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KINETICS OF ACCUMULATION OF HYDROCARBONS AND OXIDATION PRODUCTS DURING RADIOLYSIS OF A MIXTURE OF WATER-HEXAN

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Abstract: The kinetics of accumulation of hydrocarbons during the radiolysis of a mixture of n-hexane + water with different content of components at T = 300K, as well as the sum of the amount of alcohols and carbonyl compounds was studied. The rate of the processes and the radiation-chemical yields of hydrocarbons, the amount of alcohols and carbonyl compounds are determined.

Keywords: γ-radiation, radiolysis, water-hexane.

1. Introduction

Radiolytic processes in hydrocarbon systems are mainly studied in the gas phase. The patterns of the influence of the phase state and the composition of the mixture on the values of the radiation-chemical yield of hydrocarbons have not been studied. In connection with the depletion of hydrocarbon reserves and the increasing demand for energy carriers, the need to identify patterns of radiation-chemical processes in liquid water-hydrocarbon systems, which can serve as model systems for producing environmentally friendly gases, has increased [1-5]. Therefore, this paper presents the results of radiation-chemical processes for the production of hydrocarbons from the model system water-n-hexane at T = 300K.

2. Experimental part

Radiolysis of a mixture of n-C_6H_{14} + H_2O was carried out under static conditions in sealed ampoules with a volume of V = 15 cm^3 under the action of γ-radiation. The filling of the ampoules with the components of the system was carried out from their vapor state in a vacuum-adsorption unit. The accuracy of filling ampoules is about ~ 0,001. Sealing ampoules held by freezing components up to 77K. It was established experimentally that when the ampoules with the samples are sealed, hydrocarbon transformations do not occur.

The ampoules with samples were irradiated on an isotope source of ^{60}Co γ-quanta. The dosimetry of the source was carried out by chemical methods — ferrosulfate and hexane [6]. The absorbed dose in the test systems was calculated by comparing the electron densities of the test and dosimetric systems. When calculating the absorbed dose rate of the water-n-hexane system, the content of each component was taken into account.

The value of the absorbed dose rate, determined by the ferrosulfate method, was D_{dose} = 0.2 ÷ 0.15 Gy / s. For the components of the studied systems, this value was determined by the expressions:

D_{water}=0,98 D_{dose} for water,

D_{hexane}=0,66 D_{dose} for hexane

D_{ZrO2}=0,87 D_{dose} for zirconium oxide.

For all systems, the calculated values of the absorbed dose are determined taking into account the composition and electron density of the components.

The ampoules were opened in a special cell, from where the radiolysis products entered the chromatograph column. The analysis of gases for H_2, CO and O_2 contents was carried out on a Gazokhrom-3101 gas analyzer and hydrocarbons - on an Agilent-7920 chromatograph. We used distilled water, n-hexane "chemically pure". The purity of n-hexane was checked by chromatographic method.

The infrared absorption spectra of liquid-phase radiolysis products of a hexane-water mixture were obtained on a Varian 640 FTIR spectrophotometer in the frequency range $\nu = 4000 \div 400$ cm^{-1}. For this purpose, a liquid NaCl cuvette with a constant thickness d = 0,027 mm was used.

3. Results and discussion

The kinetics of accumulation of hydrocarbons during radiation-chemical processes in a water-n-hexane mixture in the liquid phase was studied. To do this, mixtures were introduced into ampoules at various ratios of components, and the radiolysis of these systems under the action of γ-quanta at 300K was also given. Figure 1 shows the kinetic curves of the accumulation of hydrocarbons at different ratios of the starting materials. Based on the initial linear section of the kinetic curves, the values of hydrocarbon accumulation rates W (C_xH_y) are determined by graphical differentiation by the expression:

$$W(C_xH_y)=d(C_xH_y)/d\tau$$

Based on the value of the rate of accumulation processes, the radiation-chemical yields of hydrocarbons are determined. Under the influence of γ-quanta on hydrocarbons, the formation of excited molecules and ions occurs, which can then decompose with the splitting of C – H and C – C bonds. For these processes to occur, it is necessary that the excitation energy be greater than the energy of the above bonds. For example, the processes occurring in hexane under the action of gamma radiation can be represented by the following scheme [12]:

$$C_6H_{14} \rightsquigarrow C_6H_{14}^+, e^-, C_6H_{14}^*$$
$$C_6H_{14}^+ + e^- \rightarrow C_6H_{14}^*$$
$$C_6H_{14}^* \rightarrow C_6H_{13}^\bullet + H$$
$$C_6H_{14}^* \rightarrow C_6H_{12} + H_2$$
$$C_6H_{14}^* \rightarrow C_nH_{2n+1}^\bullet + C_{6-n}H_{2(6-n)+1}, \text{где } n=1 \div 6$$
$$C_nH_{2n+1}^\bullet + C_nH_{2n+1}^\bullet \rightarrow C_nH_{2n} + C_nH_{2n+2},$$

As a result of the above processes, during the radiolysis of hexane, limiting and unsaturated hydrocarbons are formed with the number of carbon atoms from 1 to 6. Mainly radicals take part in the formation of C_1-C_5 hydrocarbons. EPR spectroscopy identified many radicals formed during the radiolysis of hexane [12]. They mostly arise when the C – H bond is broken, forming the C_6H_{13} and H radical. However, C – C bonds may also break to form fragmentation radicals, for example CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}. They were detected by the EPR spectroscopic method [11].

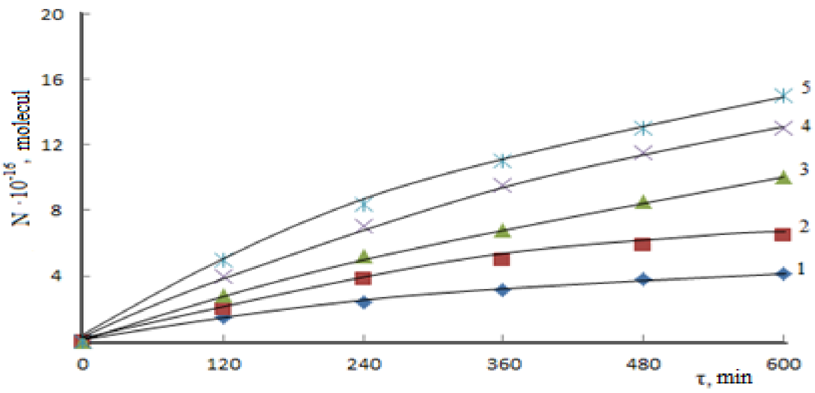

Fig.1. Kinetics of hydrocarbon accumulation during radiolysis of the mixture n-hexane + water at T = 300K, D=0,15 Gy/s, 1-pentane, 2-butane, 3- methane, 4-ethane, 5-propane

The kinetics of accumulation of hydrocarbons was studied experimentally during the radiolysis of a mixture of water-n-hexane with a 50% content of each component. The analysis was carried out in the gas phase. Figure 1 shows the kinetic curves of the accumulation of hydrocarbons during the radiolysis of a mixture of the above composition at T=300K and the dose rate D = 0,2 Gy/s.

Based on the kinetic curves, the values of the rate of accumulation and the radiation-chemical yield of individual hydrocarbons are determined. They are presented in table 1:

Table 1.

The value of the rate of accumulation and radiation-chemical yields of hydrocarbons

Hydrocarbons	**Methane**	**Ethane**	**Propane**	**Butane**	**Pentane**
$W \cdot 10^{13}$, molecule/sec	0,58	0,70	0,75	0,56	0,18
G, molecule/100eV	0,15	0,18	0,2	0,15	0,09

In general, the radiolytic decomposition processes in the water-n-hexane system can be schematically represented as follows:

$$n(H_2O + C_6H_{14})_{liq} \rightsquigarrow (n\text{-}x)(H_2O + C_6H_{14})_{liq} + CH_4 + H_2 + \Sigma C_{iliq} + \Sigma C_{iqaz}$$

where n- is the number of initial molecules of the mixture, x- is the number of molecules of the mixture in the gas phase, and the indices g- and gas- denote the liquid- and gas states, respectively.

