Processes of chemical transformations in heavy aromatic hydrocarbons of the Surakhan oil under the action of UV rays

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Abstract. Photooxidative transformations and mechanisms of oxidative reactions in aromatic groups of hydrocarbons isolated from heavy Surakhan (Azerbaijan) petroleum under atmospheric conditions have been investigated. Polycyclic aromatic hydrocarbons, which are part of the aromatic components of heavy Surakhan petroleum, after irradiation with UV rays for 1÷11 hours in the presence of oxygen undergo chemical transformations: endoperoxides polycyclic aromatic hydrocarbons, quinones, etc. are formed. It was found that oxidation products under atmospheric conditions can be formed as follows: during the oxidation of acenes (naphthalene, anthracene), which are part of the aromatic groups of petroleum components, excited aromatic hydrocarbons (donor) interact with atmospheric oxygen (acceptor) in the triplet state with the transition of the acceptor to excited state with the formation of singlet oxygen \( ^1 \text{O}_2 \), in this case the donor molecule returns to the ground state. When phenanthrene is photooxidized, quinones are formed (the reaction is irreversible).

1. Introduction

In order to use hydrocarbon resources, including oils and gases, in the future there is a purposeful utilization of oils obtained from various wells and oil residues obtained after processing natural oil at an oil refinery.

It is known that [1] upon contact of oil with atmospheric oxygen, induced oxidative processes also occur, which in recent years have become the subject of numerous studies related to the solution of a number of fundamental and practical problems: obtaining new phosphors, hydrogen energy, ecology, etc.

At present, the problem of creating chemical light sources [2] based on reversible chemical reactions with the participation of affordable and economically viable organic raw materials is very urgent. Such raw materials, in particular, are oil and oil products.

In recent years, petroleum phosphors (PPh) have been obtained from the least rationally used oil refining products - from heavy catalytic cracking gas oil and heavy pyrolysis gas oil [3]. Due to the possibility of their use in non-traditional areas for petroleum products - as reversible solar energy accumulators, photosensitizers for the decomposition of organic compounds, luminescent dyes, light
stabilizers for polymer materials, as well as in connection with their widespread use in capillary luminescence flaw detection [4-6] photooxidative transformations were investigated, as a result of which physicochemical, structural-group and spectral-luminescent changes in the properties of oil and oil products occur. The kinetic regularities of photooxidative transformations in PPh were investigated and the mechanisms of photochemical processes were revealed.

Since PPh obtained from natural oil are more photo- and thermally stable than PPh from secondary oil products, one of the directions of their utilization is to obtain PPh from high-boiling fractions (> 400°C) of natural oil.

The aim of this work is to study the physicochemical, spectral and luminescent properties of heavy Surakhan oil, as well as to study the kinetics and mechanisms of photochemical transformations in this oil under the influence of UV rays.

2. Research Object and Methodology

Heavy Surakhan oil is a brown liquid belonging to paraffinic oils and is pumped out of a well with a depth of 685 meters. This oil has the following physical and chemical parameters: molecular weight 202; density (20°C) - 841.7 kg/m³; kinematic viscosity (40°C) - 6.33 mm²/s; flash point “plus” 44°C, pour point “minus” 40°C, acid number 2.55 mg KOH/g; the sulfur content is 0.781 wt.%, the resin is 4.1 wt.%.

Heavy Surakhan petroleum (HSP) has a complex composition, it includes naphthenic paraffinic (NP-73%), aromatic (AH-16.24%) and olefinic hydrocarbons (OH-0.01%). Before the study, HSP was divided into individual aromatic hydrocarbon (AH) groups (I-IV groups AH) in accordance with the refractive index using the adsorption method (GOST-11858-85) for an accurate study of the structure-group composition (table 1). In this work, the method [7] was used to calculate the polycyclic aromatic hydrocarbons (PAH) content.

Electronic absorption spectra were measured on a spectrophotometer "JENWAY - 6850 UV/visible Spectrophotometer". The study of photoluminescence spectra and luminescence excitation spectra was carried out on a "Cary Eclipse fluorescence spectrophotometer" device at room temperature in the range 190-1100 nm using a quartz cell with a thickness of 1 cm. Experimental conditions are the same on both devices.

An illuminator with a DRSh-500 mercury lamp with an UFS-1, UFS-5 light filter was used as a light source for photo-irradiation of the samples. The samples were irradiated in the interval 1–11 hours.

As a result of spectral studies, it was found that the absorption peaks of benzene and PAH, which are part of HSP and its components, are recorded in the spectral range of 190-800 nm.

The study of the electronic spectra of the samples shows that with an increase in the concentration of solutions (solvent - hexane) of oil and its components, the absorption spectra are bathochromically shifted to the long-wavelength region of the spectrum. This is due to the condensation of alkyl-substituted PAH.

When comparing UV spectra of HSP and its components, absorption maxima were observed in the spectra of hydrocarbon components of heavy Surakhan oil related to separate AH (benzene, naphthalene, phenanthrene, etc.). This is due to the electron-phonon interactions between PAH molecules: as the distance between PAH molecules increases, the electron-phonon interactions between them weaken, so the absorption peaks for individual PAH are accurately distinguished and recorded in the electronic absorption spectra.

