The UV-C radiation mechanism to form HO$_2^\cdot$ radicals from water

I M Piskarev$^{1,4}$, K A Astaf'eva$^2$ and I P Ivanova$^3$

$^1$ Skobeltsyn Institute of Nuclear Physics, MSU, Moscow, 119234 Russia
$^2$ Lobachevsky Nizhny Novgorod State University, Nizhny Novgorod, 603022 Russia
$^3$ Nizhny Novgorod Medical State Academy, Nizhny Novgorod, 603104 Russia
$^4$ E-mail: i.m.piskarev@gmail.com

Abstract. The formation of chemically active particles in distilled water via continuous and pulsed light radiation was investigated. The source of the continuous radiation was a DKB-9 UV mercury low pressure lamp ($\lambda = 253.7$ nm). Upon UV lamp irradiation of water, hydrogen peroxide was formed in a yield of $(1 \pm 0.2) \times 10^{-7}$ mol (L s)$^{-1}$. The pulsed radiation source was the plasma of a spark electric discharge in air with a continuous radiation spectrum and a weak maximum at $\lambda = 220$ nm. The radiation affected the water through quartz glass. In this case, nitrous and nitric acids formed in the water, but no accumulation of hydrogen peroxide was detected. The formation of the active products can be explained by the interaction of exited water molecules that formed due to the radiation. The energy threshold for the formation of hydrogen peroxide corresponds to a radiation wavelength of less than 1220 nm. To directly identify HO$_2^\cdot$ radicals, we studied redox reactions in solutions containing Fe$^{2+}$, Fe$^{3+}$ and I$^{-}$ ions at pH values from 0.8 to 8.1. The quantum yield of HO$_2^\cdot$ radicals in an acidic medium under the action of the mercury lamp radiation was $0.015 \pm 0.005$.

1. Introduction
Water and light are two elements, and their interaction determines many processes on Earth. Water absorbs very little visible and UV radiation, but the absorption coefficient is not zero. In ref. [1], the formation of HO$_2^\cdot$ radicals in distilled water under the action of pulsed UV-C radiation was observed. Therefore, it is of interest to consider processes that can occur under the action of light. The purpose of this study was to evaluate the formation mechanism of HO$_2^\cdot$ radicals and the product of this interaction (hydrogen peroxide) in distilled water under the action of continuous and pulsed UV-C radiation.

2. Materials and methods
The source of continuous radiation was a non-ozone low pressure DKB-9 mercury lamp with an ultraviolet glass body, a power of 9 W, and $\lambda = 253.7$ nm. The photon flux on the surface of a water sample according to the instruction manual is $5.4 \times 10^{-8}$ mol (cm$^2$ s)$^{-1}$. The source of the pulse radiation was an IR-10 spark plasma radiation generator [2]. The power released in the pulse was 0.059 J, and the repetition frequency of the pulses was 10 Hz. The radiation spectrum is continuous with a maximum in the UV-C region at $\lambda = 220$ nm. The radiation passed through a 2.3 mm-thick quartz plate; thus, the products formed in the discharge itself did not affect the water in any way.
Samples of distilled water (5 ml) were irradiated in a Petri dish with each radiation source for 6 hours. After irradiation, the absorption spectrum of the samples was measured in the wavelength range of 250–500 nm. To identify hydrogen peroxide in the samples, 0.1 ml of a TiCl$_3$ solution prepared by dissolving 2 g of metallic titanium in 30 ml of concentrated hydrochloric acid was added. Twice distilled water (pH = 6.5) and chemically pure reagents were used.

To determine the oxidation rate of bivalent iron, a Mohr's salt solution with a concentration of 2–50 g/l in 0.4 M sulfuric acid at a pH = 0.8 was used. The processing time of the Mohr solution to UV-C radiation was 1 to 2 minutes. To estimate the rate of reduction of trivalent iron, an aqueous solution of iron nitrate (Fe(NO$_3$)$_3$ × 9H$_2$O) at a concentration of 0.04 g/l and pH = 3.4 was used. In both cases, the concentration of ferric ions, which was in the initial solution of Fe$^{3+}$ and accumulated during the oxidation of bivalent iron in the Mohr's salt, was determined from the band in the absorption spectrum at 304 nm (extinction coefficient of $\varepsilon = 2100$ L (mol cm)$^{-1}$) [3]. Oxidation of iodine ions I$^{-}$ was studied in an aqueous solution of KI that had a concentration of 5 g/l in the pH range from 1.4 to 8.1. During the oxidation of iodine ions, triiodide ions were formed. The concentration of the triiodide was determined from the optical density of the band in the UV absorption spectrum at $\lambda$ = 288 nm and $\varepsilon = 2.65 \times 10^4$ l (mol cm)$^{-1}$ [4].

