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MECHANISM OF $\text{Fe}(\text{OH})^{2+}(\text{aq})$ PHOTOLYSIS IN AQUEOUS SOLUTION

(Technical Report)

Prepared for publication by

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Mechanism of $\text{Fe}(\text{OH})^{2+}(\text{aq})$ photolysis in aqueous solution

(Technical Report)

Abstract: Experiments on laser flash photolysis (308 nm) of $\text{Fe}(\text{OH})^{2+}(\text{aq})$ complex in aqueous solution with addition of nitrobenzene demonstrate the formation of hydroxyl radical in the primary photochemical process.

1. INTRODUCTION

At present, one of the most urgent ecological problems is the contamination of natural water systems (oceans, lakes, rivers, precipitation) owing to anthropogenic processes. It may happen that in the nearest future, the power of the natural mechanisms of self-purification will be insufficient for supporting the purity of water medium at the undangerous level. To exclude this danger, it is necessary to understand the mechanisms and processes of self-purification occurring in natural water systems. It is assumed that dissociation of many organic substances in natural waters mainly depends on abiotic factors rather than organism activity [1]. One of the factors stimulating the dissociation of organic compounds is solar energy. Organic and inorganic impurities contained in oceans, rivers, and rain droplets can participate in various photochemical and further thermal reactions. To construct quantitative models of the processes occurring in these systems, one needs information on the primary photochemical processes and reactions of short-lived intermediates.

Among photoreactions in water systems, of importance are the processes involving the ions of transient metals and, in particular, iron. Iron (mainly, trivalent) is a widespread element of soil and rocks from which it enters all natural water systems through various processes. In the environment, in conditions of alkali pH of river and sea waters, iron is mainly found as dissolved hydroxides, colloids, complexes with organic and inorganic ions, and in weighed mineral particles of different sizes. Precipitation and marsh waters with pH below 4 contain also a considerable amount of free trivalent iron [2].

The mechanism of photolysis of Fe(III) hydroxocomplexes in water solutions is in the available literature [3]. This mechanism is based on intramolecular electron transfer from the coordinated OH^- anion to the central ion of the excited complex with subsequent escape of a hydroxyl radical into the bulk. It is assumed that the oxidation of organic compounds is initiated by the $\bullet\text{OH}$ radical. This mechanism is, however, based on the results of the analysis of the final products of phototransformations. So far, no information on direct experiments on the photolysis of Fe(III) complexes was available in literature. Neither $\bullet\text{OH}$ radical nor the intermediate products of its reaction with organic or inorganic compounds were recorded. At the same time, an alternative mechanism of photolysis is possible, which is based on an electron transfer from organic molecules located in the second coordination sphere to the excited complex. This mechanism is typical of photoreduction of the complexes of transient metals in polar organic solvents [4–6].

The goal of the present paper is to determine the mechanism of Fe(III) hydroxocomplex photolysis from the direct photochemical experiments. Laser flash photolysis was used to solve this problem. The main attention was concentrated on the search for the experimental evidence for hydroxyl radical formation in the primary photochemical process.

$\bullet\text{OH}$ radical in water solutions has a weak absorption in the far UV spectrum region (a band with a maximum at 225 nm and absorption coefficient of about $500 \text{ M}^{-1} \text{ cm}^{-1}$ [7]) not easily accessible for recording because of the absorption of initial complexes and organic additives. Therefore, in pulsed photochemical experiments it can be revealed using a trap, i.e., a molecule that, in reactions with $\bullet\text{OH}$ radical, forms an intermediate with a characteristic absorption spectrum. Recently, dimethylformamide

has been used as a trap [8]. However, owing to the low rate constant of $\bullet\text{OH}$ radical reaction with this molecule and a relatively small absorption coefficient of the band of the resulting intermediate, it is not convenient for quantitative measurements. Therefore, in the present work, nitrobenzene was used as the $\bullet\text{OH}$ radical acceptor. The reaction with nitrobenzene occurs with a high rate constant and gives rise to the intermediate with a higher absorption coefficient.

