THE RADIATION-CHEMICAL REMOVAL OF PHENANTHRENE FROM AQUEOUS SOLUTIONS AND MODDELING OF REMOVAL MECHANISM

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ABSTRACT

The radiolytic decomposition of phenanthrene in water solutions under γ-irradiation was investigated. Phenanthrene was chosen as a prototypical PAHs because of its association with most petroleum products and as usual is produced during petroleum refining.

1. INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are not produced on industrial scale and are mainly created during the incomplete incineration processes of organic compounds. For example, more than 200 PAHs were identified in the fire products of organic fuel, and about 150 in the exhaust gases of transport. The PAHs in atmosphere and in land penetrate into water environment by being washed with atmospheric drops (rain, snow, etc.). Apart from these, the pollution of water environment by PAHs occurs by means of oil, oil products and lubricants.

PAHs are distinguished by their high toxic influence to human health. Most of them have high transformation activity as well, and cause carcinogenic, teratogenic and mutagenic changes.

PAHs undergo different chemical transformations in water environments. These include photolysis by the influence of visible light and by microorganisms in the presense of oxygen. The degradation of PAHs increases by rising of temperature and the amount of independent chloride and with decrease of pH of water medium.

Radiation treatment is considered as effective removal method of PAHs among the new methods of destruction of PAHs in water solutions [1-9]. In [1] the removal process of naphthalene from aqueous solutions using high-energy electron beam irradiation is studied. They found that the naphthalene removal to be more efficient at higher initial naphthalene concentrations and radiation chemical yields of removal process changes from 0.2 up to 1.8 at the range (1.5-160 uM).

The removal yields in the radiolysis of cyclic aromatic compounds were determinated in [10]. It was established that the radiolytic decomposition of simple organic compounds occurs by the breakage of carbon-hydrogen bond giving the parcut radical and hydrogen atom.

In this work, we have investigated the radiolytic decomposition of phenanthrene in water solutions under γ-irradiation. Phenanthrene was chosen as a prototypical PAHs because of its association with most petroleum products and as usual is produced during petroleum refining [11-12].

2. EXPERIMENTAL

Methodics: Because phenanthrene is not dissolved in water, it is first dissolved in methanol and 300 ug/L solutions of phenanthrene are prepared by using these solutions and the solutions with different consentrations and with 0.5 L volume are prepared. The solutions are homogenized with mixing during 16 hours, and are irradiated by ^{60}Co isotope (0.69Gy/s) at different doses. So the irradiated sample contained the methanol as accompaind substance. Concentration of the methanol is changed in the range 0.25-2.5 ml/L(water). After then the extractions and cleaning process of samples for chromotografic analysis are carried out. Phenanthrene determination was provided by system HPLC/FLD (Fluorescence Detector 363) (Varian, USA) with column Chrompack CromSpher PAH (Varian CP29376), carrier solvents-Acetonitrile/Water [12] and GCMS "Thermo Electron" Trace DSQ (quadrupole mass analyzer) (Finnegan, USA) with column TR-5MS 0.25mm x 0.25 um x 30 m. Scan mode- SIM, carrier gas - He. The characteric chromatogramms and specter of phenanthrene identification given in Fig. 1.

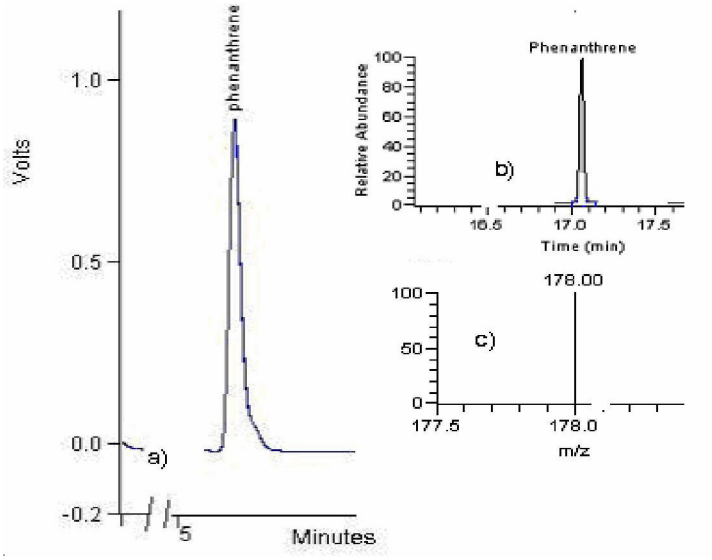

Fig 1. Chromatogramms (a-HPLCFLD, b-GCMS) and specters (c-GCMS) of phenanthrene.

