

STRUCTURAL MODIFICATION OF LIQUID HYDROCARBONS IRRADIATED BY A NANOSECOND e -BEAM

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Received June 2, 1997*

The processes of oxidation and isomerization of liquid normal alkanes of C₅–C₆ types irradiated by a 4 ns duration e -beam with the peak electron energy of 140 keV under ambient air and in rare gases are investigated experimentally. The data on the radiochemical yields of the processes of oxidation and isomerization of normal alkanes of C₅, C₆ and C₈ types are presented.

Investigation of the processes of structural modification of hydrocarbons under the action of radiation are important for understanding the ecological problems of the atmospheric chemistry. Besides, the processes of oxidation and structure branching of liquid hydrocarbons are critical to modern plasma-chemical technology of processing hydrocarbon raw materials.

Use of a high-current e -beam with the average electron energy on the order of 150 keV provides for efficient chemical reaction initiation in liquid hydrocarbons. In this case the electron path length in liquid alkanes is not long and comprises about 0.5 mm. Nevertheless, high density of the electron flux, interaction with a gas medium through a developed surface and the possibility to work at high pulse repetition rate enable a desired conversion of liquid hydrocarbons.

A small-size generator of nanosecond pulses (see Ref. 1) producing 300 kV pulses with the duration of 4 ns at a pulse repetition rates 1–200 Hz was used in our experiments. The voltage pulses were applied to a vacuum diode. Accelerating zone of the diode was formed by a plane anode (the diode body) and an explosive emission cathode. The cathode was made from copper foil bands glued on a dielectric surface. The use of metal-dielectric contact allows one to reduce the electric field strength at the cathode required for the explosive emission and increases lifetime of the cathode up to 10^7 – 10^8 pulses. The entrance window in the form of a set of holes covered by 45- μ m thick aluminium-beryllium foil was used to extract the accelerated electrons from the diode. The accelerator produces a 4-ns e -beam with the current density of 65 A/cm² over the area of 10 cm². Energy parameters of the flux were measured by the method of

foils (see Ref. 2). Energy distribution of electrons was typical for such accelerators. Total electron energy was found to be 0.2 J per pulse. Its values measured with a calorimeter IMO–2 and estimated from the energy distribution were in a good agreement.

The liquid to be investigated (n -alkanes of C₅, C₆ and C₈ types) in the volume of 2 cm³ was irradiated in a stainless steel cell 40 mm in the inner diameter and 15 mm in length. Stationary regime and that with the liquid flow were possible. In the stationary regime the cell was evacuated and then filled with a rare gas under a pressure of 10 Bar. Irradiation was performed under ambient air or in a rare gases.

Diffusion of the oxygen in liquid alkanes depends on the viscosity and can proceed during 10 s in 0.3–5 mm thick layer at the atmospheric pressure. In order to reduce this time the oxygen content in the near-surface layer was increased at the expense of air pressure or using air blown through the liquid. Besides, in our experiments heat deposition from pulsed electron flux forms a developed surface similar to that of boiling liquid which also enables enriching of the liquid with oxygen.

Analysis of stable products formed during the hydrocarbons irradiation was made using a gas-chromatography method.

Capillar flask PEG–20M 25 m in length and 0.2 mm in diameter with an inoculated phase and a detector PID were used in the experiments. Flux division coefficient was 1:100. Helium was used as a carrier gas, the sample volume was 0.8 μ l. Computer identification of peaks and quantitative processing of the results obtained were performed using “ECOCHROM” software developed at SDB IOC RAS, Moscow. Typical chromatograms obtained using irradiation in the ambient air and rare gases are presented in Figs. 1 and 2.

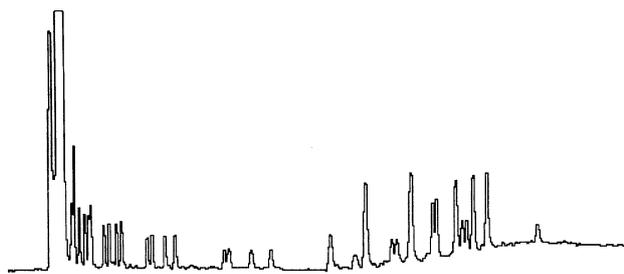


FIG. 1. Chromatograms of the radiolysis products of octane in argon.

