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# Hydroxyl radical formation upon photolysis of the $Fe(OH)^{2+}$ complex in aqueous solution

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**The laser flash photolysis (308 nm) of the $Fe(OH)^{2+}$ complex in aqueous solution with the addition of nitrobenzene demonstrated the formation of hydroxyl radicals in the primary photochemical process.**

Photochemical processes involving transition metal ions, in particular iron and copper, are responsible for the oxidation of organic and inorganic compounds in natural water.[1,2] The mechanism of photolysis of aqueous solutions of iron(III) hydroxo complexes assumes the intramolecular electron transfer from the coordinated $OH^-$ ion to the central ion of an excited complex followed by the escape of a hydroxyl radical into the bulk solution.[2] It is assumed that the oxidation of organic compounds is initiated by $^{\bullet}OH$ radical. However, this mechanism is based on the analysis of the final products of phototransformations. Neither $^{\bullet}OH$ radical nor the intermediate products of its reaction with organic or inorganic compounds were detected. At the same time, an alternative mechanism can be based on electron transfer from organic molecules located in the second coordination sphere to the excited complex. This mechanism is typical of the photoreduction of transition metal complexes in polar organic solvents.[3–5]

The $^{\bullet}OH$ radical has a weak absorption in the far UV region (maximum at 225 nm[6]), which is difficult to record owing to the absorption of initial complexes and organic additives. Therefore, in pulsed photochemical experiments, it can be revealed by a trap, *i.e.*, a compound that reacts with $^{\bullet}OH$ radicals to form an intermediate with a characteristic absorption spectrum. Earlier, dimethylformamide (DMF) has been employed as a trap.[7] However, because of the low rate constant of the reaction of $^{\bullet}OH$ radicals with DMF and a relatively small molar absorption coefficient of the absorption band of the resulting intermediate, DMF was unsuitable for quantitative measurements. Therefore, we propose nitrobenzene as an acceptor of $^{\bullet}OH$ radicals because the reaction rate constant is higher and the intermediate has a higher molar absorption coefficient.

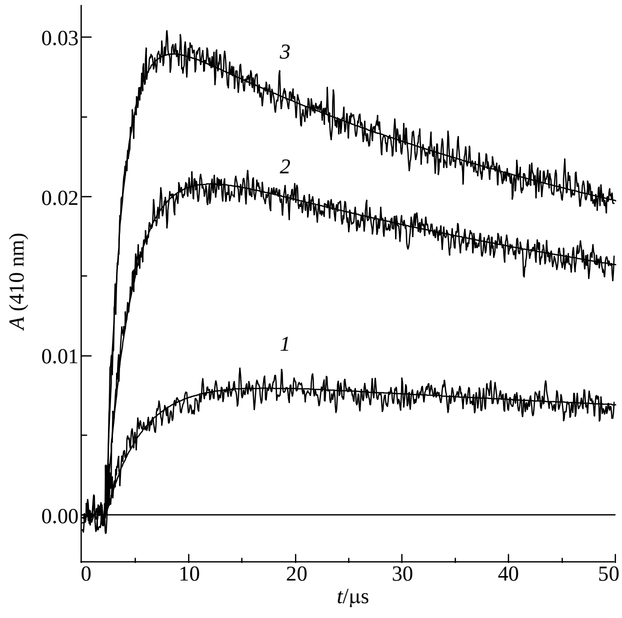

**Figure 1** Kinetic curves of changes in the absorbance at 410 nm upon laser flash photolysis (308 nm, XeCl laser) of $Fe(OH)^{2+}$ in aqueous solution with additions of nitrobenzene [cuvette thickness, 1 cm; temperature, 293 K, pH 2.9; initial $Fe(ClO_4)_3$ concentration, $5.3\times10^{-4}$ mol dm$^{-3}$]. Curves *1–3* refer to $1.6\times10^{-5}$, $6\times10^{-5}$ and $1.3\times10^{-4}$ mol dm$^{-3}$ of nitrobenzene, respectively. Smooth curves are the best fits by numerical solutions of system of differential equations for reactions (2)–(6) with parameters listed in Table 1.

