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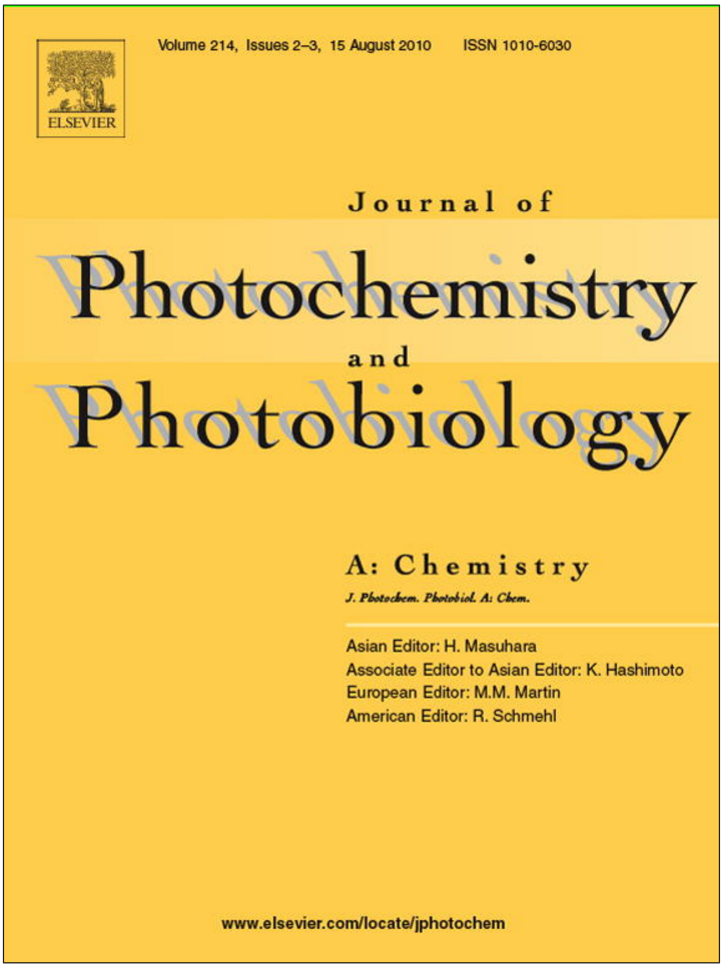

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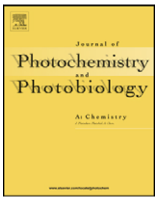

Photochemistry of $PtBr_6^{2-}$ complex in aqueous solutions. Formation and decay of $Br_2^{\bullet-}$ radical anions

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ABSTRACT

Laser flash photolysis was applied to study the photochemistry of $PtBr_6^{2-}$ complex in aqueous solutions with the presence of free Br^- anions. Laser pulse is followed by the formation of $Br_2^{\bullet-}$ radical anion, which reacts with the initial complex with the rate constant $k = 9 \times 10^8\ M^{-1}\ s^{-1}$ yielding the complex of Pt(V). Analysis of $Br_2^{\bullet-}$ quantum yield via bromide concentration testifies that a bromine atom is formed by an electron transfer from a free Br^- anion to the light-excited complex. $PtBr_6^{2-}$ photoaquation occurs via heterolytic cleavage of the Pt–Br bond. Addition of free bromide anions sufficiently decreases the quantum yield of photoaquation.

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1. Introduction

Photochemistry of $PtBr_6^{2-}$ complex in aqueous solutions was studied in [1–8]. Earlier literature data on the photochemistry of this complex based on the stationary experiments were contradictive. Controversies were touched upon both the interpretation of the experimental data and the nature of the photochemical processes. Balzani et al. [3–5] believed that the multi-stage photoaquation occurs. Quantum yield of the first stage of photoaquation (reaction 1) in the solutions with neutral pH values was shown to be 0.4 independent on the wavelength of the exciting light [4].

$$PtBr_6^{2-} \xrightarrow{h\nu} \left(PtBr_6^{2-}\right)^* \xrightarrow{H_2O} PtBr_5(H_2O)^- + Br^- \qquad (1)$$

Shagisultanova et al. [6] supposed that the experimental data on the $PtBr_6^{2-}$ photolysis in strongly acidic solutions indicated the one-stage formation of Pt(IV) complex with two molecules of water in the first coordination sphere

$$PtBr_6^{2-} \xrightarrow{h\nu} \left(PtBr_6^{2-}\right)^* \xrightarrow{2H_2O} PtBr_4(H_2O)_2 + 2Br^- \qquad (2)$$

Penkett and Adamson [2] based on the data of $PtBr_6^{2-}$ flash photolysis postulated the reaction of two-electron reduction of Pt(IV) with a bromine molecule escape to the solution bulk

$$PtBr_6^{2-} \xrightarrow{h\nu} PtBr_4^{2-} + Br_2 \qquad (3)$$

Recently we have studied the primary processes in the photochemistry of $PtBr_6^{2-}$ by means of stationary and nanosecond laser flash photolysis [7] and ultrafast kinetic spectroscopy [8]. The data obtained supported the conclusion of Balzani et al. [3–5] on the multi-stage photoaquation of $PtBr_6^{2-}$. Quantum yield of the first stage was re-measured and found to be 0.39 in an aqueous solution, 0.29 in a buffer solution with pH 6.86 and 0.6 in 1 M $HClO_4$ [7]. The characteristic time of the formation of aquated complex $PtBr_5(H_2O)^-$ on the first stage of photolysis is less than 100 ns [7]. Experiments on femtosecond kinetic spectroscopy with the excitation at 420 nm [8] have shown that photoaquation could occur from either a triplet excited $^3T_{1g}$ state of $PtBr_6^{2-}$ or from hot, vibrationally excited ground state $^1A_{1g}$. The characteristic time of photoaquation does not exceed 15 ps [8].