2. EXPERIMENTAL

A set-up for laser flash photolysis with XeCl laser excitation (308 nm, pulse duration 15 ns, mean energy 50 mJ/pulse) [5] was used in the experiments. A steady-state photolysis was performed using irradiation of either a XeCl laser or a high-pressure mercury lamp with a set of glass filters for separating the necessary wavelengths. Electron absorption spectra were recorded using Specord UV-Vis and Specord M40 (Carl Zeiss) spectrophotometers. The analysis of the final products of photochemical reactions was performed by high-performance liquid chromatography (HPLC) (SP8800-20 "Spectra Physics" chromatograph with an UV detector). For the numerical calculations of the kinetic curves, the differential equations were solved by means of the fourth-order Runge-Kutta method.

As a source of Fe(III) ions, $\text{Fe}(\text{ClO}_4)_3 \times \text{H}_2\text{O}$ (Aldrich) was used. The dependence of the electron absorption spectrum of Fe(III) in water solutions on pH is shown in Fig. 1. The absorption spectrum of $\text{FeOH}^{2+}(\text{aq})$ complex contains charge transfer bands with maxima at 208 and 300 nm (absorption coefficients at these wavelengths are 4300 and $1985 \text{ M}^{-1} \text{ cm}^{-1}$, respectively [3]). $\text{Fe}^{3+}(\text{aq})$ complex has absorption bands with maxima at 205 and 238 nm ($\epsilon_{\text{max.}} = 3670$ and $3480 \text{ M}^{-1} \text{ cm}^{-1}$, respectively) [3]. All the experiments were carried out in solutions with $\text{pH} \approx 3$. In these conditions, the ions of trivalent iron form the complexes $\text{FeOH}^{2+}(\text{aq})$ (90%) and $\text{Fe}^{3+}(\text{aq})$ (10%) [3]. Since the absorption coefficient of

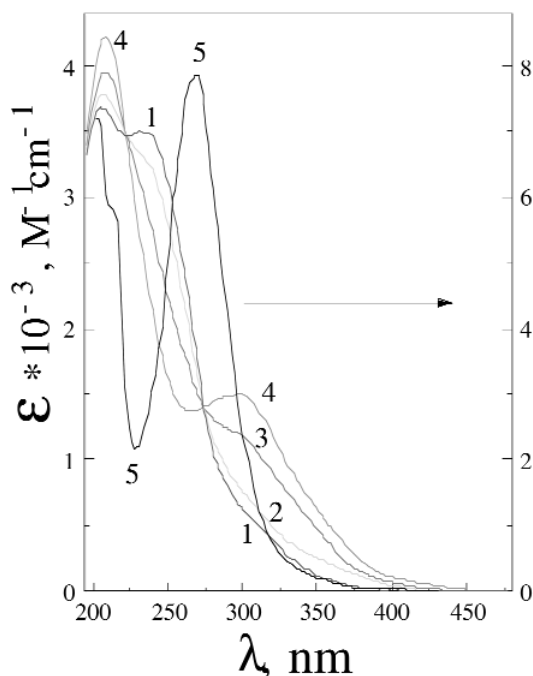


Fig. 1 Dependence of electronic absorption spectrum of water solution of iron(III) perchlorate on pH (left axis, curves 1–4 denote pH 2.1, 2.26, 2.53, 3.04) and electronic absorption spectrum of nitrobenzene (right axis). Temperature, 298 K.

hydroxocomplex at the wavelength of laser radiation (308 nm) is much higher than that of $\text{Fe}^{3+}(\text{aq})$, the only photoactive form in our experiments was the $\text{FeOH}^{2+}(\text{aq})$ complex.

Nitrobenzene (Aldrich) was employed without repurification. The optical absorption spectrum of nitrobenzene (Fig. 1) has maxima at 204 and 270 nm. In spite of a noticeable absorption at 308 nm, nitrobenzene does not display any photochemical activity under excitation at this wavelength, which is necessary for its application as a trap of hydroxyl radicals.

All experiments were performed in oxygen-free samples with a constant ionic strength 0.035 M (KClO_4). Samples were prepared with double-distilled water. The water was also additionally treated by irradiating Fe(III) perchlorate solution for several hours with the light of a high-pressure mercury lamp to remove the organic impurities.