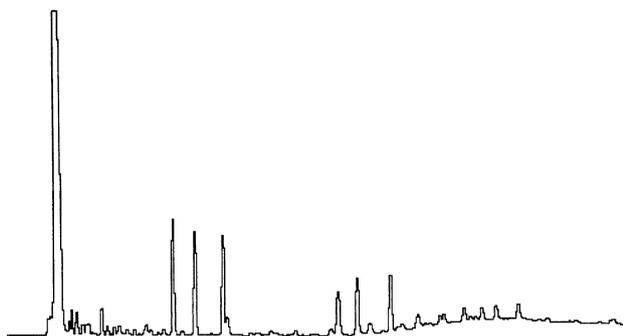


FIG. 2. Chromatograms of the radiolysis products of octane when blown through with air.

Radiolysis of products and their radiative-chemical yields (G) for normal alkanes irradiated by an e -beam in argon are listed in Table I.

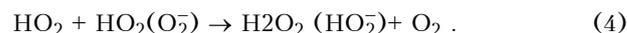
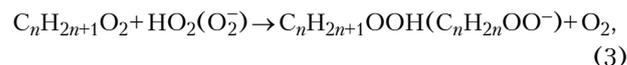
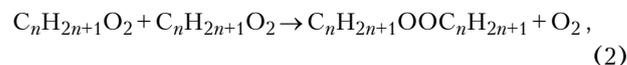
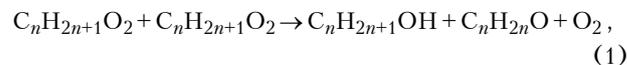
TABLE I.

Heptane, dose $2.8 \cdot 10^{21}$ eV/g in argon, $p = 1$ Bar		Octane, dose $2.7 \cdot 10^{21}$ eV/g in argon, $p = 1$ Bar	
Product	G , molecules/100 eV	Product	G , molecules/100 eV
$\Sigma i-C_6$	0.8	$C_n < C_8$	4.3
$\Sigma i-C_8$	1.7	$\Sigma i-C_9$	6.5
$\Sigma i-C_9$	0.9	$n-C_9$	0.5
$n-C_9$	< 0.1	$\Sigma i-C_{10}$	1.9
$\Sigma i-C_{10}$	0.7	$n-C_{10}$	0.5
$n-C_{10}$	< 0.1	$\Sigma i-C_{12}$	1.8
$C_{12:1}$	< 0.1	$n-C_{12}$	0.4
$\Sigma i-C_{12}$	2.7	$\Sigma i-C_{14}$	1.4
$n-C_{12}$	0.3	$n-C_{14}$	1.2
		$C_{16:1}$	0.4
		$\Sigma i-C_{16}$	14.6
		$n-C_{16}$	0.7

In this case normal alkanes with the molecular mass lower and higher than those of the initial alkanes along with the dimers and their different isomers $i-C_{2n}$ are main radiolysis products in the liquid phase. In both cases the maximal yield of isomers $i-C_{2n}$ was obtained. Only trace amounts of unsaturated hydrocarbons were found.

The mechanism of radiolysis product formation in a monomolecular and bimolecular processes is associated with reactions involving free radicals produced due to the break of C-H and C-C bonds in the excited alkane molecules. Therewith the main fraction of radicals are formed due to the break of C-H bonds. The yield of radicals with a smaller size as compared to the initial molecules is lower than that of radicals formed due to the break of C-H bonds (see Ref. 3). The break of C-C bonds can occur both in the processes of excitation and ionization. The radicals can split out the secondary hydrogen atoms from normal alkanes or they recombine with one of the other radicals. Besides, disproportionation can happen. The dominating reaction depends on the condition wherein it occurs. In conditions of our experiments when the overall cross-section area of the tracks even in the initial lengths reaches about 20% of the overall irradiated surface the reactions prevail that produce isomers of dimers and hydrocarbons with intermediate molecular mass. These hydrocarbons and dimers are formed in the process of statistical combining of various hydrocarbon radicals with the prevalence of the disproportionation reaction. Besides, an anomalous distribution of products from group C_{n+1} as compared to those from groups C_{n+2} , C_{n+3} and so on is observed when irradiating n -alkanes (C_6 , C_8) with a nanosecond e -beam. The anomaly was observed earlier by other authors (see Ref. 3). In this paper both linear and branched C_{n+1} products are predominantly formed by introducing through the C-H bonds that occurs in the process of radiolysis of methylene in a singlet state rather than through recombination of maternal radicals with the methyl ones.