This work reports the photochemistry of $PtBr_6^{2-}$ with the presence of free Br^- anions. In this case, an additional channel of photochemical reaction could appear, namely an electron transfer from an intersphere bromide anion to the light-excited complex. A bromine atom occurring in this reaction should rapidly convert to

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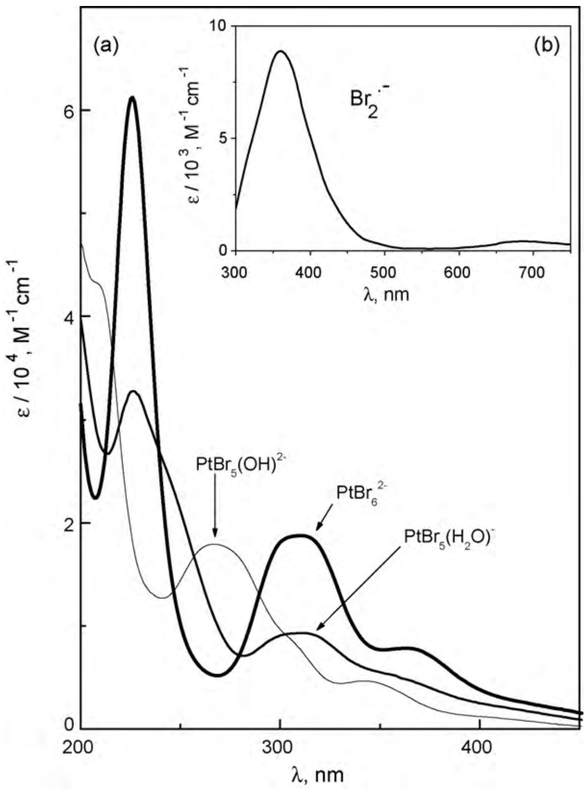

Fig. 1. UV absorption spectra of Pt(IV) complexes (a) and $Br_2^{\bullet-}$ radical anion (b) [15] in aqueous solutions. Spectra of $PtBr_5(H_2O)^-$ and $PtBr_5(OH)^{2-}$ complexes are taken from [7].

a $Br_2^{\bullet-}$ radical anion which possesses an intense absorption band in a near UV spectral region. It could be proposed that the measurements of $Br_2^{\bullet-}$ absorption in pulsed experiments allow one to determine the dependence of quantum yield via Br^- concentration, which gives information about primary processes in the photochemistry of $PtBr_6^{2-}$. The efficiency of such an approach was demonstrated in the study of $IrCl_6^{2-}$ photochemistry in aqueous [9] and alcohol [10] solutions.

2. Experimental

Solutions of $PtBr_6^{2-}$ complex were prepared from the $Na_2PtBr_6 \times H_2O$ salt synthesized as described in [11]. NaBr (Aldrich) was used as a source of free bromide anions. Deionized water was used to prepare solutions. If necessary, oxygen was removed from the samples by 20 min bubbling with argon.

UV absorption spectra were recorded using Agilent 8453 spectrophotometer (Agilent Technologies). Stationary photolysis was performed by irradiation of a XeCl laser (308 nm), a YAG laser (355 nm) or a high pressure mercury lamp with a set of glassy filters to distinguish necessary wavelengths. Laser flash photolysis experiments were performed with the use of previously described [12] setup with an excitation by a XeCl excimer laser (308 nm, 15 ns, 20 mJ/pulse) or by a YAG laser (355 nm, 5 ns, 10 mJ). For the extraction of kinetic (reaction rate constants) and spectral (molar absorption coefficients of intermediates) parameters from the experimental data, a system of differential equations corresponding to the selected reaction scheme was solved numerically by a fourth-order Runge-Kutta method, and the results were compared with the experimental kinetic curves.