The total amount of AH in the Surakhani oil and its components for the 1st group. AH, II gr. AH, III gr. AH and IV group AH, are, respectively, 34.8; 42.4; 44.6; 39.1 wt.%. On the other hand, if we compare the electronic absorption spectra of I-IV group AH in the spectral range 250-300 nm, then the value of optical densities (D) changes as follows:

1.7 (I gr. AH) < 2.9 (II gr. AH) < 3.2 (III gr. AH) < 3.5 (IV gr. AH).
When studying the electronic spectra of AH I - IV gr. it was determined that the long-wavelength boundaries of the absorption spectra of the components of AH III and IV gr., in contrast to I and II gr. continue up to 700 nm. However, in this region of the spectrum, due to the overlapping of absorption bands, it was not possible to carry out a quantitative analysis. The spectral range > 400 nm in the UV spectrum is most likely associated with alkyl-substituted PAHs and heteroatomic compounds [8].

The values of benzene and PAHs present in the HSP components and calculated from the UV absorption spectrum are shown in table 1.

### Table 1. The content of benzene and PAH in aromatic HSP groups.

| Composition and Aromatic Group | Benzene (wt.%) | Naphthalene (wt.%) | Phenanthrene (wt.%) | Anthracene (wt.%) | Total (wt.%) |
|-------------------------------|---------------|-------------------|-------------------|-----------------|-------------|
| Petroleum                     | 4.3           | 3.2               | 2.4               | Traces          | 10.1        |
| 1 group aromatics             | 20.1          | 12.1              | 2.5               | -               | 34.8        |
| 2 group aromatics             | 18.7          | 20.6              | 3.1               | -               | 42.5        |
| 3 group aromatics             | 17.4          | 20.1              | 3.04              | 4.1             | 44.6        |
| 4 group aromatics             | 15.2          | 13.7              | 4.2               | 6.1             | 39.1        |

The presence of alkyl-substituted AH in HSP and its components was confirmed by IR spectra. For aromatic hydrocarbons, this spectrum is characterized by absorption regions 1612-1620, 3030-3080 cm⁻¹. However, the shift of the absorption maxima to the region of high and low frequencies of 10-12 cm⁻¹ indicates the presence of mono-, di-, trivalent aromatic rings in the compounds. To determine the type of substituted aromatic compounds, the absorption region of 700-900 cm⁻¹ was studied, and it was determined that the studied samples contain mono – (675, 701, 702 cm⁻¹); 1.2 di - (745, 746 cm⁻¹); 1.3 di - (780, 870 cm⁻¹); 1, 2, 3 tri - (779, 780 cm⁻¹), 1, 2, 4 tri - (811, 812, 871-875, 879 cm⁻¹) substituted with AH.

Thus, the results of UV and IR studies show the presence of mono-, bi- and tricyclic AH in the composition of HSP and its components. This oil can also contain heterocyclic compounds.

Before studying the luminescence spectra, the composition of HSP and its components exposed to UV light was considered as a preliminary qualitative analysis. In this case, the content of the investigated solutions was determined by the color of the luminescence of the spot of the given solution, impregnated on a paper filter (the solvent is benzene). As a result of visual studies, the following luminescence colors were observed: oil (yellowish brown); I group AH (purple); II group AH (blue-violet); III group AH (turquoise) and IV group AH (yellow-pink).

In order to improve the accuracy of visual observations for each component of the aromatic group, samples of various concentrations (solvent hexane) were prepared and their luminescence was investigated (table 2).

Although mono - and bicyclic AH, which are the main components of I gr. AH, emit colorless fluorescent light [9], phenanthrene emits violet fluorescent light. In the case of II gr. AH fluorescent light of various shades of violet is observed, which refers to phenanthrene and its alkyl substituents. There are also alkyl-substituted naphthalenes in this group. III gr. AH have turquoise backlighting: a mixture of blue and green colors. This color can be attributed to a mixture of 9, 10-diphenylanthracene (blue fluorescence) and 9, 10-bis 2-phenylethylanthracene (green fluorescence). In addition, blue-violet fluorescence is observed at various concentrations, which indicates the presence of alkyl-substituted phenanthrene and anthracene hydrocarbons (table 2).

The results obtained were confirmed by the photoluminescence method, and the study of the spectral-luminescent properties of AH in HSP and its components revealed that they consist mainly of mono-, bi- and tricyclic AH and their alkyl-substituents (table 3).

An increase in the intensity of the luminescence maxima was observed upon excitation of the samples at the maxima of shorter wavelengths corresponding to PAH.
After irradiation with HSP (1-11 hours of radiation), the intensity of absorption, luminescence excitation, and luminescence peaks of PAHs recorded for all AH groups decreases. In this case, the optical density in the spectral region of about 200 nm for all groups increases. This indicates the formation of endoperoxides in the components of the aromatic group of PAH after UV irradiation.