From the diagram it can be seen that hydrocarbon products can be formed both in the gaseous and in the liquid state. Comparisons of the results we observed for hydrocarbon yields with literature data on the radiolysis of pure hexane show that the spectrum of products in both systems is about the same, but the absolute values differ [7-10]. This difference can be explained by the fact that a certain part of the hydrocarbons is in a dissolved state in the original system. The reason for the difference may be the interaction of the radiolysis products of the original products. The decrease in the amount of hydrocarbons in comparison with the radiolysis of pure hexane indicates the influence of the products of radiolysis of water in particular O_2 and OH, which interact with alkyl radicals to form alcohols and carbonyl compounds. Possible mechanisms for their formation are as follows:

$$C_nH_{2n+1}^{\bullet} + OH \rightarrow C_nH_{2n+1}OH, \text{ где } n=1\div6$$
$$H + O_2 \rightarrow HO_2,$$
$$C_nH_{2n+1}H + HO_2^{\bullet} \rightarrow C_nH_{2n+1}O_2^{\bullet} + H_2,$$
$$C_nH_{2n+1}O_2^{\bullet} + C_nH_{2n+1}O_2^{\bullet} \rightarrow C_nH_{2n+1}OH + C_nH_{2n}O + O_2$$

To identify specific oxygen-containing compounds, an infrared analysis of the irradiated H_2O + C_6H_{14} mixture was carried out at a volume ratio of 50%. C=O vibrations were detected at frequencies of 1740–1695 cm^{-1}, as well as C–H stretching vibrations at frequencies of 2900–2700 cm^{-1} and C–H deformation vibrations at frequencies of 975–780 cm^{-1}. These vibrations were attributed to aldehydes.

Aliphatic aldehydes were also detected at frequencies of 1440-1325cm^{-1}. Also on the spectra detected peaks corresponding to ketone carbonyl groups:

-CH_2-CO-CH_2 at frequencies of 1725-1703 cm^{-1}

and

-CH=CH-CO- at frequencies of 1685-1665 cm^{-1}

Alcohols were also found among radiolysis products (fig.2). They correspond to the following spectrum bands:
unrelated OH group at frequencies of 3650-3590cm^{-1}

Deformation vibrations of OH and valent oscillations of C–O:

primary alcohols	near 1050cm^{-1} and 1350-1260cm^{-1}
secondary alcohols	near 1100 cm^{-1} and 1350-1260 cm^{-1}
tertiary alcohols	near 1150cm^{-1} and 1480-1310cm^{-1}

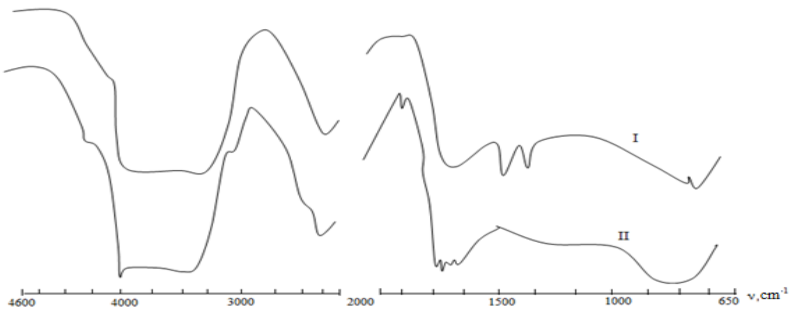

Fig. 2. IR- spectra of the irradiated system n-C_6H_{14}+H_2O at 5 hours (I) and 15 hours (II) at D=0,15 Gy/s

The identification of the above substances was carried out using methods and tables [13-14]. At the same time, oxygen-containing compounds were analyzed by liquid chromatography. Based on the data obtained, a summation of the amount of alcohols and a summation of the amount of carbonyl compounds was performed separately and is shown in fig.3. kinetics of accumulation of these substances during the radiolysis of the mixture in a volume ratio of 50%.