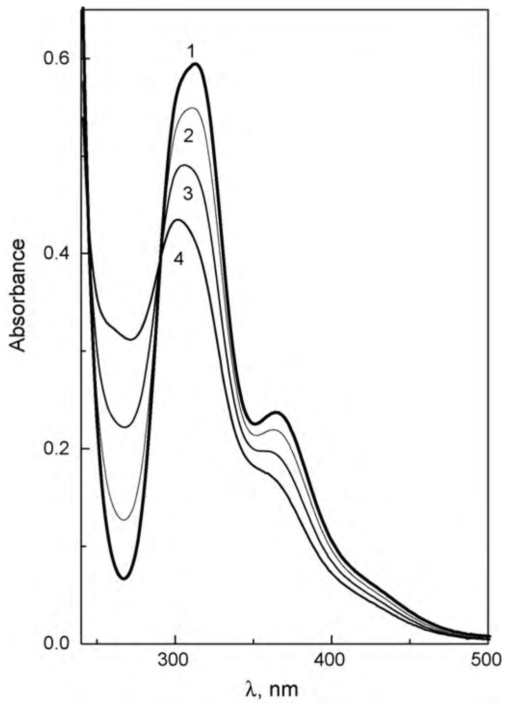

Fig. 2. Stationary photolysis of $PtBr_6^{2-}$ complex (3.5×10^{-5} M) in aqueous solutions with addition of 1 M NaBr. Excitation by XeCl laser pulses (308 nm). Curves 1–4 correspond to 0, 3, 9, 20 laser pulses.

3. Results and discussions

3.1. UV spectra of reagents, products and intermediates

UV spectra of complexes related to this work are shown in Fig. 1. The spectrum of the initial $PtBr_6^{2-}$ complex (Fig. 1a) coincides with known from the literature [5]. The spectra of $PtBr_5(H_2O)^-$ and $PtBr_5(OH)^{2-}$ complexes were reported in [7]. $PtBr_5(H_2O)^-$ and $PtBr_5(OH)^{2-}$ complexes are the primary products of thermal [13] and (or) photochemical [7] aquation of $PtBr_6^{2-}$. Ratio between $PtBr_5(H_2O)^-$ and $PtBr_5(OH)^{2-}$ concentrations is determined by acidic properties of the $PtBr_5(H_2O)^-$ complex (pK_a = 4.4 [14]).

$$PtBr_5(H_2O)^- \xrightarrow{pK_a=4.4} PtBr_5(OH)^{2-} + H^+ \tag{4}$$

The UV spectrum of $Br_2^{\bullet-}$ radical anion, which is a probable intermediate of $PtBr_6^{2-}$ photolysis, taken from [15] is shown in Fig. 1b.

3.2. Stationary photolysis of $PtBr_6^{2-}$ in aqueous solutions in the presence of free Br^- anions

Fig. 2 demonstrates the changes in the UV spectrum of $PtBr_6^{2-}$ in a course of its photolysis in the presence of large (1 M) amounts of free bromide anions. The initial pH value of the solution was neutral. Spectral changes practically coincide with that of occurred when $PtBr_6^{2-}$ is irradiated in the absence of free Br^- anions [7] and correspond to the photoaquation of the initial complex. Conservation of an isosbestic point at 291 nm is characteristic for the formation of $PtBr_5(OH)^{2-}$ complex.

The UV spectrum of the initial complex is restored in the dark after photolysis (Fig. 3a). It proves that the irradiation of $PtBr_6^{2-}$ in the presence of free Br^- anions leads to photoaquation. In the course of the dark backward reaction the same isosbestic point as in the stage of photolysis (291 nm) is conserved. Fig. 3b shows the kinetic curves of dark reactions recorded at 313 and 269 nm, which are satisfactorily fitted by a two-exponential function with the characteristic times of 36 ± 3 and 350 ± 60 s.

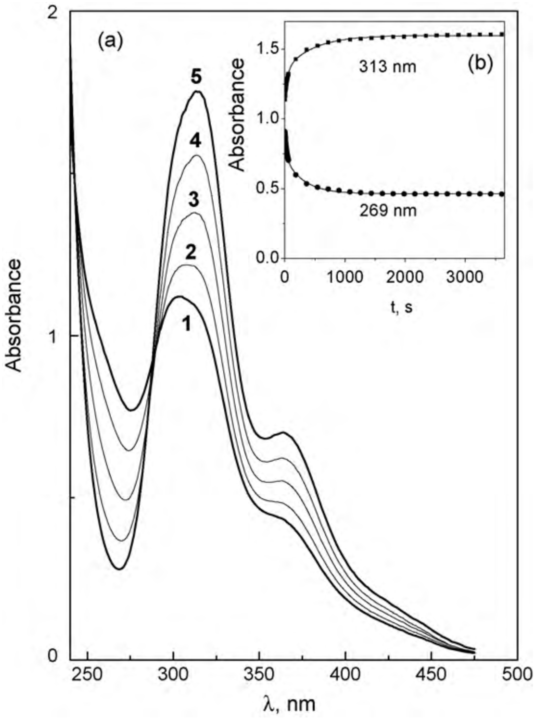

Fig. 3. Thermal reaction after the photolysis of aqueous $PtBr_6^{2-}$ solution (9.3×10^{-5} M) in the presence of 4 M NaBr. (a) curve 5 – spectrum of the initial complex; curves 1–4 correspond to 0; 30; 180; 3780 s after irradiation. (b) Kinetic curves (dots) and two-exponential fits (full lines).