3. RESULTS AND DISCUSSION

Preliminary studies of radiolytic decomposition process were conducted for the different phenanthrene concentrations in distilled water (not aerated).

The kinetic curves are given in Fig. 2. The calculated radiation chemical yields of phenanthrene decomposition are given in Fig 3.

The dates show that, phenanthrene removal yields are increasing by raising of initial concentrations of phenanthrene and changes from (1.5 – 8) x 10^{-2}.

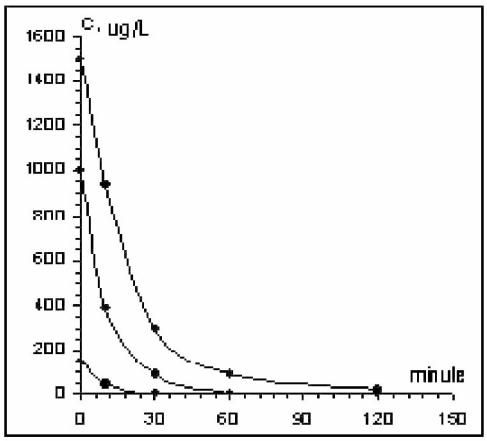

Fig.2. Radiation-chemical degradation of phenanthrene at its various initial concentrations in water solutions.

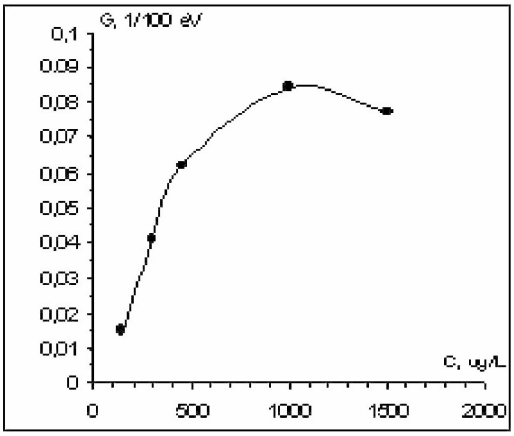

Fig.3. Dependence of radiation-chemical yields of phenanthrene degradations on its initial concentrations in water solutions.

The yields and spectrum of active particles, formed in the water radiolysis is given as:

$$H_2O \rightarrow 2.7\,\dot{O}H + 2.6e^-_{aq} + 0.6\,\dot{H} + 0.45H_2 + 0.7H_2O_2 + 2.6H^+$$

Where the numbers in this equation are the production of G-values of each relevant species (1/100eV).
Each of these particles can react with phenanthrene. But rate constant of the reactions for OH radicals and H atoms with phenanthrene molecules is not determinated. It is known only the rate constant for the e_{aq}^- reaction with phenanthrene: [13]

$$Phenanthrene + e^-_{aq} \rightarrow Phenanthrene\ \ radical\ anion$$

$$Solvent - H_2O$$

$$K = 4 \cdot 10^{19}\, L/mol \cdot \sec$$

But the observed G-values for the phenanthrene degradations processes is less than radiation-chemical yield of e^-_{aq} ($G_{e^-_{aq}}$ = 2.6) . This may be related with competitive reactions of e_{aq}^- with other accompanied compounds in water, for example dissolved O_2 and methanol.

Modeling:
Elementary reactions in water radiolysis:

Number	Reaction	Rate constant at 20 °C, l/mol·s	E_a, kC/mol
1	$2e_{aq} \rightarrow H_2 + 2OH^-$	$5,5 \times 10^9$	20,5
2	$e_{aq} + H \rightarrow H_2 + OH^-$	$2,5 \times 10^{10}$	12,6
3	$e_{aq} + OH \rightarrow OH^-$	3×10^{10}	12,6
4	$e_{aq} + O^- \rightarrow 2OH^-$	$2,2 \times 10^{10}$	12,6
5	$e_{aq} + HO_2 \rightarrow HO_2^-$	2×10^{10}	12,6
6	$e_{aq} + O_2^- \rightarrow OH^- + HO_2^-$	$1,3 \times 10^{10}$	18,8
7	$H_2O_2 + e_{aq} \rightarrow OH + OH^-$	$1,2 \times 10^{10}$	15,1
8	$e_{aq} + HO_2^- \rightarrow OH^- + O^-$	$3,5 \times 10^9$	12,6
9	$O_2 + e_{aq} \rightarrow O_2^-$	$1,8 \times 10^{10}$	13,0
10	$e_{aq} + H^+ \rightarrow H$	$2,3 \times 10^{10}$	12,2
11	$e_{aq} + H_2O \rightarrow OH^- + H$	19	18,8
12	$2H \rightarrow H_2$	$7,8 \times 10^9$	12,6
13	$H + OH \rightarrow H_2O$	2×10^{10}	12,6
14	$H + HO_2 \rightarrow H_2O_2$	2×10^{10}	12,6
15	$H + O_2^- \rightarrow HO_2^-$	2×10^{10}	12,6
16	$H_2O_2 + H \rightarrow OH + H_2O$	9×10^7	13,6
17	$O_2 + H \rightarrow HO_2$	$2,1 \times 10^{10}$	12,6
18	$OH^- + H \rightarrow e_{aq} + H_2O$	$2,2 \times 10^7$	26,0
19	$2OH \rightarrow H_2O_2$	$5,5 \times 10^9$	8,0
20	$OH + O^- \rightarrow HO_2^-$	2×10^{10}	12,6
21	$OH + HO_2 \rightarrow O_2 + H_2O$	$6,3 \times 10^9$	12,6
22	$OH + O_2^- \rightarrow O_2 + OH^-$	$8,2 \times 10^9$	12,6
23	$H_2O_2 + OH \rightarrow HO_2 + H_2O$	$2,7 \times 10^7$	14,0
24	$OH + HO_2^- \rightarrow OH^- + HO_2$	$7,5 \times 10^7$	12,6
25	$H_2 + OH \rightarrow H + H_2O$	$4,2 \times 10^7$	19,0
26	$OH + OH^- \rightarrow O^- + H_2O$	$1,2 \times 10^{10}$	12,6
27	$2O^- \rightarrow OH^- + HO_2^-$	1×10^9	12,6
28	$O_2^- + O^- \rightarrow O_2 + 2OH^-$	6×10^8	12,6
29	$H_2O_2 + O^- \rightarrow O_2^- + H_2O$	5×10^8	12,6
30	$O^- + HO_2^- \rightarrow OH^- + O_2^-$	4×10^8	12,6
31	$H_2 + O^- \rightarrow OH^- + H$	8×10^7	12,6
32	$O^- + H_2O \rightarrow OH^- + OH$	$1,75 \times 10^6$	18,8
33	$2HO_2 \rightarrow H_2O_2 + O_2$	$8,3 \times 10^5$	24,7
34	$H_2O_2 + HO_2 \rightarrow O_2 + OH + H_2O$	0,2	20,0
35	$O^{2-} + HO_2 \rightarrow O_2 + HO_2^-$	$9,7 \times 10^7$	8,8
36	$HO_2 \rightarrow H^+ + O_2^-$	$7,5 \times 10^5$	12,6
37	$2O_2^- + 2H_2O \rightarrow H_2O_2 + O_2 + 2OH^-$	0,3	12,6
38	$H_2O_2 + O_2^- \rightarrow O_2 + OH^- + OH$	0,13	20,0
39	$O_2^- + HO_2^- \rightarrow O_2 + OH^- + O^-$	0,13	20,0
40	$H^+ + O_2^- \rightarrow HO_2$	$5,1 \times 10^{10}$	12,6
41	$H_2O_2 \rightarrow 2OH$	$1,33 \times 10^7$	71,2
42	$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$	1×10^{10}	12,6
43	$HO_2^- + H_2O \rightarrow H_2O_2 + OH^-$	$1,13 \times 10^6$	12,6
44	$H^+ + HO_2^- \rightarrow H_2O_2$	2×10^{10}	12,6
45	$H^+ + OH^- \rightarrow H_2O$	$1,4 \times 10^{11}$	12,6
46	$H_2O \rightarrow H^+ + OH^-$	$2,52 \times 10^5$	45,4
47	$O_2 + O^- \rightarrow O_3^-$	3×10^9	-
48	$O^- + O_3^- \rightarrow 2O_2^-$	7×10^9	-
49	$H_2O_2 + O_3^- \rightarrow O_2 + O_2^- + H_2O$	$1,6 \times 10^6$	-
50	$HO_2^- + O_3^- \rightarrow O_2 + OH^- + O_2^-$	$8,9 \times 10^5$	-
51	$O_3^- \rightarrow O_2 + O^-$	300	-
52	$H_2 + O_3^- \rightarrow O_2 + OH^- + H$	$2,5 \times 10^5$	-
53	$H^+ + O^- \rightarrow OH$	1×10^{10}	-
54	$OH^- + HO_2 \rightarrow O_2^- + H_2O$	1×10^{10}	-

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