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Hydrogen Peroxide Formation in Aqueous Solutions under UV-C Radiation

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Abstract—The formation of hydrogen peroxide in bidistilled water under the influence of UV-C radiation from a DKB-9 low-pressure mercury lamp has been studied. The yield of hydrogen peroxide was $(1 \pm 0.2) \times 10^{-7}$ mol (L s)⁻¹. The wavelengths of radiation under the influence of which the formation of H₂O₂ is possible

have been estimated. It has been assumed that the intermediate product of the reaction is the HO_2^{\bullet}/O_2^{-} radical. To identify it, oxidation–reduction reactions in aqueous solutions containing Fe²⁺, Fe³⁺, and I⁻ ions at

pH values from 0.8 to 8.1 have been studied. The quantum yield of HO₂ radicals in an acidic medium under the influence of radiation from the mercury lamp is 0.015 ± 0.005 .

Keywords: hydrogen peroxide, HO_2^{\bullet}/O_2^{-} radical, Fe^{2+} and I^{-} oxidation, UV-C radiation **DOI**: 10.1134/S0018143918030128

INTRODUCTION

Mechanisms of the interaction of UV-C radiation that can pass through air (200–280 nm) with the matter have been studied for a long time are well documented. There are monographs summarizing these studies [1, 2]. One of the mechanisms is the direct absorption of a photon by an energy level of a molecule (provided that such a level exists) followed by the transition of the molecule to an excited state in which it can undergo further transformations. If there is no such energy level in the molecule, and dissolved oxygen is present in the water, then reactions of type I and II with a sensitizer in the triplet state are possible. Any

impurity in water can act as a sensitizer. The O_2^- radical ion is formed in type I reaction, the reaction of type II generates singlet oxygen [3].

In natural waters, there are always substances that can play the role of a sensitizer; therefore, hydrogen peroxide is formed in natural water under the influence of visible and UV radiation [4, 5]. In the case of UV-C radiation with $\lambda < 246$ nm, the decomposition of water molecules with the formation of hydroxyl radicals is feasible in the absence of sensitizers in water. However, the probability of this process is low [6]. Hydroxyl radicals are formed with a noticeable probability under the influence of vacuum ultraviolet at $\lambda <$ 180 nm.

Gudkov et al. [7] studied the formation of hydrogen peroxide in bidistilled water under the influence of sunlight and artificial illumination with an electric bulb. The treatment of a 20-mL sample of water with solar radiation for 1 to 5 h resulted in the formation of 30 to 200 nmol (concentration from 1.5×10^{-6} up to 1×10^{-5} mol/L) of hydrogen peroxide. Illumination with an electric bulb for the same time gave 8 to 16 nmol (concentration from 4×10^{-7} up to 8×10^{-7} mol/L) of hydrogen peroxide. The participation of HO₂/O₂⁻⁻ radicals in this process was shown.

In [8, 9], it was shown that HO_2^{-}/O_2^{-} radicals can be formed in water by the action of UV-C radiation. The radicals are in the following equilibrium:

$$\text{HO}_2^{\bullet} \leftrightarrow \text{O}_2^{\bullet-} + \text{H}^+, \quad \text{p}K_a = 4.8.$$
 (1)

Depending on the acidity of the medium, the radi-

cal exists in different forms. In [9], the yield of HO_2 on a beam of pulse and continuous UV-C radiation in an

acidic medium was estimated. The interaction of HO_2 radicals with one another should lead to the formation of hydrogen peroxide. However, hydrogen peroxide was not detected in [8, 9].

The formation of $HO_2^{\bullet}/O_2^{\bullet-}$ radicals can be considered as a new mechanism of the interaction of photons of visible and ultraviolet ranges with aqueous solutions. Therefore, it is of interest to obtain information

on the formation of HO'_2/O'_2 radicals under the influence of UV-C radiation in pure water and in aqueous solutions of substances that cannot exist in the triplet

state, do not enter type I and II reactions at any rate, and are barely capable of the direct absorption of photons.

The purpose of this work is to determine the yield of hydrogen peroxide in bidistilled water and the generation rate of $HO_2^{\cdot}/O_2^{\cdot-}$ radicals in aqueous solutions under the influence of UV-C radiation and to assess

the possible mechanism of the formation of $HO_2^{\cdot}/O_2^{\cdot-}$ radicals.