Kinetics of the substitution of a water molecule to Br^- anion (the reaction of anation) in the $PtBr_5(H_2O)^-$ complex was studied by Elding and Gustafson [16,17] in strongly acidic solutions (0.5 M $HClO_4$). The dependence of the observed anation rate constant (k_{obs}) on the concentration of Br^- was described in [16] by an equation:

$$k_{obs} = k_1[Br^-] + k_2[Br^-]^2$$

where $k_1 = 1.8 \times 10^{-3}$ M^{-1} s^{-1} and $k_2 = 4.5 \times 10^{-2}$ M^{-2} s^{-1}.

The presence of a quadratic term was explained by the formation of an intersphere complex between $PtBr_5(H_2O)^-$ and Br^- [16]. When Br^- concentration is about 4 M, the upon mentioned values of k_1 и k_2 give the value of the characteristic anation time of about 1.5 s.

When photoaquation of $PtBr_6^{2-}$ occurs at pH values close to neutral, the reaction product is $PtBr_5(OH)^{2-}$ complex, which electric charge is higher than that of $PtBr_5(H_2O)^-$ occurred in acidic solutions. Therefore, one can expect the rate of anation to decrease. That is really so. Fig. 3b shows that the characteristic lifetime of $PtBr_5(OH)^{2-}$ is about 35 s, which is ca. 20 times higher than in acidic solutions. The complexity of the kinetic curves (at least, two-exponential approximation is necessary) could be due to the multi-stage kinetics of OH^- to Br^- substitution.

3.3. *Laser flash photolysis of $PtBr_6^{2-}$ in the presence of free Br^- anions: evidence of $Br_2^{\bullet-}$ radical anions formation*

Nanosecond laser flash photolysis of $PtBr_6^{2-}$ in aqueous solutions with no added Br^- anions results in an instant decrease in absorption of the initial complex without any further changes [7]. The kinetic curves are threshold-like [7]. No detectable intermediates occur. Therefore, the photoaquation of the $PtBr_6^{2-}$ complex is a fast reaction occurring during the time of a laser pulse (less than 10 ns).

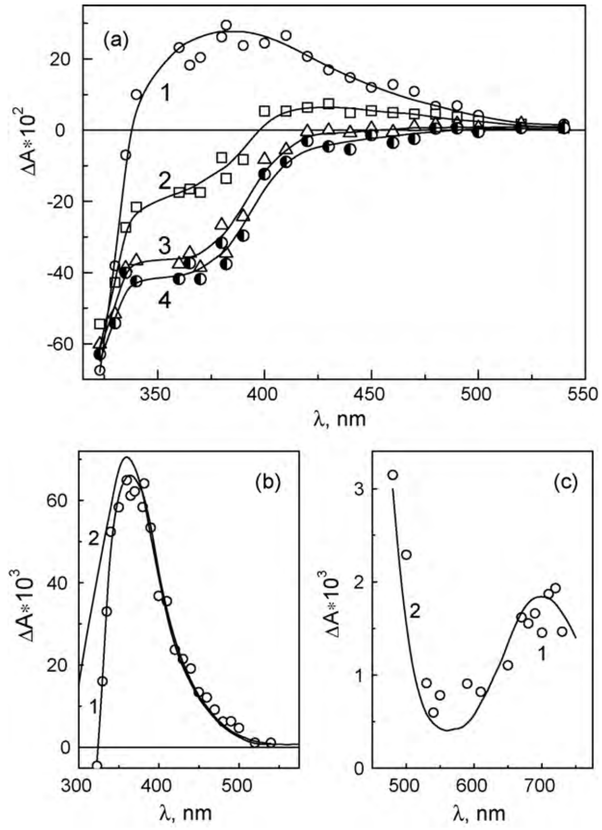

Fig. 4. Intermediate absorption spectra caused by laser flash photolysis (308 nm) of aqueous $PtBr_6^{2-}$ solution (4.2×10^{-5} M) in the presence of 4 M NaBr (a) curves 1–4 correspond to 0, 10, 50, 175 μs after laser pulse. (b) 1 – difference in spectra 1 and 4 shown in (a), 2 – spectrum of $Br_2^{\bullet-}$ radical anion [15]. (c) 1 – intermediate absorption after the laser pulse in the red spectral region, 2 – $Br_2^{\bullet-}$ spectrum.

Addition of large amounts of NaBr to the solutions of $PtBr_6^{2-}$ leads to the occurrence of intermediate absorption and dramatic changes in the shape of the kinetic curves. Instead of instant bleaching in the region of 340–500 nm after the laser pulse, an intermediate absorption appears. Fig. 4a demonstrates the temporal changes in the intermediate absorption at high concentration of NaBr (4 M). Fig. 5a shows a typical kinetic curve. All the processes of changes in the intermediate absorption terminate to 200 μs. Decrease in the concentration of NaBr leads to the decrease in the yield of the intermediate absorption, which is evident from the kinetic curve shown in Fig. 5b corresponding to 1 M NaBr. In the last case, laser pulse results in an instant increase in absorption followed by its additional decrease corresponding to the decay of an intermediate absorption.