3. RESULTS AND DISCUSSION

3.1 Kinetic scheme of $\text{FeOH}^{2+}(\text{aq})$ photolysis in the presence of nitrobenzene

A slow disappearance of an initial complex was observed under steady-state irradiation of $\text{FeOH}^{2+}(\text{aq})$ in the region of the long-wave charge transfer band. The resulting $\text{Fe}^{2+}(\text{aq})$ complex has only weak absorption bands (the maximum absorption coefficient at 238 nm is $60 \text{ M}^{-1} \text{ cm}^{-1}$) [9]. Accordingly, experiments on laser flash photolysis of $\text{FeOH}^{2+}(\text{aq})$ solutions without organic additives showed only an instant decrease in optical density in the region of wavelengths $\lambda > 320 \text{ nm}$ assigned to initial complex disappearance.

After addition of nitrobenzene (10^{-5} – 10^{-4} M) to the samples, the laser flash photolysis experiments showed the formation of an intermediate absorption (Fig. 2). A characteristic time of an increase

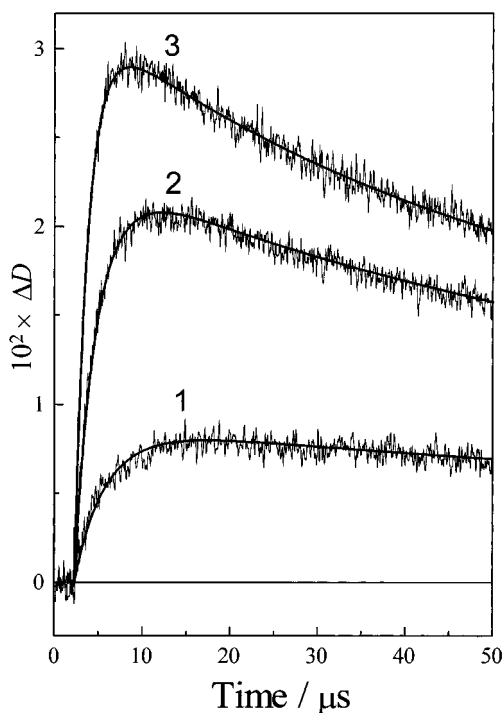


Fig. 2 Kinetic curves of change in optical density at 410 nm upon laser flash photolysis (308 nm, XeCl laser) of $\text{Fe(OH)}^{2+}(\text{aq})$ in aqueous solution with additions of nitrobenzene (cuvette thickness, 1 cm; temperature, 293 K, pH = 2.9; ionic strength, 0.035 M (KClO_4); initial concentration of $\text{Fe(ClO}_4)_3$, $5.3 \times 10^{-4} \text{ M}$). Curves 1–3 denote to 1.6×10^{-5} , 6×10^{-5} and $1.3 \times 10^{-4} \text{ M}$ of nitrobenzene. Smooth curves are the best fits by numeric solutions of system of differential equations corresponding to eqs. 2–6 with parameters listed in Table 1.

of this signal reduces with enhancing concentration of nitrobenzene. The intermediate absorption spectrum has a maximum at a wavelength of 410 nm (Fig. 3, curve 1) and corresponds to that of the nitrohydroxycyclohexadienyl radical $\text{Ph}(\bullet\text{OH})\text{NO}_2$ (Fig. 3, curve 2) [10].

$\bullet\text{OH}$ radical can add to a nitrobenzene molecule in three different positions to form three isomers. However, the data on the difference between the optical spectra of isomers are unavailable in the literature. Therefore, their spectra are assumed to coincide. The proposed mechanism of reactions is described by kinetic schemes 1–6 in which the primary reaction 1 responsible for hydroxyl radical formation corresponds to the concepts published [3].