EXPERIMENTAL

An OUFb-04 ultraviolet bactericidal irradiator with a 9-W ozone-free, low-pressure DKB-9 mercury lamp with a housing made of uviol glass was the radiation source. The lamp operates continuously, gives mono-chromatic radiation with a wavelength of 253.7 nm. The photon flux according to the manufacturer's certificate data was $I_0 = 5.4 \times 10^{-8}$ mol (cm² s)⁻¹ at a distance of 3 cm from the surface of the lamp. The average lifetime of the lamp is 6000 h, but the average operating time is 1000 h due to contaminations of the inner surface of the glass. Therefore, the actual intensity was measured before the experiments and after the entire set of experiments.

To determine the radiation intensity of the lamp, the yield of the decomposition of hydrogen peroxide samples was measured. The concentration of hydrogen peroxide was 0.01 mol/L, pH 3.8. The acidic pH of the solution is due to the peroxide stabilizer. The treatment of peroxide with lamp radiation was carried out in a glass beaker with a diameter of 40 mm and a depth of 60 mm. The concentration of peroxide in the initial and treated solution was determined by titrating the entire volume of the treated sample with 0.05 N potassium permanganate solution in an acidic medium at a temperature of 80°C. It was found that the thickness of the total absorption layer was 55 mm. For the total absorption layer, the concentration dependence of the peroxide remained after irradiation with the mercury lamp for 5 to 30 min was determined. The distance from the surface of the liquid to the lamp was 30 mm.

In order to determine the radiation intensity of the lamp from these data, a decrease in the concentration of peroxide under irradiation was calculated in terms of the known mechanism [10]. The calculation was performed using the MathCad package 14. The emission intensity of the lamp was set as a parameter.

The yield of hydrogen peroxide generated by UV radiation from the mercury lamp in pure bidistilled water was measured. To this end, water of 5 mL in volume was irradiated in a Petri dish for 5 h. The distance from the surface of the liquid to the lamp was 30 mm. To identify the peroxide, freshly prepared TiCl₃ solution was added into the irradiated water sample. Titanium trichloride was prepared by dissolving 0.3 g of titanium metal in 50 mL of concentrated hydrochloric

acid. To a 5 mL sample of treated water, 0.1 mL of titanium trichloride solution was added. Titanium trichloride forms a complex with hydrogen peroxide having a maximum in the absorption spectrum at $\lambda =$ 410 nm [11]. The method was calibrated using hydrogen peroxide solutions of a known concentration, to which TiCl₃ was added.

The redox properties that allow the products, generated in an aqueous solution by UV irradiation, to be identified as HO_2^{-}/O_2^{-} radicals have been investigated using several detection systems.

To determine the divalent iron oxidation rate, a solution of Mohr's salt with a concentration from 2 to 50 g/L in 0.4 M sulfuric acid, pH 0.8 was used. The concentration of trivalent iron in Mohr's salt caused by the spontaneous oxidation of ferrous ion during storage of the reagent did not exceed 0.5%. The treatment time of Mohr's salt solution with UV-C radiation was 1 and 2 min.

To estimate the rate of reduction of trivalent iron, an aqueous solution of iron nitrate $Fe(NO_3)_3 \cdot 9H_2O$ with a concentration of 0.04 g/L, pH 3.4 was used. In both cases, the concentration of trivalent iron Fe^{3+} , which was in the initial solution and accumulated during oxidation of divalent iron in Mohr's salt, was determined from the 304-nm band in the absorption spectrum (molar absorption coefficient $\varepsilon = 2100 \text{ L} \text{ (mol cm)}^{-1}$) [12].

Oxidation of iodide ions. An aqueous solution of KI with a concentration of 5 g/L was used. The initial acidity value was 5.6. The measurements were performed at pH values from 1.4 to 8.1. The pH was set by introducing sulfuric acid and alkali NaOH into the stock solution. The volume of the acid or alkali did not exceed 2% of the volume of the prepared solution. When iodide ions are oxidized, triiodide ions are formed. The concentration of triiodide was determined from the absorbance of the UV band at $\lambda = 288$ nm, $\varepsilon = 2.65 \times 10^4$ L (mol cm)⁻¹ [13].