The difference in the intermediate absorption spectra at the times of $t = 0$ and $t = 200$ μs are shown in Fig. 4b. This difference coincides with the UV spectrum of $Br_2^{\bullet-}$ radical anion having a strong band with the maximum at 360 nm. The correctness of the identification of the intermediate absorption is supported by recording of absorption in the region of 750 nm (Fig. 4c), which is a characteristic feature of $Br_2^{\bullet-}$ spectrum [15]. The discrepancy between spectrum of $Br_2^{\bullet-}$ and experimental spectrum in the region of $\lambda < 360$ nm (Fig. 4b) is explained by the disappearance of the initial $PtBr_6^{2-}$ complex.

It should be noted that the intermediate absorption spectra do not demonstrate absorption which could be attributed to Pt(III) complexes, either $PtBr_6^{3-}$ or to products of its dissociation and (or) hydrolysis. It means that the complexes of trivalent platinum do not have appreciable absorption in the experimentally available spectral region of 300–700 nm.

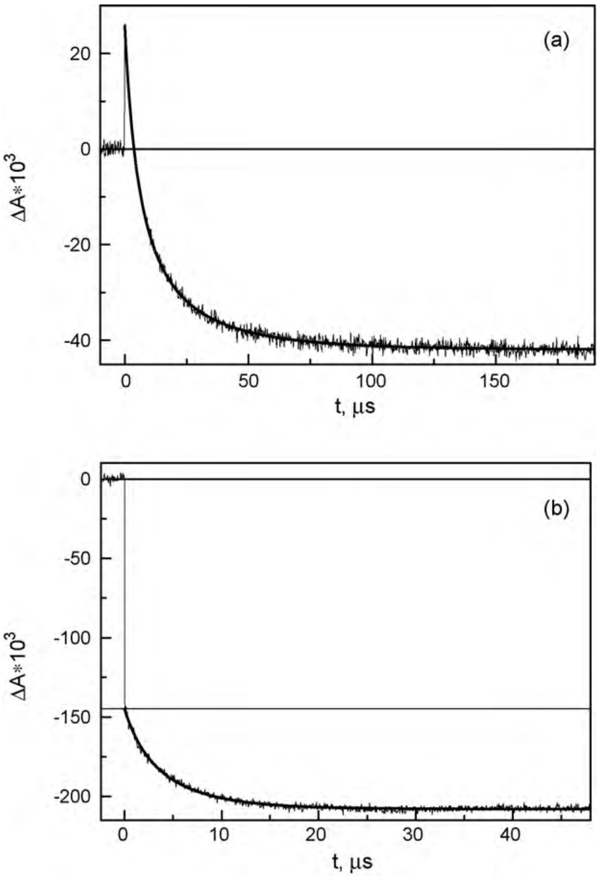

Fig. 5. Kinetic curves at 370 nm caused by laser flash photolysis (355 nm) of aqueous $PtBr_6^{2-}$ solution (4.2×10^{-5} M) in the presence of 4 M NaBr (a) and 1 M NaBr (b). Experimental curves and fits (bold lines; see text).

Information concerning the mechanism of $Br_2^{\bullet-}$ formation could be obtained from the dependence of its yield via the concentration of free bromide anions. The yield of radical anions is determined by the amplitudes and shapes of the kinetic curves, which could be precisely calculated from the known kinetic mechanism of $Br_2^{\bullet-}$ disappearance.

3.4. *Decay of $Br_2^{\bullet-}$ radical anions*

The usual channel of $Br_2^{\bullet-}$ disappearance is its disproportionation

$$Br_2^{\bullet-} + Br_2^{\bullet-} \to Br^- + Br_3^- \tag{5}$$

The rate constant of this reaction k_5 was repeatedly measured in the literature [18–21]. Its value at ionic strength of the solution ≤0.02 M falls within the range $(1.9\text{–}2.4) \times 10^9\ M^{-1}\,s^{-1}$. Effect of the ionic strength on the k_5 value was studied in [19]. The increase of KBr concentration in solution from 0.01 to 1 M results in the increase of k_5 from 1.9×10^9 to $2.5 \times 10^9\ M^{-1}\,s^{-1}$ [19] due to shielding of negatively charged particles by an ionic atmosphere. If initial concentration of radical anions is about $(1\text{–}10) \times 10^{-6}$ M and $k_5 \approx 2.5 \times 10^9\ M^{-1}\,s^{-1}$, one can estimate that the characteristic time of $Br_2^{\bullet-}$ disappearance in reaction (5) falls within the range 400–40 μs.

Kinetic curves (Fig. 5) show that in our case the disappearance of intermediate absorption is sufficiently faster (ca. 10 μs). Therefore, an additional channel of $Br_2^{\bullet-}$ decay should exist. This additional reaction is of a first order via $PtBr_6^{2-}$, because the effective rate constant of $Br_2^{\bullet-}$ disappearance linearly depends on the concentration of the initial complex (Fig. 6). The slope of this straight line allows one to determine the rate constant of the reaction between $Br_2^{\bullet-}$ and $PtBr_6^{2-}$, $k_6 = (9.0 \pm 0.2) \times 10^8\ M^{-1}\,s^{-1}$.