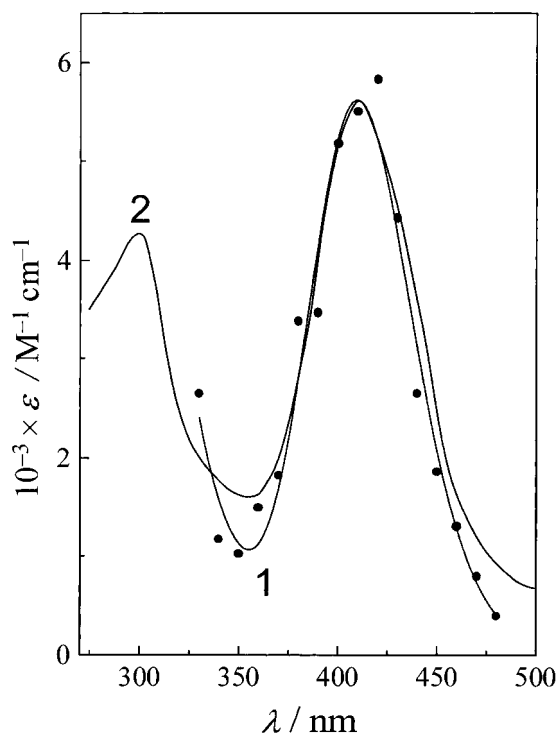
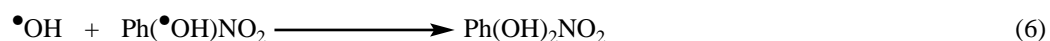
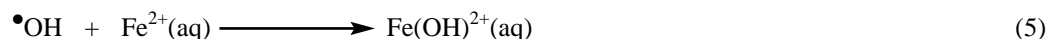


Fig. 3 Electronic absorption spectrum of intermediate arising from laser flash photolysis (308 nm, XeCl laser) of $\text{Fe}(\text{OH})_{\text{aq}}^{2+}$ in aqueous solution with additions of nitrobenzene [Temperature, 293 K, pH = 2.9, ionic strength, 0.035 M (KClO_4); initial concentrations of $\text{Fe}(\text{ClO}_4)_3$ and nitrobenzene, 3.1×10^{-4} and 1.1×10^{-4} M]. Dots: experimental points corresponding to 7.6 μs after laser pulse; curve 1: fit of the experimental spectrum by a Gaussian curve; curve 2: spectrum of $\text{Ph}(\bullet\text{OH})\text{NO}_2$ radical taken from [10] (pulsed radiolysis of aqueous solutions of nitrobenzene at pH = 7). Maximal values at 410 nm are made coincident.

The experimental kinetic curves were fitted by a numerical solution of the system of differential equations for reactions 2–6 (Fig. 2, smooth curves). The least-squares fit was used to find a set of parameters that agree with the literature data and give the best description of the experimental kinetic curves. The initial concentration of $\bullet\text{OH}$ radicals was determined from a decrease in the optical density in the $\text{FeOH}^{2+}(\text{aq})$ absorption band (330 nm) just after the laser pulse. As variable parameters, we used the absorption coefficient of the band of $\text{Ph}(\bullet\text{OH})\text{NO}_2$ radical, the rate constant of this radical disappearance ($2k_d$), the effective absorption coefficient of the products of reaction 4 at the wavelength of kinetic curve recording (410 nm), and the rate constant of reaction 6.

Two of the four variable parameters, referring to the $\text{Ph}(\bullet\text{OH})\text{NO}_2$ radical, (absorption coefficient and rate constant of reaction (4)) are available in the literature [10]. The problem of the products of reaction (4) is to be considered in Section 3.2.

3.2 The reaction products of $\text{Ph}(\bullet\text{OH})\text{NO}_2$ radicals

Reaction 4 can be both the disproportionation of $\text{Ph}(\bullet\text{OH})\text{NO}_2$ radicals and their recombination followed by secondary reactions [10,11]. Figure 4 shows changes in the optical absorption spectrum in experiments on steady-state photolysis of iron(III) perchlorate in the presence of nitrobenzene. A decrease in optical absorption upon photolysis in the region of 200–350 nm (Fig. 4a) is determined by consumption of $\text{FeOH}^{2+}(\text{aq})$ and nitrobenzene. In the region of 350–500 nm (Fig. 4b), the absorption is observed to appear in the initial photolysis stage and disappear under longer irradiation. This absorption belongs to nitrophenols having bands in the visible and nearest UV region [12] and forming in reaction 4.