The detecting solutions were exposed to the radiation of the mercury lamp in Petri dishes with a diameter of 40 mm. The volume of the treated liquid in all the experiments was 5 mL, the thickness of the liquid layer was 7 mm. The distance from the surface of the liquid to the surface of the lamp is 30 mm.

The pH was measured with an EKONICS Expert-001 instrument (Russia). The UV absorption spectra were recorded with an AKVILON SF-102 spectrophotometer (Russia) operating wavelength range 200–1100 nm. The optical path length of the cell was 10 mm. We used reagent grade chemicals and bidistilled water with pH 5.5. To process the experimental results, the MathCad 14 software package was used.

RESULTS

Determination of DKB-9 Mercury Lamp Radiation Intensity

Let us estimate the possibility of decomposition of hydrogen peroxide used as a radiation detector under the action of radicals. If the radical $HO_2^{\cdot}/O_2^{\cdot-}$ is formed, it exists predominantly in the form of HO_2^{\cdot} , since its pK_a is value 4.8 and the hydrogen peroxide solution used in the work has pH 3.8. The reaction with hydrogen peroxide is as follows:

$$H_2O_2 + HO'_2 \rightarrow H_2O_2 + HO'_2.$$
 (2)

Neither hydrogen peroxide nor HO₂ radicals are consumed in this reaction, only the transfer of hydrogen atoms takes place. The formation of hydroxyl radicals in water by the action of radiation with $\lambda =$ 253.7 nm is impossible. Therefore, the mechanism of decomposition of peroxide can only be the direct absorption of photons by hydrogen peroxide molecules followed by their degradation. The initial concentration of peroxide was (0.01 \pm 0.0005) mol/L to become $[H_2O_2] = (0.0032 \pm 0.0004) \text{ mol/L after}$ 30-min irradiation. Calculation reported in [10] describes the experimental data at an intensity of $I_0 =$ $(5.7 \pm 0.5) \ 10^{-8} \ \text{mol} \ (\text{cm}^2 \ \text{s})^{-1}$. At the end of the set of experiments, the intensity decreased by 10%. Such a reduction lies within the errors of all measurements, so it could be ignored.

Formation of Hydrogen Peroxide

In [8], we observed the generation of HO₂ radicals under the influence of UV-C radiation. The interaction of HO₂ radicals should lead to the formation of H₂O₂. Figure 1 shows the absorption spectrum of a solution of pure hydrogen peroxide, the absorption spectrum of a sample of bidistilled water immediately after irradiation with a mercury lamp for 5 h, and the spectrum of the same irradiated sample after the addition of titanium trichloride to it.

Figure 1 (curve 3) shows the appearance of a peak at 410 nm characteristic of the hydrogen peroxide complex with TiCl₃. Based on this spectrum, the concentration of hydrogen peroxide in the sample of water treated for 5 h was found to be $[H_2O_2] = (0.006 \pm$ 0.001)% or 2 × 10⁻³ mol/L. Hence, the yield of hydrogen peroxide generated by radiation from of the DKB-9 lamp is $(1 \pm 0.2) 10^{-7}$ mol (L s)⁻¹.

The absorbance in the range 250-400 nm of water exposed to UV radiation for 5 h (Fig. 1, curve 2) is much larger than that the solution of pure hydrogen peroxide (Fig. 1, curve 1), although the concentration of pure peroxide in the sample is greater according to curve 1. This means that irradiation with the UV lamp



Fig. 1. Identification of hydrogen peroxide in a sample of bidistilled water treated with mercury lamp UV radiation; (1) pure hydrogen peroxide solution with a concentration of 0.01%; (2) water sample treated with UV radiation for 5 h; (3) a sample treated for 5 h after the addition of 0.1 mL of TiCl₃.

gives rise to other compounds. The formation of NH_4^+ ions was identified in [8].

