THE HYDROGEN GENERATION DURING WATER-HEXANE SYSTEM RADIOLYSIS

A.A.Garibov, K.T.Eyubov, T.N. Agayev

Institute of Radiation Problems of Azerbaijan National Academy of Sciences, Baku-Azerbaijan

Kinetics of molecular hydrogen accumulation during water-n-hexane compound radiolysis at different component content is investigated in given work. It is determined that as a result of transmission of ionizing radiation energy and interaction of active intermediate products with initial components radiochemical hydrogen yield in the compound exceeds additive sum of yields in separate components.

Radiolysis of hydrocarbons-water compounds is of great interest during revelation of new ways of transformation and use of ionizing radiation with the help hydrogen- universal energy carrier[1-10]. The results of these investigations may be helpful during more precise determination of process mechanism passing in experimental conditions under the influence of ionizing radiation in hydrocarbon-water compounds and also in natural conditions of oil and gas fields under the influence of natural radionuclides radiation.

Stated work is devoted to the investigation of kinetics of molecular hydrogen accumulation at radiolysis of water-n-hexane model system.

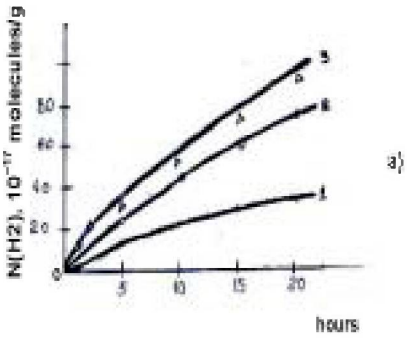
Radiolysis of water-n-hexane system is realized in statistic conditions in sealed ampoules under the influence of γ-radiation. Filling of ampoules with the system's components is carried out from their vapor state on vacuum-adsorption mounting. Filling accuracy of ampoules makes approximately ±0,001. Sealing of ampoules was realized by freezing the components up to 77K. It was established experimentally that during the soldering process of ampoules with the samples, the transformation of hydrocarbons doesn't take place.

Irradiation of ampoules with samples was carried out on isotope source of γ-quantum ^{60}Co. Source dosimetry was carried out by chemical methods – ferrasulphate, hexane [11]. Adsorbed dose in investigated system was calculated by comparing electron density of investigated and dosimetric systems [11-13]. During calculation of adsorbed dose rate of water-n-hexane system the content of each compound was taken into consideration. The value of adsorbed dose rate determined by ferrasulphate method was D_{dose} = 1,42 gy/s. For the investigated system's components this value was determined by the expression D_{water} = 0,98 D_{dose} for water and D_{hexane}= 0,66 D_{dose} for hexane. For all the systems calculated values of adsorbed dose are determined taking into account the content and electron density.

Opening of ampoules were made in special location wherefrom radiolysis products entered into the chromatograph column. Analysis of H_2 , CO, O_2 is carried out on Gaschrom-3101 gas-analyzer. Distilled water and pure n-hexane are used in this work. Hexane purity is checked by chromatographic method.

Taking into consideration that the objective of the work is revelation of effective ways of getting universal energy carrier from water-hydrocarbon impurities system, the kinetics of molecular hydrogen accumulation during γ-radiolysis of water-n-hexane system was investigated.

"Water-n-hexane systems with different content of n-hexane were prepared and their radiolysis at the temperature T=296K was carried out. The kinetics of molecular hydrogen accumulation at radiolysis of water-n-hexane compound at different proportions was investigated. It is shown kinetic curves of the molecular hydrogen accumulation on Figure.1.a.



a)

On basis of kinetic curves the value of speed and radiochemical yields of molecular hydrogen was calculated. Radiolysis of pure water and n-hexane was carried out in identical conditions. Radiochemical yields of molecular hydrogen at pure water and n- hexane radiolysis are accordingly equal to 0,45 and 5,30 molecules/100 eV [1,10].

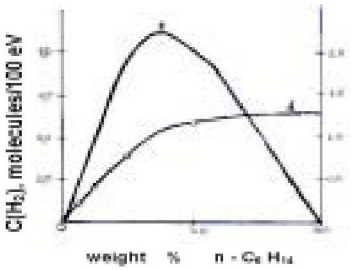
Supposing that during radiolysis of water-n-hexane compound radiolysis processes of the components pass according to the mechanism of private systems and radiolysis products do not interact with each other, for H_2 accumulation speed during radiolysis of the given compound it's possible to draw up the following expression:

$$dH_2/d\tau=(x_1G_1 + x_2G_2) \cdot I \cdot 10^{-2} \qquad (1),$$

where x_1, x_2, G_1 and G_2 is the share of each component in the compound (%) and correspondingly values of radiochemical yields (molecules/100ev) during radiolysis of pure components, I-dose rate (eV/g·sec).

The dependence of H_2 radiochemical yield from n-hexane content in water-n-hexane compound is shown in Figure.1.b (curve1).