We examined laser flash photolysis[4] (excitation by a XeCl laser at 308 nm) of iron(III) perchlorate in aqueous solutions with pH 3. Under these conditions, about 90% trivalent iron ions form the $FeOH^{2+}$ complex and the remaining ions form the $Fe^{3+}_{aq}$ complex.[2] Because the molar absorption coefficient of the hydroxo complex at the above wavelength is much higher than that of $Fe^{3+}_{aq}$, the only photoactive form was the $FeOH^{2+}$ complex. All the experiments were performed in oxygen-free solutions with the constant ionic strength 0.03 M ($KClO_4$) using twice-distilled water. To remove organic impurities, the solutions of $Fe^{III}$ perchlorate were irradiated with light of a high-pressure mercury lamp for several hours.

Adding nitrobenzene ($10^{-5}$–$10^{-4}$ M) to the solutions resulted in the kinetic curves of intermediate absorption appearance and decay (Figure 1). The characteristic time of an increase in this signal depends on the nitrobenzene concentration. The spectrum of intermediate absorption has a maximum at a wavelength of 410 nm (Figure 2, curve *1*) and corresponds to the nitrohydroxycyclohexadienyl radical[8] $Ph(^{\bullet}OH)NO_2$ (Figure 2, curve *2*). The $\cdot OH$ radical can add to a nitrobenzene molecule at three positions to form three isomers. However, the data on the optical spectra of these isomers are unavailable in the literature. The assumed mechanism of reactions follows the kinetic scheme given below:

$$Fe(OH)^{2+} \xrightarrow{h\nu} Fe^{2+}_{aq} + {}^{\bullet}OH \qquad (1)$$

$${}^{\bullet}OH + PhNO_2 \longrightarrow Ph({}^{\bullet}OH)NO_2 \qquad (2)$$

$$2\,{}^{\bullet}OH \longrightarrow H_2O_2 \qquad (3)$$

$$2\,Ph({}^{\bullet}OH)NO_2 \longrightarrow \text{products} \qquad (4)$$

$${}^{\bullet}OH + Fe^{2+}_{aq} \longrightarrow Fe(OH)^{2+} \qquad (5)$$

$${}^{\bullet}OH + Ph({}^{\bullet}OH)NO_2 \longrightarrow Ph(OH)_2NO_2 \qquad (6)$$

The experimental kinetic curves were fitted by numerical solutions of the system of differential equations for reactions (2)–(6) by the fourth-order Runge–Kutta method (Figure 1, smooth curves). The least-squares fit was used to choose the set of parameters, which agrees with the published data and gives the best description of experimental kinetic curves. The initial concentration of $^{\bullet}OH$ radicals was determined from a decrease in the absorbance of $Fe(OH)^{2+}$ (330 nm) just after a laser pulse. As variable parameters, we used the molar absorption coefficient of $Ph(^{\bullet}OH)NO_2$, the rate constant of radical disappearance ($2k_4$) and the effective molar absorption coefficient of the products of reaction (4) at a wavelength of 410 nm.

Reaction (4) can represent both disproportionation and recombination of $Ph(^{\bullet}OH)NO_2$ radicals followed by secondary reactions.[8,9] Nitrophenols are the only products of these transformations, which can exhibit absorption in the visible and near-UV regions.[10] The published data on the yield of nitrophenols

**Table 1** Rate constants of reactions (2)–(6 ) and molar absorption coefficients (410 nm) of the Ph($^\bullet$OH)NO$_2$ radical and final products of photoreaction.

| Parameter | This work | Published data |
|---|---|---|
| $k_2/10^{-9}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | 4.7$^a$ | 4.7$^8$ |
| $k_3/10^{-9}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | 5.2$^a$ | 5.2$^6$ |
| $2k_4\,\varepsilon_R^{-1}/10^{-5}$ cm s$^{-1}$ | 4.8±0.5 | 4.3 (pH 1)$^8$ |
| $k_4/10^{-9}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | 1.37±0.15 | 0.8 (pH 1)$^8$ |
| $\varepsilon_R$/dm$^3$ mol$^{-1}$ cm$^{-1}$ | 5660±160 | 3700$^8$ |
| $\varepsilon_P^{eff}$/dm$^3$ mol$^{-1}$ cm$^{-1}$ | 90±50 | ≈30$^8$; ≈120$^{9,b}$ |
| $k_5/10^{-8}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | 4.3$^a$ | 4.3$^6$ |

[a] A published value was used in the simulation. [b] Estimation from the yields and molar absorption coefficients of products.

in reaction (4) are rather contradictory. According to ref. 9 (decomposition of nitrobenzene using Fenton’s reagent and analysis of final products), it is about 1/2 of initial nitrobenzene. In this case, the relative yields of *ortho*-, *meta*- and *para*-isomers are almost the same. Asmus *et al.*[8] gave a value of ~1/8 (pulse radiolysis with the estimation by an absorption spectrum corresponding to the final part of kinetic curves). In our case, the quantitative analysis of the products of reaction (4) is difficult because of a photochemical reaction between nitrophenols and the Fe(OH)$^{2+}$ complex. Therefore, the effective molar absorption coefficient of the products was varied upon the treatment of the data of pulsed experiments.