Oxidation of Divalent Iron

Figure 2 shows the dependence of the concentration of ferric ion formed in an acidic solution of Mohr's salt under the influence of mercury lamp radiation per 1 min, on the concentration of ferrous ion. Oxidation of iron can be due to the interaction with

HO₂. With increasing treatment time to 2 min, the Fe³⁺ concentration increases proportionally. The concentration of Fe³⁺ increases with increasing Fe²⁺ concentration and reaches a maximum at [Fe²⁺] = 40–50 g/L (100–130 mmol/L). The maximum concentration of trivalent iron formed is [Fe³⁺] = 195 \pm 10 µmol/L. Such a character of the dependence can be

due to the decay of radiation-induced HO₂ radicals in the solution in the reaction with one another at low ferrous ion concentrations [14]. As a result, the yield of oxidized iron turns out to be lower at low Fe²⁺ concentrations and reaches a plateau at high Fe²⁺ concentrations. Therefore, based on the maximum concentration of the ferric ions formed, we can estimate the yield

of HO_2^{\bullet} radicals. The interaction of divalent iron in an

acidic medium with HO_2^{\bullet} radicals is described by the reactions:

Fe²⁺ + HO₂ + H⁺
$$\rightarrow$$
 Fe³⁺ + H₂O₂,
 $k_3 = 1.5 \times 10^6 \,\text{L}\,(\text{mol s})^{-1},$
(3)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-},$$

 $k_4 = 56 L (mol s)^{-1},$
(4)

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Fig. 2. Dependence of the concentration of ferric ion $[Fe^{3+}]$, $\mu mol/L$, formed by irradiation with light from a mercury lamp for 1 minute in an acidic solution of trivalent iron, on the concentration of $[Fe^{2+}]$, mmol/L.

$$Fe^{2+} + OH^{-} \rightarrow Fe^{3+} + OH^{-},$$

 $k_5 = 10^9 L (mol s)^{-1},$
(5)

HO₂ + HO₂ → H₂O₂ + O₂,

$$k_6 = 9.6 \times 10^8 \,\mathrm{L} \,(\mathrm{mol} \,\mathrm{s})^{-1}$$
. (6)

Hereinafter, data on the reaction rate constants from the reference book [15] were used. It can be seen from reactions (3)–(6) that three trivalent iron ions are formed per one primary HO₂ radical. In this case, we neglect the consumption of the hydrogen peroxide generated by the primary UV-C radiation. Based on the saturation concentration [Fe³⁺] = 195 ± 10 µmol/L, the HO₂ generation rate in water is (1.08 ± 0.1) × 10⁻⁶ mol (L s)⁻¹. The rate of generation of the radicals in a 5 mL Petri dish with a surface of 7 cm² is (7.7 ± 0.8) × 10⁻¹⁰ mol (cm² s)⁻¹.

The reduction of the trivalent iron built-up during irradiation under the conditions of the present work (acidic medium) is impossible. This conclusion is confirmed by the experimental data obtained in this study.

Reduction of Trivalent Iron

No reduction of ferric ions in a $Fe(NO_3)_3 \cdot 9H_2O$ solution was detected. In the case of UV-C irradiation of the solution, only an increase in the absorbance at 304 nm due to trivalent iron was observed. The effect may be explained in terms of the fact that during the storage of $Fe(NO_3)_3 \cdot 9H_2O$, trivalent iron had been partially reduced to divalent iron, which underwent oxidation in this experiment. The absence of reduction of trivalent iron means that species with reducing properties are not produced by the action of radiation



Fig. 3. Dependence of the concentration of triiodide $[I_3]$, μ mol/L, formed by irradiation with light from a mercury lamp for 1 minute in KI solution, on the pH of the aqueous solution.

in an acidic medium. The reaction of HO_2 radicals with trivalent iron in an acidic medium is impossible.

Oxidation of Iodide Ions

The dependence of the concentration of triiodide formed in a KI solution during 1-min irradiation with the mercury lamp is shown in Fig. 3. At pH values from 1.4 to 1.9, the triiodide concentration does not change within the limits of error, it is maximal, making $134 \pm 13 \ \mu mol/L$. The concentration of I_3^- decreases rapidly with increasing pH, at pH 4.4 the decrease slows down considerably, and the concentration of $I_3^$ remains almost unchanged starting from pH 6.1. Qualitatively, the character of the dependence is caused by the fact that the value of the dissociation constant for the $HO_2^{\bullet}/O_2^{\bullet-}$ radical is $pK_a = 4.8$. In a strongly acidic medium, it exists as HO_2^{\bullet} , which oxidizes iodide ions; at pH > 6, it exists predominantly in the reductant form of O_2^- , and oxidation of iodide ions becomes impossible.