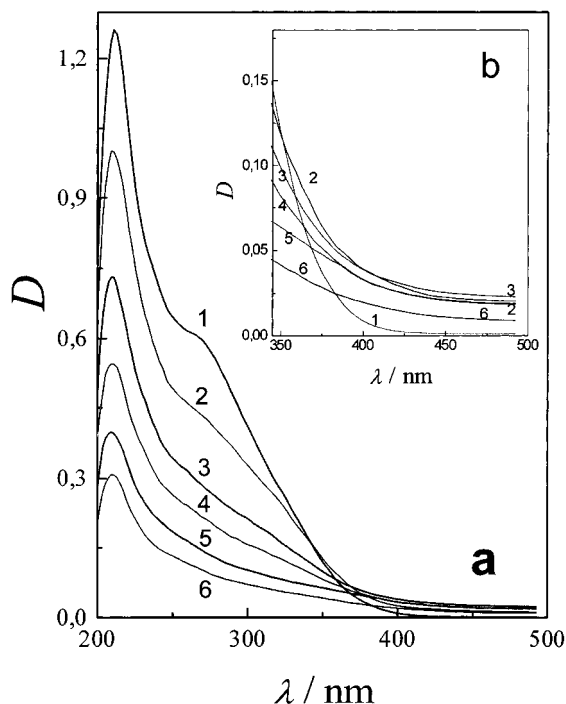


Fig. 4 Iron(III) perchlorate photolysis (high-pressure mercury lamp with glass filters, $\lambda_{\text{max}} = 313$ nm) in water solutions with addition of nitrobenzene. Changes in the optical absorption spectrum (cuvette thickness, 0.5 cm; temperature, 298 K; pH = 2.7; ionic strength, 0.035 M (LiClO_4); initial concentrations of $\text{Fe}(\text{ClO}_4)_3 \times \text{H}_2\text{O}$ and nitrobenzene, 8.3×10^{-4} M and 1.3×10^{-4} M, correspondingly). a) the whole spectra; b) long-wave part of the spectra. Curves 1–6 denote 0, 2, 7, 12, 20, 35 min of irradiation.

The disappearance of nitrophenols is likely to depend on the reaction with $\bullet\text{OH}$ radical which becomes important with decreasing concentration of nitrobenzene in the progress of photolysis. Nitrophenols dissolved in water without $\text{Fe}(\text{OH})^{2+}(\text{aq})$ complex are stable under irradiation at 308 nm. The formation of nitrophenols was demonstrated using HPLC of the irradiated solutions containing $\text{Fe}(\text{OH})^{2+}(\text{aq})$ and nitrobenzene (Fig. 5). Since nitrophenols can both be accumulated and disappear, it is necessary to vary the effective absorption coefficient of products upon the treatment of kinetic curves in pulse experiments. This, probably, causes discrepancy in the literature data on the yield of nitrophenols in reaction 4. According to ref. 11 (dissociation of nitrobenzene with the help of Fenton reagent with analysis of final products), it amounts to 1/2 of the consumed nitrobenzene (the relative yields of ortho-, meta-, and para- isomers are almost the same). The authors of ref. 10 give the value 1/8 [pulse radiolysis of nitrobenzene in water solutions with estimation using the absorption spectra in the end region of the kinetic curves (like in Fig. 4b)].

3.3 Kinetic parameters of reactions 2–6 and the evidence for hydroxyl radical appearance from $\text{Fe}(\text{OH})^{2+}(\text{aq})$ photolysis

The results of the modeling of experimental curves with different concentrations of nitrobenzene and $\text{Ph}(\bullet\text{OH})\text{NO}_2$ radicals (varied by change in laser pulse intensity) are summarized in Table 1. The literature values for the rate constants of the reactions between $\bullet\text{OH}$ radical and nitrobenzene (reaction 2) and radical reactions 3 and 5 allow one to get a fair agreement between calculated and experimental