3. Experimental results

The absorption spectra of the irradiated solutions are shown in Figure 1 (curves 1 and 2). The absorption spectrum of TiCl$_3$ in distilled water (0.1 ml of TiCl$_3$ solution per 5 ml of water) is also provided in curve 4. As shown, the TiCl$_3$ reagent itself did not make an appreciable contribution to the optical density of the samples in the wavelength range of 200–500 nm. The absorption spectrum of quartz glass (curve 3) shows that glass passed at least 70% of the photon flux in the entire range from 200 to 500 nm.

![Figure 1. The absorption spectra of solutions after the addition of the TiCl$_3$ solution: 1 – water irradiated for 6 hours with the spark discharge plasma; 2 – water irradiated for 6 hours with the low pressure mercury lamp, $\lambda$ = 253.7 nm (dotted line – same sample without addition of TiCl$_3$); 3 – absorption spectrum of quartz glass; 4 – absorption spectrum of distilled water after the addition of TiCl$_3$.](image)

The TiCl$_3$ reacts with hydrogen peroxide to form a complex that has an absorption line at 410 nm. As shown in Figure 1, a line appeared after the addition of TiCl$_3$ to the sample of distilled water irradiated by the mercury lamp (curve 2). Calibration of solutions with a known concentration of hydrogen peroxide allowed us to determine the yield of H$_2$O$_2$ upon irradiation with $\lambda$ = 253.7 nm, and a yield of $(1 \pm 0.2) \times 10^{-7}$ mol (l s)$^{-1}$ was obtained. The pH value of water after irradiation with the mercury lamp slightly increased (from 6.5 ± 0.05 to 6.9 ± 0.05).

For the water sample irradiated with spark discharge plasma, after the addition of TiCl$_3$, the absorbance in the region of $\lambda$ = 410 nm was close to zero (curve 1). The spectrum shows a peak at $\lambda$ = 300 nm and a group of peaks in region of 330–390 nm. The peak position at 300 nm corresponds
to the absorption of nitric acid (NO$_3^-$ ions) with an absorbance relative to baseline of 0.09 ± 0.006. The acidity was pH = 1.9 ± 0.05. The extinction coefficient of nitric acid, which we directly measured, was 7 l (mol cm)$^{-1}$. Hence, [NO$_3^-$] = 0.013 ± 0.001 mol/l. This concentration of nitric acid corresponds to pH = 1.88, which is within the error that coincides with the actual measured pH value. Hence, we concluded that the 300 nm peak is associated with nitric acid.

It can be assumed that a group of peaks in the 330–390 nm region is associated with nitrous acid.

![Figure 2. Identification of the product giving an absorption line in the 330–390 nm region: 1 – absorption spectrum of nitrous acid at pH = 2.3; 2 – spectrum of the water sample after irradiation with the spark discharge plasma for 6 hours, pH = 1.9; 3 – absorption spectrum of NO$_2^-$ ions in a 0.05 mol/l NaNO$_2$ solution.](image)

To identify the product that has absorption peaks in the 330–390 nm region, the absorption spectrum of nitrous acid formed in reaction (1) was measured:

$$2\text{NaNO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HNO}_3.$$  

(1)

The concentration of NaNO$_2$ is 5 × 10$^{-3}$ mol/l. Sulfuric acid (diluted at 1 : 4) was introduced dropwise to pH = 2.3. The spectrum is shown in Figure 2, curve 1. Curve 3 shows the absorption spectrum of the 5 × 10$^{-3}$ mol/l NaNO$_2$ solution. When sulfuric acid was introduced into the NaNO$_2$ solution, the peak corresponding to curve 3 disappeared. A group of peaks from 330 to 390 nm appeared (curve 1, nitrous acid). The coincidence of the shape of the nitrous acid spectrum (curve 1) with peaks formed by the spark discharge plasma irradiation (curve 2) confirmed that the product formed under pulse discharge plasma radiation was nitrous acid.