As it is seen radiochemical yield of hydrogen increases with the increase of n-hexane content in compound and at high concentrations within accuracy corresponds to the yield of molecular hydrogen during radiolysis of pure hexane. Dependence of difference of experimentally observed and calculated radiochemical yields values $\Delta G=G_{exper}$ (H_2)-G_{calcul} (H_2) from compound content is shown in Figure 1.b (curve2).



b)

As it is seen dependence of ΔG from n-hexane content has extreme character. Maximum value ΔG is observed in the range of values of n-hexane concentration c_{hexane}=30-40%. Creation of molecular hydrogen during radiolysis of pure water and hexane at the T=296k may be presented by the following processes [12]:

$$H_2O \quad H + OH \qquad (2)$$

$$H + H \rightarrow H_2 \qquad (3)$$

$$n\text{-}C_6H_{14} \quad n\text{-}C_6H_{13} + H \qquad (4)$$

$$H + H \rightarrow H_2 \qquad (5)$$

In experimental conditions dissolubility of n-hexane in water is equal to 0,0138g/100g of water. Maximum quantity of n-hexane molecules dissolved in experimental conditions in 0,5g of water makes $N_{max}=2,3\cdot10^{18}$ molecules. The surface area between phases in experimental conditions is determined according to the value of geometrical sectional area of ampoules and it is equal to $S=283mm^2$.

According to the value of elementary area occupied by the molecule of n-hexane $w_m=0,51$ nm^2 [14] the number of n-hexane molecules in monomolecular layer between phases in radiolysis conditions was determined and it is equal to $N=5,5\cdot10^{14}$ molecules. Maximum deviation in values of hydrogen accumulation speed in experimental conditions corresponds to the following value $\Delta W(H_2)=1,06\cdot10^{14}$ molecules/g·sec. If we accept that the creation of molecular hydrogen is taking place according to reactions (3) and (5) then for obtaining such value is necessary decomposition of initial substances molecules ~$2\Delta W$ (H_2), i.e. $2,12\cdot10^{14}$ molecules.

As 2,3 $\cdot 10^{18}$ n-hexane molecules were in direct contact with water molecules in experimental conditions, it's possible to explain observed deviations from additive sum by the transfer of energy from water molecules to n-hexane molecules as well as by the interaction of intermediate products of radiolysis.

Ionization potential and excitation level of water molecules is higher than of n-hexane ones. That's why transfer of energy between the components may be realized by ionization as well as by excited state. H and OH radicals formed at radiolysis according to reactions (2) and (4) may react with n-hexane molecules [16]:

$$OH + C_6H_{14} \rightarrow C_6H_{13} + H_2O \qquad (6)$$

$$H + C_6H_{14} \rightarrow C_6H_{13} + H_2 \qquad (7)$$

As a result of process (7) quantity of formed hydrogen increases during compound's radiolysis.

Maximum shift into the range of great water content in compound counts in favour of proposed mechanism $\Delta G\,(H_2)=f(c_{hexane})$ into the range of great water content in the compound.

In that way radiolysis of water-n-hexane mixed fluid in regard to radiolysis of the components passes with the great yield of molecular hydrogen. Radiochemical processes in hydrocarbon-polluted waters may be used for getting hydrogen.

References

1. Radiation chemistry of hydrocarbons. Edited by G.Feldiak, "Energyatomizdat", 1985
2. Buxton G.Y.//Proc. Nato Adv. Study. Inst., Capri, 7-18 Sept., 1981. Dordrecht e.a., 1982 p.241
3. Shimizu Y., Nagai S.// Radiat. Phys. And Chem. – 1989. –33, №6.-p567
4. Soebianto Y., Yamaguchi T.// Radiat. Phys and Chem.-1992.-39, №3.-p251
5. Ohta N., Shiga T.// Bull. Fac. Eng. Hiroshima Univ.-1992.-41, №1.-p25
6. Samarina E.P., Kuzina S.I.// 10 All-Union conference on genetics and mechanism of chemical reactions in solids. Chernogolovka, July 1989: Reports thesis V.2.-Chernogolovka,1989.-p.14.
7. Dey G.R.., Naik D.B., Rao K.A.// Barc.[Rept].-1996.-P/005.-p.55
8. Ponomarev A., Sirtlanov A.S., Pikayev A.K.// Reports of RAS.2000.372, №2, p.195
9. Shiga T., Ohta N.// Bull. Fac. Eng. Hiroshima Univ.-1992.-40, №2.-p127
10. Bugayenko V.L., Byakov V.M.// Institute of theoretical and experimental physics.-1991.- №74-91.-24
11. Pikayev A.K. Modern chemistry. Main regulations, experimental technique and methods. M., "Science" 1985, p.289
12. Garibov A.A., Velibekova G.Z., Rufullayev R.I., Agayev T.N.// Questions of atomic science and technique. Nuclear technique and Technology series, 2nd edit., 1989, p.29
13. Garibov A.A., Velibekova G.Z.,Bakirov M.Y., Djafarov Y.D.// Questions of atomic science and technique. Atomic-hydrogen energy and technology series, 1985, 3rd edit., p.57
14. Kelcev N.V. Basis of adsorption technique. Moscow, Chemistry, 1984, p.40
15. Gordon A., Ford R. Satellite of chemist. "World" publish., 1976, p.263.
16. Pikayev A.K., Kabakchi S.A. Reactivity of primary products of water radiolysis. Reference-book -M.:Energyizdat., 1982

Captions of pictures:

Figure 1

a. Kinetics of molecular hydrogen accumulation during radiolysis of water-n-hexane compound at T=296K and D_{dose} = 1,42 gy/s: curve1(11,5 weight %); curve2(c_{hexane} =21,8 weight %); curve3(c_{hexane}=50 weight %)
b. Dependences of radiochemical yield of hydrogen(1) and difference of additive sum values of radiochemical yields of molecular hydrogen, determined by experimental and calculated methods, (2) during radiolysis of water-n-hexane system at T=296K from hexane content in compound.