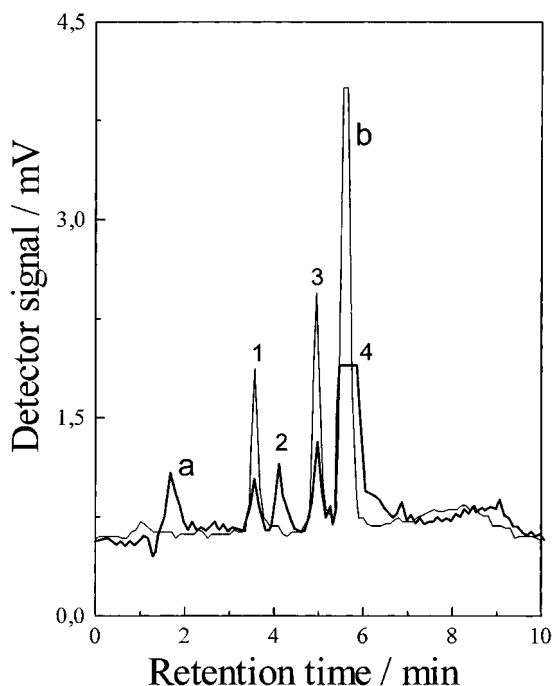


Fig. 5 HPLC detection of final products of iron(III) perchlorate photolysis in water solution with additions of nitrobenzene. Chromatograph, SP8800-20 (Spectra Physics); column, 4×150 mm, Diasorb-130-C16-T, $7 \mu\text{m}$; UV detector; registration at 280 nm; eluent: A: water; B: acetonitrile; linear gradient: 0 min – 30% of B, 20 min – 100% of B; flow speed, 1 mL/min; injection $20 \mu\text{L}$. Curve a) chromatogram of a hundred times diluted irradiated (XeCl laser, 308 nm, 20 mJ/pulse, 300 pulses) solution of 1.2×10^{-2} M $\text{Fe}(\text{OH})^{2+}(\text{aq})$ and 1.4×10^{-2} M of nitrobenzene. Curve b) chromatogram of a reference solution (nitrobenzene, 2×10^{-5} M; *p*-nitrophenol, 6×10^{-6} M; *o*-nitrophenol, 7×10^{-6} M). Recognition of peaks: 1: *p*-nitrophenol; 2: *m*-nitrophenol; 3: *o*-nitrophenol; 4: nitrobenzene.

Table 1. Rate constants of reactions 2–6, absorption coefficient (410 nm) of Ph(\bullet OH)NO₂ radical (ϵ_R), and effective absorption coefficient (410 nm) of final products of photoreaction (ϵ_{eff}^p).

Parameter	This work	Literature data (reference)
$k_2 \times 10^{-9} / \text{M}^{-1} \text{s}^{-1}$	4.7*	4.7 [10]
$k_3 \times 10^{-9} / \text{M}^{-1} \text{s}^{-1}$	5.2*	5.2 [7]
$2k_4/\epsilon_R \times 10^{-5} / \text{cm s}^{-1}$	4.8 ± 0.5	4.3(pH = 1) [10]
$k_4 \times 10^{-9} / \text{M}^{-1} \text{s}^{-1}$	1.37 ± 0.15	0.8 (pH = 1) [10]
$\epsilon_R / \text{M}^{-1} \text{cm}^{-1}$	5660 ± 160	3700 [10]
$\epsilon_{\text{eff}}^p / \text{M}^{-1} \text{cm}^{-1}$	90 ± 50	≈ 30 [10]; ≈ 120 [11]**
$k_5 \times 10^{-8} / \text{M}^{-1} \text{s}^{-1}$	4.3*	4.3 [7]

* literature data were used for fitting.

** estimation using output and absorption coefficients of reaction products.

kinetic curves (Fig. 2). The values of both $2k_4$ and ϵ_R necessary for reaching coincidence between the calculated and experimental kinetic curves exceed those obtained in ref. 10. However, the $2k_4/\epsilon_R$ ratio determined for the second-order kinetic curves directly from the experimental data, almost coincides with that measured in ref. 10.

The absorption coefficient of the band of Ph(\bullet OH)NO₂ was calculated in ref. 10 using the value of the radiation yield of radicals in water solutions saturated with N₂O (for conversion of e⁻(aq) into \bullet OH radical). However, a hydrogen atom that can add to a nitrobenzene molecule to form the \bullet Ph(H)NO₂ radical, also contributes to the radiation yield value. The authors [10] suggest that the spectra of these two radicals fully coincide up to the value of the absorption coefficient. This assumption is rather doubtful and can cause a lower value of absorption coefficient in ref. 10 as compared with that obtained in this work.

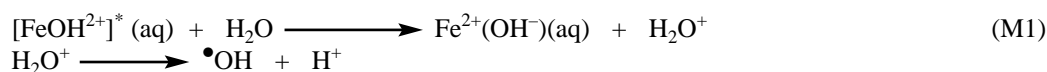
The value of k_6 is unavailable in the literature. The calculations show, however, that even at $k_6 \approx k_{\text{diff}}$ (diffusion limit of bimolecular reaction rate constant) the contribution of reaction 6 to the process of \bullet OH radical disappearance is no more than 4% and is of no importance for the treatment of experimental data.