Experiments on oxidation of n -alkanes were performed in air at an enhanced pressure or using air blowing through the initial product. Oxygen, because of its high reactive ability with respect to electrons and free radicals has strong effect on hydrocarbon radiolysis. Radiolysis of n -alkanes in the presence of oxygen yields radicals $C_nH_{2n+1}O_2$, HO_2 , and O_2^- that interact according to the conventional reaction scheme:



Main products of the irradiation of C_5 , C_6 , and C_8 liquid alkanes by a nanosecond e -beam at air pressure of 3–5 Bar or when blowing them through with air are carbonyl compounds and spirits (see Tables II and III) resulting from disproportionation of peroxide alcyne

radicals according to reaction (1). Acids and peroxide compounds were not found.

TABLE II.

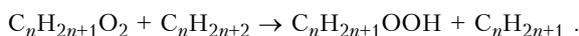
Pentane, dose 3.3×10^{21} eV/g in air, $p = 1$ Bar		Hexane, dose 2.8×10^{21} eV/g, blown through with air	
Product	G, mol/100 eV	Product	G, mol/100 eV
pentaaldehyde	35.2	hexaaldehyde	8.3
heptanone-2	7.5	hexanone-2	10.5
<i>n</i> -heptanole	4.3	<i>n</i> -hexonole	6.4
heptanole-2	5.5	hexanole-2	9.8
$C_n > C_5$	13.5	$C_n > C_6$	6.1
		<i>n</i> -C ₁₂ , Σi -C ₁₂	4.2

TABLE III.

Octane, dose 2.8×10^{21} eV/g, blown through with air		Octane, dose 2.8×10^{21} eV/g in air, $p = 3.5$ Bar	
Product	G, mol/100 eV	Product	G, mol/100 eV
octaaldehyde	4.2	octaaldehyde	5.5
octanone-2	4.2	octanone-2	4.5
octanone-3	3.9	octanone-3	4.4
octanole-1	3.1	octanole-1	1.7
octanole-2	2.6	octanole-2	2.0
octanone-3	0.9	octanone-3	2.0
$C_n < C_8$	0.2	$C_n < C_8$	1.6
$C_n > C_8$	3.3	$C_n > C_8$	1.3
<i>n</i> -C ₁₆ , Σi -C ₁₆	5.9	<i>n</i> -C ₁₆ , Σi -C ₁₆	1.2

Reasonably high yield of the products for pentane and hexane attracts our attention. This is because the main portion of the *e*-beam energy is given in the form of heat and part of the product is in the gaseous phase wherein the oxidation process is highly efficient and

oxidation according to the chain mechanism is quite probable. Under our experimental conditions the following reaction is possible:



The chain termination occurs in the reaction between radicals $C_nH_{2n+1}O_2$ and C_nH_{2n+1} between each other and between the same radicals (see Ref. 4).

In addition to oxidation the isomerization was also observed in the experiments in the presence of air. The tendencies of structural modification of *n*-alkane molecules with air pressure are listed in Table III. Therewith, the content of the oxidation products and the fraction of carbonil compounds increase while that of spirits reduces. Increase of air pressure up to 3 Bar improves the yield of products with $C_n < C_8$ by one order of magnitude, while proportions of the products $n - C_n$, $\Sigma i - C_n$ ($8 < n < 15$) and $n - C_{16}$, $\Sigma i - C_{16}$ were reduced by factors 2.5 and 5, respectively. This means that the reactions splitting out hydrogen atoms from *n*-alkanes by the radicals become dominant over the reaction between radicals as the pressure increases.

Thus, the use of a high-current *e*-beam for radiolysis of the liquid alkanes in different gas media makes it possible an efficient direct initiation of oxidation and isomerization processes.

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