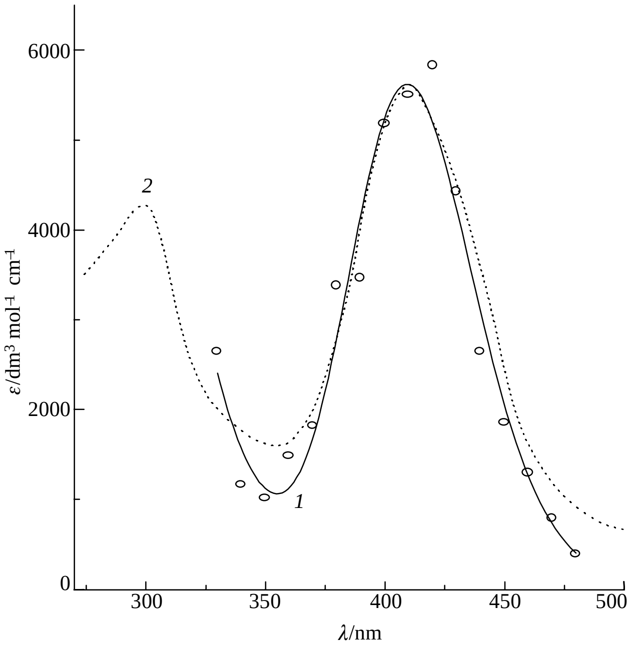

**Figure 2** Optical absorption spectrum of an intermediate arising from laser flash photolysis (308 nm, XeCl laser) of Fe(OH)$^{2+}$ in aqueous solution with additions of nitrobenzene [temperature, 293 K, pH 2.9; initial concentrations of Fe(ClO$_4$)$_3$ and nitrobenzene $3.1\times10^{-4}$ and $1.1\times10^{-4}$ mol dm$^{-3}$, respectively]. Dots indicate experimental points corresponding to 7.6 μs after a laser pulse; a full line shows the fit of an experimental spectrum by a Gaussian curve; dashed line indicates the spectrum of the Ph($^\bullet$OH)NO$_2$ radical taken from ref. 8 (pulsed radiolysis of aqueous nitrobenzene solutions at pH 7).

The results of fitting of more than 30 experimental kinetic curves (with different nitrobenzene concentrations and laser pulse intensities) are summarised in Table 1. Note that the optimum values of $2k_4$ and $\varepsilon_R$ exceed the previous data.[8] However, the $2k_4/\varepsilon_R$ ratio, which was determined from the experimental second-order kinetic curves, almost coincides with that given in ref. 8. The value of $k_6$ is unavailable in the literature. Varying it as a parameter shows that even when this rate constant reaches a diffusion limit, the contribution of reaction (6) is not more than 4% of the initial amount of $^\bullet$OH radicals and has no effect on the treatment of experimental data. The molar absorption coefficient of Ph($^\bullet$OH)NO$_2$ was calculated[8] from the radiation yield of radicals in aqueous solutions saturated with N$_2$O (for conversion of $e^-_{aq}$ into $^\bullet$OH radicals). However, a hydrogen atom, which can add to a nitrobenzene molecule to form Ph($^\bullet$H)NO$_2$ radical, also contributes to the radiation yield. It was assumed[8] that the spectra of these two radicals fully coincide up to the value of molar absorption coefficients. This assumption causes certain doubts and can be a reason for a lower molar adsorption coefficient in ref. 8 as compared to our data.

Thus, we detected the Ph($^\bullet$OH)NO$_2$ radical and found that the reaction rate constants of its formation ($k_2$) and $^\bullet$OH radical recombination ($k_3$) are consistent with the published data. We unambiguously concluded that the organic radical results from the reaction of $^\bullet$OH radicals with nitrobenzene and directly confirmed the formation of hydroxyl radicals upon photoreduction of the FeOH$^{2+}$ complex in aqueous solution.

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