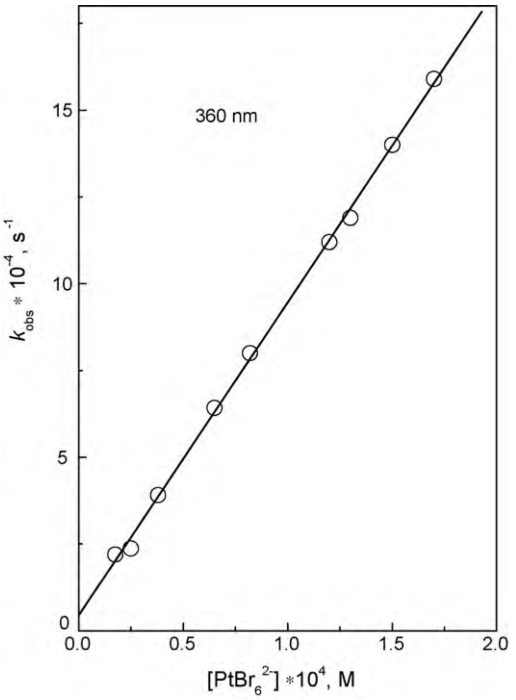

Fig. 6. Dependence of the effective rate constant (k_{obs}) of $Br_2^{\bullet-}$ disappearance (360 nm) on $PtBr_6^{2-}$ concentration in aqueous solutions with addition of 1 M NaBr.

$$Br_2^{\bullet-} + PtBr_6^{2-} \to PtBr_6^- + 2Br^- \tag{6}$$

At high intensity of a laser pulse and large depth of photoaquation, a sufficient part of the initial $PtBr_6^{2-}$ complex could be transformed to the $PtBr_5(OH)^{2-}$ complex, which could also react with $Br_2^{\bullet-}$ radical anion.

$$Br_2^{\bullet-} + PtBr_5(OH)^{2-} \to PtBr_5(OH)^- + 2Br^- \tag{7}$$

It is not possible to distinguish the reactions (6) and (7). Therefore, in further calculations we assume that the rate constants of these reactions are equal.

As a result, under conditions of this work the main channel of $Br_2^{\bullet-}$ disappearance is the reaction with $PtBr_6^{2-}$ resulted in the formation of Pt(V) complex. It is worth noting that the similar reaction occurs when aqueous solutions of $PtCl_6^2$ complex are irradiated in the presence of free chloride anions [14]. In the last case, oxidation of $PtCl_6^2$ by $Cl_2^{\bullet-}$ radical anion leads to the formation of $PtCl_6^-$ complex.

The rate constant of a diffusion-controlled reaction between two charged particles of the same sign of charge could be calculated as [22]

$$k_{diff} = 4\pi R_O D (e^{R_O/R} - 1)^{-1} \tag{8}$$

where R_O is the Onsager radius of the reacting particles (for the $Br_2^{\bullet-}$–$PtBr_6^{2-}$ pair $R_O = 2e^2/(\varepsilon kT) \approx 13.4$ Å); R is the reaction radius, and D is the mutual diffusion coefficient of the reagents. Assuming that the reaction radius is equal to the sum of the Van der Waals radii of reagents ($R(Br_2^{\bullet-}) = 3.3$ Å [23], $R(PtBr_6^{2-}) = 4.2$ Å, because the Pt–Br bond length is 2.2 Å [24] and Br^- anion radius is 2 Å [25]), we obtain $R = 7.5$ Å. Diffusion coefficients for $Br_2^{\bullet-}$ and $PtBr_6^{2-}$ could be estimated using Stokes–Einstein equation $D = \frac{kT}{6\pi\eta R}$, which gives for the mutual diffusion coefficient the value of $D = 1.2 \times 10^{-5}\ cm^2/s$.

Inserting the estimated values of R_O, R and D to the formula (8), one can calculate the value of the diffusion-controlled rate constant for reactions (6) and (7) as $k_{diff} = 2.3 \times 10^9$ M^{-1} cm^{-1}, which corresponds to zero ionic strength of the solution. When ionic strength is about 1 M, one can expect a moderate increase of k_{diff}. Therefore, the experimental value of the rate constant k_6 is about 2.5 times less than the diffusion rate constant.

It should be noted that we have not found the spectral manifestations of Pt(V) complexes. It could be proposed that Pt(V) complexes disappear in the reaction with Pt(III) intermediates formed by an electron transfer from a free bromide anion to the light-excited $PtBr_6^{2-}$ complex.

3.5. Quantum yield of $PtBr_6^{2-}$ photolysis in the presence of free Br^- anions

Determination of the quantum yield of $PtBr_6^{2-}$ photolysis in the presence of free bromide anions in stationary experiments is hampered by the relatively fast reaction of the $PtBr_5(OH)^{2-}$ complex anation (Fig. 2). However, pulsed experiments allow one to determine both quantum yield of photolysis (using the decrease in $PtBr_6^{2-}$ absorption) and quantum yield of $Br_2^{\bullet-}$ formation (using its absorption at 360 nm).

