

Structural Modification of Liquid Hydrocarbons Irradiated by E-beam of Nanosecond Duration

V.M. Orlovskii

*Institute of High-Current Electronics SB RAS, 2/3, Akademichesky ave., Tomsk, 634055, Russia
Phone: +8(3822) 49-14-43, Fax: +8(3822) 49-24-10, E-mail: orlovskii@loi.hcei.tsc.ru*

Abstract – Processes of oxidation and isomerization of liquid normal alkanes C_5 – C_8 at irradiation by the bunch of electrons of 4 ns duration with energy of 140 keV in the peak in air and in medium of inert gases are investigated experimentally. Data on the radiochemical yield of the processes of oxidation and isomerization of *n*-alkanes C_5 , C_6 , and C_8 are presented.

1. Introduction

Processes of oxidation and transformation of liquid hydrocarbons to more developed structures are of great importance in modern plasma chemical technologies of processing of hydrocarbon raw material. Use of a high current stream of electrons with energy 140 keV allows to initiate effectively chemical reactions in liquid hydrocarbons. In this case pass of electrons in liquid alkanes is insignificant and about 0.5 mm, nevertheless high density of the stream of electrons, interaction with the gas environment through the developed surface and the opportunity of process recurrence with high pulse repetition frequency allow to convert purposefully liquid hydrocarbons.

2. Test stand and methods of measurements

Experiments were carried out with the radiochemical reactor created on the basis of the small-sized generator of nanosecond voltage pulses by amplitude of 200 kV, duration of 4 ns and repetition frequency of 1–200 Hz. The reactor worked in the following way: a voltage pulse from the generator of nanosecond pulses was given on the vacuum diode, the case of which is made from two coupled cylinders with internal diameter of 108 mm. Accelerating area of the vacuum diode is formed out of the planar anode (the diode case) and the cathode, operating in a explosive emission mode. The cathode is made from copper foil bands by thickness of 25 μm , width of 4 mm and height of 10 mm pasted on the glass fibre laminate substrate at 5 mm distance from each other and fixed in the cathode holder. Use of contact “metal – dielectric” allowed to decrease electric field intensity which is necessary for explosive emission initiation on the cathode and thus to increase number of pulses up to 10^7 – 10^8 . In addition to plasma of cathode torches, in such system owing to formation of a surface discharge, plasma of an edge of the glass fibre laminate substrate starts to emit. Arising correlation between emitters led to more even

selection of the current from a surface of the cathode. To extract accelerated electrons from the vacuum diode an output window with system of the apertures closed by an Al–Be foil with thickness of 45 μm was used. The accelerator formed behind the foil the stream of electrons with sectional area of 10 cm^2 , density of 65 A/cm^2 and duration of 4 ns. Energy distribution of electrons extracted from the vacuum diode was characteristic for accelerators of this type with 140 keV in the peak. Total energy of electrons for a pulse, measured by means of a calorimeter IMO-2 and calculated from energy distribution of electrons coincided well enough and was 0.2 J for a pulse.

2 ml of the investigated liquid was irradiated in a stainless steel cuvet with internal diameter of 40 mm and depth of 15 mm. The cuvet allowed to irradiate at a stationary mode, or at a liquid flow mode. At a stationary mode of irradiation the cuvet can be vacuumized and be filled up with inert gas with pressure up to 10 atm. Irradiation was carried out in air and in medium of inert gases. The analysis of the stable products received during irradiation of hydrocarbons, was carried out by the gas chromatography method.

Diffusion of oxygen in liquid alkanes depends on viscosity and can occur for a layer of 0.3–0.5 mm at air pressure during 10 s. Concentration of oxygen in a superficial layer increases due to air pressure or air purge through liquid for reduction of this time. Besides, due to heat evolution at irradiation of a liquid layer by the pulse stream of electrons, the developed surface like boil formed in our experiments, that also promoted enrichment of liquid by.

3. Test results and their interpretation

Products of radiolysis and their radiochemical yields (G) at irradiation of normal alkanes C_6 and C_8 by the stream of electrons in argon medium are shown in Table 1.

The basic radiolysis products in a liquid phase are in this case normal alkanes with molecular mass less and more, than molecular mass of the initials, and also dimers and their various isomers. In both cases the maximal output of isomers *i*- C_{2n} was observed. Non-saturated hydrocarbons were noted in trace quantities.

The mechanism of radiolysis product formation in monomolecular and bimolecular processes is connected with attraction of reactions in which the free radicals resulting from the break of O–H and C–C linkages of excited molecules of alkanes participate.