### Table 2. Results of visual control of the luminescence of heavy Surakhan oil of various concentrations.

| Studied components | Studied components (%) | Luminescence color |
|--------------------|------------------------|--------------------|
| Initial substance  |                        | Purple             |
| I group AH         | 2.69                   | light purple       |
|                    | 1.45                   | light purple       |
| Initial substance  |                        | bluish purple      |
| II group AH        | 2.68                   | purple             |
|                    | 1.35                   | light purple       |
| Initial substance  |                        | Turquoise          |
| III group AH       | 2.76                   | Blue               |
|                    | 1.40                   | bluish purple      |
| Initial substance  |                        | yellow-pink        |
| IV group AH        | 2.90                   | dark yellow        |
|                    | 1.48                   | yellow-blue        |

### Table 3. Distribution of mono-, bi- and tricyclic aromatic hydrocarbons in HSP and its components over some luminescence maxima.

| Aromatic groups TSN | Monocyclic AH and their alkyl-substituted | Bicyclic AH and their alkyl-substituted | Tricyclic AH and their alkyl-substituted |
|---------------------|-------------------------------------------|----------------------------------------|------------------------------------------|
| I group AH          | 290, 291, 292, 308                        | 329, 336, 340, 355                     | 403, 408, 410, 443, 444, 475, 498, 521, 391, 417 |
| II group AH         | —                                         | 330, 331, 332, 337, 340, 341, 342, 354, 360 | 420, 425, 433, 445, 460, 521, 475, 492, 493, 475, 498, 375, 395, 400, 415, 444 |
| III group AH        | —                                         | 315, 316, 332, 344, 357, 368            | 447, 551, 460, 493,620                   |
| IV group AH         | —                                         | 359, 365, 377                          | 410, 425, 445, 462, 473, 497, 522        |

After 7 hours of irradiation, I gr. AH optical density of the absorption maximum band corresponding to naphthalene hydrocarbons decreases and a new absorption band is formed at \( \lambda = 200 \) nm. This absorption band is associated with the photooxidation of naphthalene hydrocarbons, so that 1, 4-naphthaquinone can be obtained as a result of the oxidation process [10]:

Oxidation of component II gr. AH slightly differs from the oxidation process of the I gr. AH: in this component, the optical density of the absorption band observed at 275 nm and belonging to the anthracene hydrocarbon decreases; a new absorption maximum is formed at 251 nm after 1 hour of irradiation. As the irradiation dose increases, this maximum is hypsochromically shifted to 240 nm (the hypsochromic shift occurs as a result of the introduction of an electron-donor substituent in the PAH molecule and the replacement of long-wavelength \( \pi\pi^* \) bands by \( l \rightarrow \alpha\pi \) bands [11]). The absorption intensities of benzene (204 nm) and naphthalene (225 nm) hydrocarbons decrease with increasing irradiation time, and they change hypsochromically, which indicates the formation of
oxymolecules. Component III gr. AH was irradiated with an interval of 1-11 hours. In this case, the optical density of the maximum absorption of naphthalene hydrocarbons \( (D = 0.9603) \), like that of the other two components, decreases, and after 7 hours of irradiation the absorption band disappears (figure 1). After 9 hours of irradiation, a new absorption maximum begins to form in the sample at < 200 nm, which, upon subsequent irradiation (201 nm), shifts bathochromically, and the optical density increases sharply. In the IV gr. AH, in contrast to the other three components, the absorption bands overlap more, which is associated with an increase in the electron-phonon interactions between PAH molecules.

![Diagram of reaction scheme]

**Figure 1.** UV-absorption spectra of dilute solutions of sample. I and II group aromatics: ----) before irradiation, ----) 1 minutes, ----) 7 hour, ----) 11 hours; III and IV group aromatics: ----) before radiation, ----) 1 hour, ----) 7 hours, ----) 11 hours.

However, even in this case, the optical densities of the recorded absorption peaks - benzene (203 nm), naphthalene (218 nm), phenanthrene (258 nm) - decrease after 7 hours of irradiation. At the end of irradiation, the absorption maximum of phenanthrene hydrocarbons reaches 240 nm (figure 1). After 11 hours, the UV spectrum recorded an absorption maximum at 192 nm with a high optical density \( (D = 2.9) \), which can be attributed to endoperoxides. Oxidation of anthracene hydrocarbons in aromatic hydrocarbons with the formation of endoperoxides occurs according to the following scheme:

![Diagram of reaction scheme]
New absorption bands (240, 241, and 251 nm) formed upon irradiation in HSP are associated with quinones, which are formed as a result of photooxidation of phenanthrene hydrocarbons present in this oil:

3. Conclusion
Thus, after UV irradiation of the HSP components in the spectral range of 190-1100 nm, the absorption maxima of AH are hypsochromically shifted. At a sufficient dose of irradiation with the splitting of electronically excited molecules of these hydrocarbons (various C-C and C-H bonds), hydrogen atoms, free radicals, biradicals and carbenes are formed, which then recombine, combine, and isomerize. After irradiation, HSP is formed, as well as quinones, endoperoxides, tetroxides.

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