The values of quantum yields at different Br^- concentrations were obtained by fitting of the experimental kinetic curves at 360 nm by the solutions of a system of differential equations corresponding to the selected reaction mechanism. Fitting of the kinetic curves is necessary to take in account the amount of the initial complex disappeared in reaction (6). The simulation of the kinetic curves was performed on the assumption that both $PtBr_5(OH)^{2-}$ complex and $Br_2^{\bullet-}$ radical anion were formed as a result of competitive reactions. Disappearance of intermediates in reactions (5)–(7) was taken into account. The varied parameters of simulation were rate constants k_5 and $k_6 = k_7$ and initial yields of $Br_2^{\bullet-}$ and $PtBr_5(OH)^{2-}$. Molar absorption coefficient of all the reagents was taken from the literature (see Fig. 1) and was not varied. Examples of the experimental curves with fits are shown in Fig. 5.

Optimal values of the rate constants obtained by simulation are collected in Table 1. The rate constant of disproportionation k_5 measured in this work is characteristic for the diffusion-controlled reaction between two charged particles of the same sign of charge and is in agreement with the values obtained previously [20]. An increase in ionic strength of solutions from 0.5 to 4 M results in increase of k_5 by a factor of 1.5. For ionic reactions (6) and (7) the rate constants obtained by simulation are also close to the rate constant of a diffusion-controlled reaction, which rises with an increase in the ionic strength.

Spectral and kinetic data treatment shows that the total quantum yield of $PtBr_6^{2-}$ photolysis drops in a factor of 5 with an increase in Br^- concentration from 0.5 to 4 M (Fig. 7). As this takes place, the quantum yield of $Br_2^{\bullet-}$ formation increases, but the dramatic decrease in the photoaquation quantum yield leads to the drop of the total quantum yield. It is important that the dependence of quantum yield vs. Br^- concentration is negligible in the region of 0–0.5 M, and the changes become observable at $[Br^-] > 0.5$ M. At higher concentration of bromide ions the reducing channel of photolysis is dominant (85% at 4 M NaBr).

It is necessary to stress that in the experiments on the stationary photolysis of $PtBr_6^{2-}$ only the process of photoaquation is observed, even with 4 M NaBr in solution. The reason probably is that the reactions between Pt(III) and Pt(V) complexes occurs, which results in the formation of only Pt(IV) complexes. The typical scale of characteristic times of these reactions falls within the time interval 10 ms–10 s.

$$\text{Pt(III)} + \text{Pt(V)} \rightarrow 2\text{Pt(IV)} \tag{9}$$

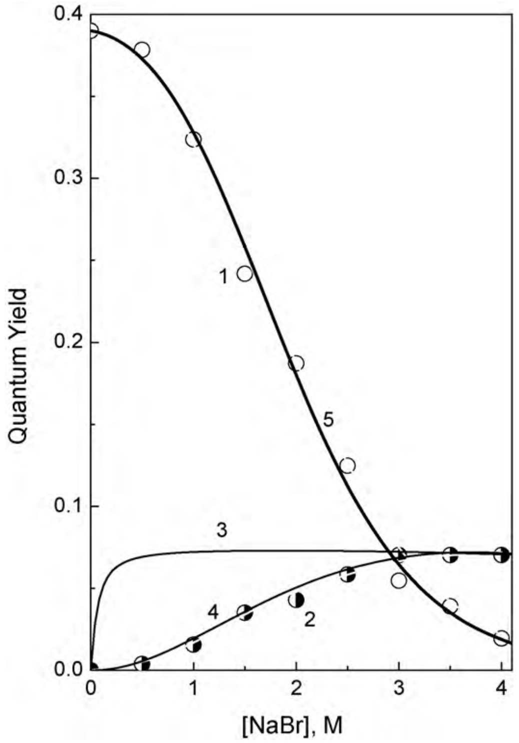

Fig. 7. Dependencies of quantum yields of $PtBr_6^{2-}$ photoaquation (1) and $Br_2^{\bullet-}$ formation (2) on the concentration of free Br^- anions. Dots – experimental data. Solid lines – calculations using Eqs. (20) (curve 3), (22) (curve 4), and (24) (curve 5). For details of calculations see text.

3.6. Mechanism of bromine atom and $Br_2^{\bullet-}$ radical anion formation

Photoaquation of $PtBr_6^{2-}$ complex can occur via two different mechanisms [7]. Firstly, a dissociative mechanism is possible. It includes a heterolytic cleavage of Pt–Br bond followed by penetration of a water molecule into the coordination sphere of Pt(IV). In this case platinum cation remains tetravalent in the case of the whole process.

$$PtBr_6^{2-} \underset{k_{-10}}{\overset{h\nu}{\rightleftarrows}} \left(PtBr_6^{2-}\right)^* \xrightarrow[k_{10}]{} \left(PtBr_5^{2-}...Br^-\right) \tag{10}$$

$$\left(PtBr_5^{2-}...Br^-\right) \xrightarrow{H_2O} [PtBr_5(H_2O)]^- + Br \tag{11}$$

The second mechanism is determined by an electron transfer form a bromide anion inside the coordination sphere of a light-excited complex with the formation of an intermediate $[PtBr_5(H_2O)^{2-}...Br]$ typically called “a radical pair”

$$PtBr_6^{2-} \underset{k_{-12}}{\overset{h\nu}{\rightleftarrows}} \left(PtBr_5^{2-}...Br^{\bullet}\right)^* \tag{12}$$

$$\left(PtBr_5^{2-}...Br^{\bullet}\right)^* \xrightarrow{H_2O} \left[PtBr_5(H_2O)^{2-}...Br^{\bullet}\right] \tag{13}$$

$$\left[PtBr_5(H_2O)^{2-}...Br^{\bullet}\right] \rightarrow [PtBr_5(H_2O)]^- + Br^- \tag{14}$$

In this case platinum cation of the $[PtBr_5(H_2O)^{2-}...Br^{\bullet}]$ radical pair is in trivalent state till a backward electron transfer occurs.