Table 1

Hexan, dose $2.8 \cdot 10^{21}$ eV/g Medium – 1 atm of argon		Octane, dose $2.8 \cdot 10^{21}$ eV/g Medium – 1 atm of argon	
Product	G , mol./100 eV	Product	G , mol./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

The basic part of radicals is presented at the same time by the radicals that are formed at the break of C–H linkages. The output of radicals of smaller size, than a parental molecule, makes smaller value, than the output of radicals with the break of C–H linkages [1]. The break of C–C linkages can occur both at excitation, and at ionization. Radicals can liberate secondary atom of hydrogen from normal alkanes, or recombine with one of other radicals. The disproportionation can occur at that. The type of reaction depends on conditions of its realization. In our conditions of irradiation, when already on initial points of tracks their total sectional area is approximately 20% from an irradiated surface, there are dominating reactions basic products of which are isomers of dimers and hydrocarbons with intermediate molecular mass.

Hydrocarbons with intermediate molecular mass and dimers are formed by statistical combination of various hydrocarbon radicals with predominance of disproportionation reactions. Besides, irregular distribution of products of a group S_{n+1} in comparison with products of a group C_{n+2} , C_{n+3} , etc. at irradiation of alkanes (C_6 , C_8) by the stream of electrons of nano-second duration is observed. Registered anomaly was

observed earlier by other researchers [1] which noted that group S_{n+1} products both linear and branched, are formed in general by means of C–H linkages and by introduction of methylene appearing at radiolysis in a singlet condition, and not by recombination of parent radicals with methyl radicals.

Experiments on oxidation of n -alkanes were carried out in air at high pressure and at air purge of an initial product.

The basic products at irradiation of liquid n -alkanes C_5 , C_6 , C_8 by the stream of electrons of nano-second duration at air purge or at air pressure of 3.5 atm are carbonyl compounds and spirits (see Tables 2 and 3), resulting from disproportionation of peroxide alkyl radicals. Acids and peroxide compounds were not found out. Great enough output of products for pentane and hexane attracts attention. It is concerned that at irradiation by the stream of electrons the considerable part of energy evolves as heat and the part of the product is in a gas phase where processes of oxidation are more effectively and oxidation by the chain mechanism may [2]. In spite of oxidation processes the process of isomerization in air is observed also in experiments.

Table 2

Pentane, dose $3.3 \cdot 10^{21}$ eV/g Medium – 1 atm of air		Hexan, dose $2.8 \cdot 10^{21}$ eV/g Medium – 1 atm of air	
Product	G , mol./100 eV	Product	G , mol./100 eV
Penta-aldehyde	35.2	Hexane-aldehyde	8.3
Hexanone-2	7.5	Hexanone-2	10.5
n -hexanol	4.3	n -hexanol	6.4
Heptanol-2	5.5	Hexanol-2	9.8
$C_n > C_5$	13.5	$C_n > C_6$	6.1
		$n-C_{12}, \Sigma i - C_{12}$	4.2

Table 3

Octane, dose $2.8 \cdot 10^{21}$ eV/g Medium – 1 atm of air		Octane, dose $2.8 \cdot 10^{21}$ eV/g Medium – 3.5 atm of air	
Product	G, mol./100 eV	Product	G, mol./100 eV
Octa-aldehyde	4.2	Octa-aldehyde	5.5
Octanon-2	4.2	Octanon-2	4.5
Octanon-3	3.9	Octanon-3	4.4
Octanol-1	3.1	Octanol-1	1.7
Octanol-2	2.6	Octanol-2	2.0
Octanol-3	0.9	Octanol-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
$n-C_{16}, \Sigma i - C_{16}$	5.9	$n-C_{16}, \Sigma i - C_{16}$	1.2

Experiments on oxidation of n-alkanes were carried out in air at high pressure and at air purge of an initial product. The basic products at irradiation of liquid n-alkanes C_5 , C_6 , C_8 by the stream of electrons of nanosecond duration at air purge or at air pressure of 3.5 atm are carbonyl compounds and spirits (see Tables 2 and 3), resulting from disproportionation of peroxide alkyl radicals. Acids and peroxide compounds were not found out. Great enough output of products for pentane and hexane attracts attention. It is concerned that at irradiation by the stream of electrons the considerable part of energy evolves as heat and the part of the product is in a gas phase where processes of oxidation are more effectively and oxidation by the chain mechanism may [2]. In spite of oxidation processes the process of isomerization in air is observed also in experiments.

Structural changes of the n-alkane C_8 at irradiation by the stream of electrons (dose $2.7 \cdot 10^{21}$ eV/g) at air pressure of 3.5 atm in presence of a catalyst $SnBr_4$ in a chromatogram stated with low resolution of peak series of high-molecular products, the content of which is 35–40%.

4. Conclusion

It is shown, that use of the e-stream for radiolysis of liquid n-alkanes in various gas media allows to initiate effectively and purposefully processes of oxidation and isomerization.

Use of the catalyst $SnBr_4$ at irradiation of liquid n-alkanes in air and at high pressure allows to form effectively high-molecular products, the content of which is 35–40%.

References

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