Thus, we have observed the process of Ph(\bullet OH)NO₂ radical appearance and showed the coincidence of the rate constants of its formation (k_2) and \bullet OH radicals recombination (k_3) with the literature values. This allows us to conclude that the organic radical results from the reaction between \bullet OH radical and nitrobenzene. This is a direct confirmation of the hydroxyl radical formation in the photoreduction of FeOH²⁺(aq) complex.

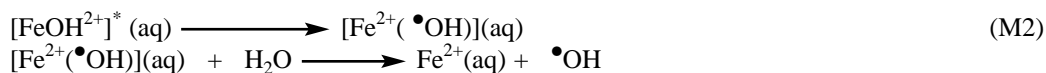
3.4 Possible processes of \bullet OH radical formation upon the excitation of FeOH²⁺(aq) complex

One can suggest the different mechanisms of \bullet OH radical formation in reactions involving the light-excited [FeOH²⁺]^{*}(aq) complex:

1. The outer-sphere electron transfer from water molecule to [FeOH²⁺]^{*}(aq) ion resulting in H₂O⁺ ion



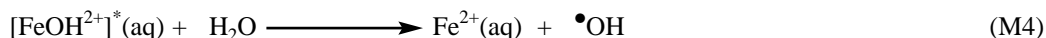
2. The intrasphere electron transfer from hydroxide ion with subsequent escape of \bullet OH radical into the bulk



3. Electron transfer from the second coordination sphere accompanied by proton transfer into the solvent volume



4. Hydrogen atom transfer from the second to the first coordination sphere



From thermodynamic considerations, mechanism (M1) is impossible because of the great value of ionization potential of water molecules even in the liquid phase (8.8 eV [13]). Mechanisms M2–M4 are energetically admissible and it seems impossible to choose among them on a basis of the presented kinetic data.

We have tried to determine the mechanism of hydroxyl radical formation basing on the temperature dependence of photolysis quantum yield. The idea is that when realizing mechanisms M3 and M4, based on tunneling, the activation energy of quantum yield should tend to zero. Process M2 includes the reaction of exchange of a hydroxyl radical to a water molecule in the first coordination sphere of Fe^{2+} ion. It should possess considerable activation energy typical of the reactions of photoaquation (e.g., for $\text{FeOH}^{2+}(\text{aq})$ ion, the activation energy of water molecule exchange in the first coordination sphere is 34.7 kJ/mol [14], and that for $\text{Fe}^{3+}(\text{aq})$ it is 66.9 kJ/mol [15]). Thus, in the case of great activation energy of quantum yield, one could suggest, with great probability, the realization of mechanism M2.

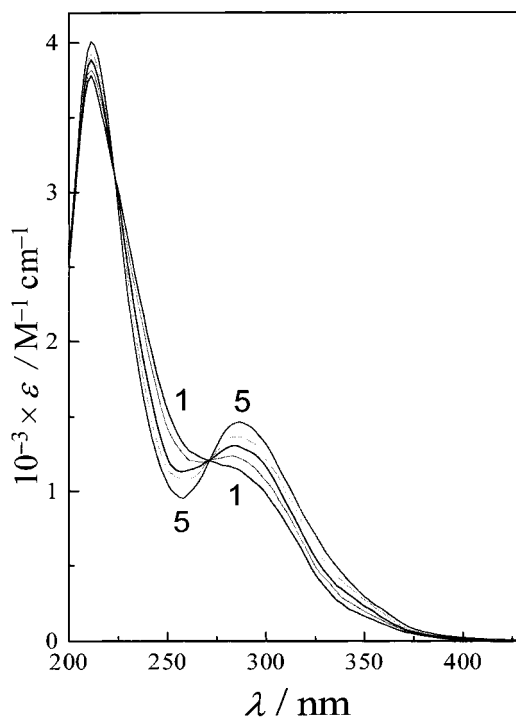


Fig. 6 Temperature dependence of electronic absorption spectrum of water solutions of Fe(III) (cuvette thickness, 1.0 cm; pH = 2.7; ionic strength, 0.035 M (LiClO_4); initial concentration of $\text{Fe}(\text{ClO}_4)_3 \times \text{H}_2\text{O}$, 2.0×10^{-4} M). Curves 1–5 denote temperatures 298, 306, 312, 319, 324 K.