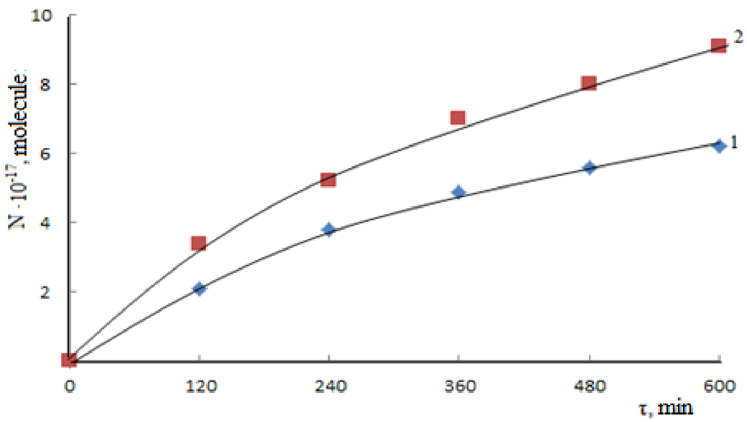

Fig. 3. The kinetics of formation of oxidation products during the radiolysis of the system n-C_6H_{14}+H_2O at T=300K and dose rates D=0,15 Gy/s, 1- alcohols, 2-carbonyl compounds

From figure 2. it can be seen that with 15-hour irradiation at a dose of 30 kGy, the absorption bands of hexane disappear in the range of 1500-1200 cm^{-1}, which means its almost complete decomposition.

Using this graph, the rates of accumulation and the radiation-chemical yields of carbonyl compounds and alcohols were calculated, which are listed in table 2:

Table 2.

Values of accumulation rate and radiation-chemical yields of carbonyl compounds and alcohols

Material	**Carbonyl compounds**	**Alcohols**
$W \cdot 10^{13}$, molecule/s	9,2	8,0
G, molecule/100eV	2,1	1,7

Thus, the radiation-chemical processes occurring in mixtures of water and hydrocarbons under the influence of irradiation allow us to solve the problems of obtaining efficient energy carriers and the utilization of polluted water.

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SU-HEKSAN QATIŞIĞININ RADİOLİZİ ZAMANI KARBOHİDROGENLƏRİN VƏ OKSİDLƏŞMƏ MƏHSULLARININ ƏMƏLƏGƏLMƏ KİNETİKASI

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Xülasə: Komponentlərin müxtəlif nisbətlərində n-heksan+su qatışığının radiolizi zamanı T=300K temperaturda karbohidrogenlərin əmələgəlmə kinetikası, eləcə də spirtlərin və karbonil birləşmələrin miqdarı təyin edilmişdir. Karbohidrogenlərin radiasiya-kimyəvi çıxımları, proseslərin sürətləri təyin edilmişdir.

Açar sözlər: γ-şüalanma, radioliz, heksan+su.

КИНЕТИКА НАКОПЛЕНИЯ УГЛЕВОДОРОДОВ И ПРОДУКТОВ ОКИСЛЕНИЯ ПРИ РАДИОЛИЗЕ СМЕСИ ВОДА-ГЕКСАН

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Резюме: Исследована кинетика накопления углеводородов при радиолизе смеси н-гексан+вода при различном содержании компонентов при Т=300К, а также суммирование количества спиртов и карбонильных соединений. Определена скорость процессов и радиационно-химических выходов углеводородов.

Ключевые слова: γ-излучение, радиолиз, вода-гексан.