DISCUSSION

A possible mechanism for the formation of oxidants could be the process $H_2O \rightarrow OH^+ + H^+$. The dissociation energy of the water molecule is 499 kJ/mol [16]. This corresponds to a quantum energy of 5.03 eV or a wavelength of $\lambda \sim 246$ nm. Therefore, hydroxyl radicals cannot be generated by ultraviolet radiation with $\lambda = 253.7$ nm of the lamp. In [8], the experimental results were explained by the formation of HO₂⁻ radicals by the action of UV radiation. A mechanism was proposed for the formation of HO₂⁻ radicals by pulsed UV-C irradiation in an acidic medium through excited states of water molecules [9].

$$\mathrm{H}_{2}\mathrm{O} + h\mathrm{v} \to \mathrm{H}_{2}\mathrm{O}^{*}.$$
 (7)

The linear decadic absorption coefficient of water is ~0.8 m⁻¹ at $\lambda = 200$ nm, it reaches a minimum ~2 × 10^{-2} m⁻¹ at $\lambda \sim 470$ nm, and then almost monotonically increases with increasing wavelength up to ~20 m⁻¹ at $\lambda = 970$ nm [17]. Absorption for the peak at $\lambda = 970$ nm is measured directly using an SF-102 spectrophotometer, the molar absorption coefficient is $\varepsilon = (3.1 \pm 0.1) \times 10^{-3}$ L (mol cm)⁻¹. Excited at wavelengths of 200–1200 nm are vibrational and electronic levels of water molecules [7] whose energy is insufficient for changing the structure of the molecule, so they can serve only as an energy storage.

It can be assumed that the water molecules excited by UV-C radiation cause the formation of hydrogen peroxide:

$$H_2O^* + H_2O \to H_2O_2 + H_2.$$
 (8)

In the presence of dissolved oxygen, another process is possible:

$$H_2O^* + O_2 \to H_2O_2 + 1/2O_2.$$
 (9)

Let us assess the feasibility of reactions (8) and (9) in terms of energy. The standard enthalpy of the formation of liquid water at 298 K is -285.8 kJ/mol, that of hydrogen peroxide is -187.8 kJ/mol, and the enthalpies of formation for the simple substances H₂ and O₂ are conventionally taken to be zero [16]. Reactions (8) and (9) are endothermic; the enthalpy change for reaction (8) is

$$\Delta H = -187.8 - 2(-285.8) = 383.8 \text{ kJ/mol},$$

which corresponds to the wavelength of $\lambda = 311.7$ nm. The enthalpy change in (9) is

$$\Delta H = -187.8 - (-285.8) = 98 \text{ kJ/mol},$$

 $\lambda = 1220.7 \text{ nm}.$

Hence, it can be seen that reaction (8) water is possible in the case of irradiation at $\lambda < 311.7$ nm and reaction (9) can occur under irradiation at $\lambda < 1220.7$ nm.

Hydrogen peroxide can form through intermediates, such as HO_2^{\cdot}/O_2^{-} radicals. The oxidation of Fe²⁺ and I⁻ in an acidic medium and the nonoccurrence of

oxidation in a neutral or alkaline medium confirm this possibility. The quantum yield of HO_2 radicals in an

acidic medium in the case of continuous irradiation with a light beam at $\lambda = 253.7$ nm is 0.015 \pm 0.005.

In [18], we investigated redox processes in a methemoglobin solution irradiated with UV-C light of a mercury lamp of the same type as that was used in this work. Methemoglobin (oxidized form of hemoglobin) reduction to deoxyhemoglobin has been observed:

$$Hb(Fe^{3+}) + O_2^{-} \rightarrow Hb(Fe^{2+}) + O_2.$$
 (10)

The acidity of methemoglobin solution is pH 7.4. In such a medium, HO_2^{-}/O_2^{-} radical exists in the form of the negative radical ion O_2^{-} , which can freely interact with the positive Fe³⁺ ion.

CONCLUSIONS

The results of the study suggest the existence of a mechanism for the effect of UV-C radiation on aqueous solutions through the formation of $\text{HO}_2^{\cdot}/\text{O}_2^{-}$ radicals.

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