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FORMATION OF FATTY ACIDS IN PHOTOCHEMICAL
CONVERSIONS OF SATURATED HYDROCARBONS

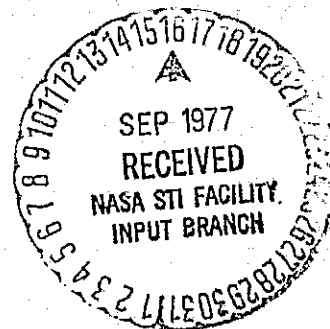
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16. Abstract Abiogenic synthesis of fatty acids was studied in photochemical conversions of saturated hydrocarbons. It was shown that, in a hydrocarbon-water-CaCO ₃ suspension, the action of 254 nm UV rays caused the formation of fatty acids with a 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 ₃ and octane-water-CaCO ₃ systems.					
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FORMATION OF FATTY ACIDS IN PHOTOCHEMICAL CONVERSIONS OF SATURATED HYDROCARBONS

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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 C₂₀H₄₂ 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°), 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 $\text{Na}_2\text{S}_2\text{O}_5$ (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/cm²·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-CaCO₃ system, 25 ml of a 30% solution of formaldehyde in water was added. After irradiation, the test mixture was separated from the CaCO₃ 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% HClO₄ (12.3 ml) while heating, and by the subsequent addition of distilled water (7 ml) and 434 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.

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 C₁-C₉ fatty acids were used as the standards.

Results and Discussion

The analysis of the water and hydrocarbon phases of the irradiated hydrocarbon-water- CaCO_3 emulsions demonstrated the presence of aliphatic acids in both phases. The higher molecular weight acids accumulated predominantly in the hydrocarbon layer.

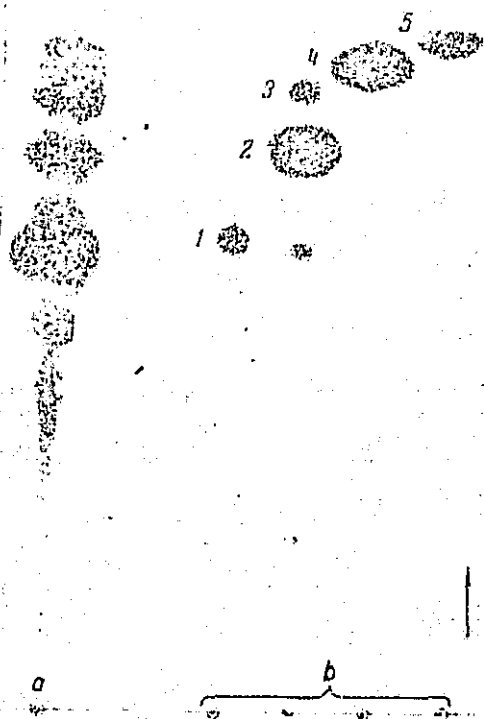


Fig. 1. Chromatogram of hydroxamic derivatives of fatty acids synthesized in UV irradiated (100 hours) heptane-water- CaCO_3 emulsion (a) and hydroxamic acid derivatives of the markers (b): 1. acetic, 2. propionic, 3. butyric, 4. valeric, and 5. caproic acids.

A chromatogram of the hydroxamic acid derivatives of the fatty acids accumulated in the water phase, during irradiation of the heptane-water- CaCO_3 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_3 system, with the use of an Apiezon-L liquid phase, enabled the C_5 - C_7 fatty acids to be more distinctly brought out in it. In the hydrocarbon layer of the irradiated heptane-water- CaCO_3 system, analyzed by the same method, C_5 - C_7 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.

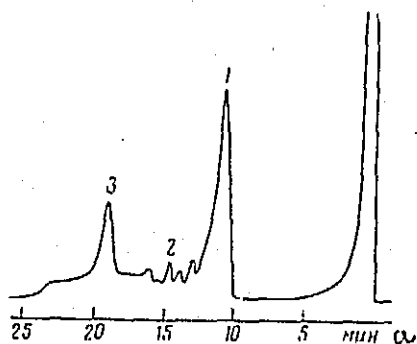


Fig. 2. Chromatogram of methyl esters of fatty acids synthesized in UV irradiated (100 hours) heptane-water- CaCO_3 emulsions; hydrocarbon layer: 1. methyl ester of valeric acid; 2. methyl ester of caproic acid; 3. methyl ester of enanthic acid. Key: a. min

Photochemical synthesis of aliphatic acids also occurs in an octane-water- CaCO_3 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_2 - C_6 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_3 system irradiated with UV rays for the same period of time. The hydrocarbon (octane) layer contains organic acids with C_4 , C_6 , C_8 , identified by gas-liquid chromatography.

In order to remove dissolved oxygen from the emulsion, the octane-water- CaCO_3 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_2 - C_8 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^{-4} to 10^{-3} M.

We anticipated that the introduction of formaldehyde into the carbohydrate-water- CaCO_3 system would promote the lengthening of the carbon chain of the fatty acids synthesized. Upon introduction

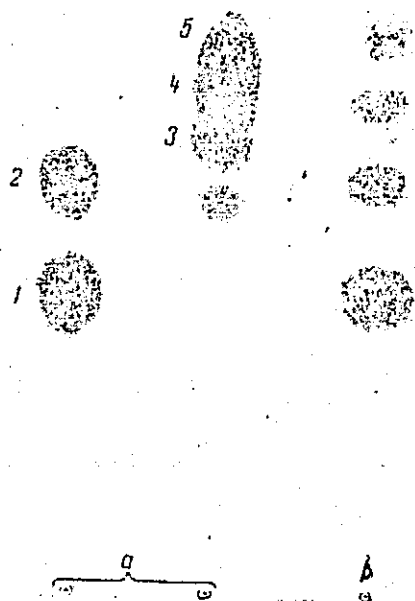


Fig. 3. Chromatogram of hydroxamic acid derivatives of fatty acids synthesized in UV irradiated (100 hours) octane-water- CaCO_3 emulsion (b) and hydroxamic acid derivatives of markers (a); 1. acetic, 2. propionic, 3. butyric, 4. valeric, 5. caproic acids.

of CH_2O into an octane-water- CaCO_3 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 $\text{C}_1\text{-C}_8$ 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_3 system with CH_2O 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_3 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_3 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.

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