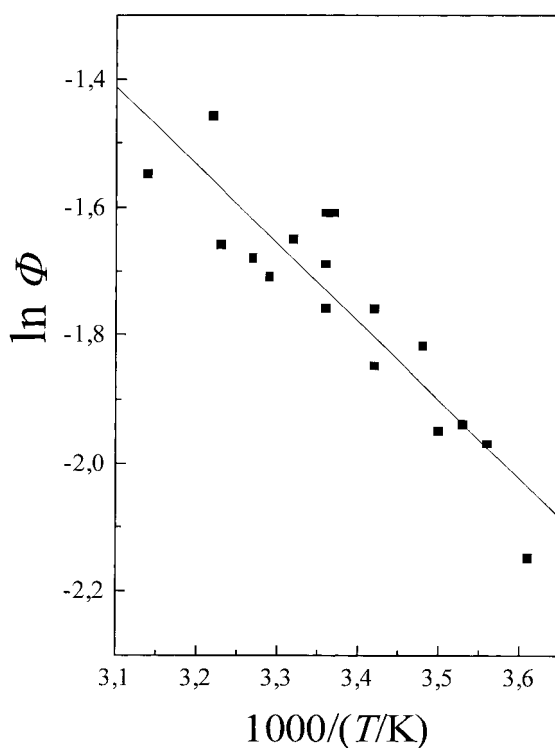


Fig. 7 Temperature dependence of quantum yield of $\bullet\text{OH}$ radical measured using laser flash photolysis (308 nm) of water solutions of $\text{Fe}(\text{ClO}_4)_3 \times \text{H}_2\text{O}$ with additions of nitrobenzene.

Note, however, that the opposite assertion is not correct, that is, the low value of activation energy does not allow one to reject mechanism M2. This is due to the fact that the photochemical excitation of the complex can substantially decrease the barrier of ligand exchange. Thus, the activation energy of $\text{Cr}(\text{acac})_2$ complex photoaquation is 15.5 kJ/mol, whereas that of the dark process is 104.5 kJ/mol [16].

In our experiments, the method of laser flash photolysis was used to measure the quantum yield of hydroxyl radical upon photolysis of $\text{FeOH}^{2+}(\text{aq})$ complex in the presence of nitrobenzene. As a standard, the oxygen-free methanol solution of the IrCl_6^{2-} complex was used. The quantum yield of the photolysis of this complex was determined in ref. 17. The absolute value of $\bullet\text{OH}$ radical quantum yield at 298 K was found to be 0.2 ± 0.02 , which is in fair agreement with the value of 0.195 obtained upon excitation at 310 nm [3].

In temperature measurements, a change in the optical absorption spectrum of $\text{Fe}(\text{III})$ solutions was taken into account (Fig. 6). The conservation of isosbestic points at 224 and 272 nm indicates the existence of transition between $\text{Fe}^{3+}(\text{aq})$ and $\text{FeOH}^{2+}(\text{aq})$ related to the temperature dependence of the equilibrium constant. No changes in the absorption coefficients of complexes with varying temperature were found.

The temperature dependence of the quantum yield of $\text{FeOH}^{2+}(\text{aq})$ photolysis in the range of 277–318 K is presented in Fig. 7. The activation energy of the process is $E_a = 10.0 \pm 1.3$ kJ/mol. As mentioned above, the low activation energy does not allow one to choose among the different photolysis mechanisms M2, M3, and M4. In order to understand the mechanism of the hydroxyl radical formation upon the photolysis of $\text{FeOH}^{2+}(\text{aq})$, it is probably necessary to improve the time resolution of pulse experiments.

CONCLUSIONS

In this work, the direct experimental evidence has been first obtained for $\bullet\text{OH}$ radical formation from photolysis of $\text{FeOH}^{2+}(\text{aq})$ complex. The quantum yield of radicals coincides with the literature value. The data were obtained on the temperature dependence of hydroxyl radical yield; the activation energy is 10.0 ± 1.3 kJ/mol. The high quantum yield and reactivity of $\bullet\text{OH}$ radical determine considerable contribution of the photochemistry of Fe(III) complexes to the oxidation of organic compounds in natural waters.

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