The oxidation of bivalent iron was observed, which may be due to HO$_2^*$ radicals, but the reduction of trivalent iron was not observed. Hence, the rate of generation of HO$_2^*$ radicals in water was determined to be (1.08 ± 0.1) × 10$^{-6}$ mol (l s)$^{-1}$. The oxidation of iodine ions was observed only in acid medium, but it was not observed in neutral and alkaline medium.

4. Discussion

Water molecules excited by UV-C radiation are assumed to lead to the formation of hydrogen peroxide:

$$\text{H}_2\text{O}^* + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2.$$  

(2)

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

$$\text{H}_2\text{O}^* + \text{O}_2 \rightarrow \text{H}_2\text{O}_2 + \frac{1}{2}\text{O}_2.$$  

(3)

Let us estimate the energy possibility of reactions 2 and 3. The standard enthalpy of liquid water formation at a temperature of 298 K is 285.8 kJ/mol. For hydrogen peroxide, it is 187.8 kJ/mol. The enthalpy of the formation of H$_2$ and O$_2$ was assumed to be zero. Reactions 2 and 3 are endothermic, and the enthalpy change for reaction 2 is ΔH = −187.8 − 2(−285.8) = 383.8 kJ/mol, which corresponds to a wavelength of $\lambda = 311.7$ nm.

The change in enthalpy for reaction 3 is ΔH = −187.8 − (−285.8) = 98 kJ/mol, $\lambda = 1220.7$ nm.
Hence, reaction 2 is possible in water upon ultraviolet radiation with \( \lambda < 311.7 \) nm, and reaction 3 is possible upon radiation with \( \lambda < 1220.7 \) nm. In water, there are levels populated throughout the range of 200–1220 nm, although their oxidation probability is small [5].

For the \( \text{HO}_2^* \) radicals, there is an equilibrium:

\[
\text{HO}_2^* \leftrightarrow \text{O}_2^{-} + \text{H}^+, \quad \text{pK}_a = 4.8.
\]  

(4)

In acidic medium, the radicals exist in the form of an oxidizer, and in a neutral or alkaline environment, they exist in the form of a reducing agent, \( \text{O}_2^{-} \). Therefore, in our acid medium, the reduction of ferric iron was not observed, and in the neutral medium, the oxidation of iodine was not observed.

In ref. [6], the oxidation reduction processes in a solution of methemoglobin upon UV-C irradiation using a mercury lamp of the same type as used in this work were investigated. Methemoglobin (oxidized form of hemoglobin) was restored to deoxyhemoglobin:

\[
\text{Hb(Fe}^{3+}) + \text{O}_2^{-} \rightarrow \text{Hb(Fe}^{2+}) + \text{O}_2.
\]  

(5)

The acidity of a solution of methemoglobin was \( \text{pH} = 7.4 \). In such a medium, \( \text{HO}_2^* \) radicals exists in the form of a negative ion-radical, \( \text{O}_2^{-} \), which can interact with the positive ion, \( \text{Fe}^{3+} \).

The primary product formed in water containing dissolved gases (oxygen and nitrogen) is nitrous acid [1, 2]. Hydrogen peroxide, which could be formed upon plasma irradiation, is consumed when interacted with nitrous acid:

\[
\text{HNO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O}.
\]  

(6)

Therefore, the formation of hydrogen peroxide upon plasma irradiation was not observed.

5. Conclusions

The results of this work allowed us deduce the mechanism of the effect of UV-C radiation on aqueous solutions in which \( \text{HO}_2^* \) radicals are formed.

References

[1] Piskarev I M, Astafeva K A, Ivanova I P 2017 Biophysics 62 (4) 547–52
[2] Piskarev I M 2016 Res. J. of Pharmaceutical, Biological and Chemical Sci. 7 (4) 1171–89
[3] Pikaev A K 1975 Dosimetry in radiation chemistry (Moscow: Nauka) p 147
[4] Kireev S V, Shnyrev S L 2015 Laser Phys. 25 075602
[5] Wozniak B, Dera J 2007 Atmospheric and Oceanographic Science Library (New York: Springer Science Business Media) LLC. Part 2.2. 48
[6] Piskarev I M, Burhina O E, Ivanova I P 2016 High Energy Chemistry 50 (1) 71