acids under the study conditions still has not been determined. However, the similarity and composition of the organic acids synthesized in the hydrocarbon emulsions, with and without dissolved air, permits suggestion of the intermediate formation of active products of the photolysis of the initial compounds in thin layers on the surfaces of the CaCO<sub>3</sub> particles. A characteristic of the systems studied is oxidation of the hydrocarbons in the absence of air.

Thus, with exposure to UV radiation in heptane or octane-water CaCO<sub>3</sub> systems, the synthesis of acetic, propionic, butyric, valeric, caproic, enanthic and caprylic (in the case of octane) acids takes place, i.e., acids with the number of carbon atoms in the chain less than or equal to the number of atoms in the initial hydrocarbon.

If the possibility of photolysis of water vapor or water in the liquid state as a result of exposure to shortwave UV radiation under the prebiological conditions of earth is assumed, the formation of active intermediate products in this process could promote the conversion of the hydrocarbons into oxygen containing derivatives, fatty acids in particular. It should be emphasized that such an important question as the abiogenic formation of higher fatty acids, which evidently were the base of lipoprotein membranes and films, still has not been answered experimentally. However, the detection of saturated fatty acids in the organic residues of the most ancient (Precambrian) rock deposits [5] is evidence of formation of this class of compounds in the early stages of evolution. The preservation of these compounds for a period of ~ 3.5 billion years permits them to be classified as "fossil" molecules. Did these fossil molecules form as a result of abiogenic processes in the period of prebiological evolution, or were they are result of the vital activities of the original organisms, is a question which is important to the understanding of the transition from chemical evolution to biological evolution.

## REFERENCES

(Journals)

1. Allen, W. and C. Ponnamperna, Currents, Mol. Biol. 1, 24 (1967).
2. Anders, E., Proc. Lunar Planetary Explor. Colloquium 2/4, 55 (1961); Ann.N.Y. Acad. Sci. 93, 649 (1962).
3. Dodonova, N.Ya. and A.I. Sidorova, Biofizika 6, 149 (1961); Biofizika 7, 31 (1962).
4. Groth, W. and H. Weysenhoff, Ann. Physik. 4, 69 (1959).
5. Han, J. and M. Calvin, Nature 224/5219, 576 (1969).
6. Lowe, C., M. Ress, and R. Markham, Nature 199, 219 (1963).
7. Mahan, B.H. and R. Mandal, J. Chem. Phys. 37/2, 207 (1962).
8. Miller, S., in the collection Voznikoveniye zhizni na Zemle [The Origin of Life on Earth], AN SSSR Press, Moscow, 1959, p. 131.
9. Obukhova, L.K., in the collection Okisleniye uglevodorodov v zhidkoy faze [Oxidation of Hydrocarbons in the Liquid Phase], AN SSSR Press, Moscow, 1959, p. 249.
10. Oparin, A.I., Voznikoveniye zhizni na Zemle [The Origin of Life on Earth], AN SSSR Press, Moscow, 1957.
11. Oró, J. and T. Han, Science 153, 53 (1966).
12. Ponnamperna, C. and F. Woeller, Nature 203/4942, 272 (1964).
13. Rodopulo, A.K. and I.A. Yegorov, Vinodeleniye i vinogradarstvo SSSR 4, 4 (1963).
14. Siecu, L.W. and R.H. Johnson, J. Phys. Chem. 67/11, 2281 (1963).
15. Studier H., R. Hayatsu and E. Anders, Geochim. et Cosmochim. Acta 32, 151 (1968).
16. Wilson, A.T., Nature 188, 1007 (1960).