Formation of a bromine atom and hence $Br_2^{\bullet-}$ radical anion in the presence of free bromide anions also can follow two different mechanisms. The first possibility is a capture of a bromine atom of the $[PtBr_5(H_2O)^{2-}...Br^{\bullet}]$ radical pair by a free Br^- anion [26]

$$\left[PtBr_5(H_2O)^{2-}...Br^{\bullet}\right] + Br^- \rightarrow PtBr_5(H_2O)^{2-} + Br_2^{\bullet-} \tag{15}$$

Table 1

Calculation and simulation of the kinetic curves of intermediate absorption at the wavelength of 360 nm in the framework of reaction scheme (5–7). Molar absorption coefficients: $Br_2^{\bullet-}$ – 9000 $M^1\ cm^{-1}$; $PtBr_6^{2-}$ – 6800 $M^{-1}\ cm^{-1}$; $PtBr_5(OH)^{2-}$ – 3600 $M^{-1}\ cm^{-1}$; $k_7 = k_6$.

$[Br^-]$, M	$k_5 \times 10^{-9}$, $M^{-1}\ s^{-1}$	$k_7 \times 10^{-9}$, $M^{-1}\ s^{-1}$	$\frac{\varphi_{PtBr_5(OH)^{2-}}}{\varphi_0}$	$\frac{\varphi_{Br_2^{\bullet-}}}{\varphi_0}$	$\frac{\varphi_{Br_2^{\bullet-}}}{\varphi_{PtBr_5OH^{2-}}}$
0	–	–	1	0	0
0.5	2.0	0.9	0.97	0.01	0.010
1	2.2	1.0	0.83	0.04	0.048
1.5	2.5	1.5	0.62	0.09	0.145
2	2.8	1.7	0.48	0.11	0.229
2.5	3.0	2.0	0.32	0.15	0.469
3	3.1	1.8	0.14	0.18	1.286
3.5	3.0	2.0	0.10	0.18	1.800
4	3.0	1.7	0.05	0.18	3.600

The second possibility is an intersphere electron transfer from a free bromide anion to the light-excited complex.

$$\left(PtBr_6^{2-}\right)^* + Br^- \rightarrow \left[PtBr_6^{3-}\ldots Br^\bullet\right] \tag{16}$$

The radical pair $[PtBr_6^{3-}\ldots Br^\bullet]$ could disappear as a result of a backward electron transfer.

$$\left[PtBr_6^{3-}\ldots Br^\bullet\right] \rightarrow PtBr_6^{2-} + Br^- \tag{17}$$

If the concentration of free Br^- anions is high enough, a bromine atom could be captured in the reaction.

$$\left[PtBr_6^{3-}\ldots Br^\bullet\right] + Br^- \rightarrow PtBr_6^{3-} + Br_2^{\bullet-} \tag{18}$$

In both cases the efficiency of a bromine atom escape from $[PtBr_5(H_2O)^{2-}\ldots Br^\bullet]$ or $[PtBr_6^{3-}\ldots Br^\bullet]$ radical pairs to the solution bulk is low because of the backward electron transfer. If a bromine atom escapes to the solution bulk, it should react with a free Br^- anion with a diffusion rate constant [27].

$$Br^\bullet + Br^- \rightarrow Br_2^{\bullet-} \tag{19}$$

Measuring the relative yield of $Br_2^{\bullet-}$ radical anion as a function of Br^- concentration, one could estimate the ratio of the rate constants of a bromine atom escape to the bulk and a backward electron transfer. Assume that Br atoms escape to the bulk. In this case, a capture of all the escaped atoms should happen at a relatively low concentration of bromide anions. Only Pt(III) intermediates could compete with Br^- anions for bromine atoms. The concentration of Pt(III) is definitely lower than the concentration of initial $PtBr_6^{2-}$ complex. Therefore, the concentration of Br^- necessary to capture all the bromine atoms could be estimated as $[Br^-] \geq [PtBr_6^{2-}] \approx 10^{-4}$ M. However, in the experiments $Br_2^{\bullet-}$ radical anions become observable only at very high concentration of Br^- (>1 M). Hence, a free Br^- anion should capture a bromine atom of the radical pair before the backward electron transfer occurs.

Fig. 7 demonstrates an S-type dependence of the $Br_2^{\bullet-}$ quantum yield via free Br^- anions concentration. At 3.5–4 M Br^- it reaches a limiting value of $\varphi\left(Br_2^{\bullet-}\right) \approx 0.07$, which is sufficiently less that the quantum yield of photoaquation in the absence of free bromide ($\varphi_0 = 0.39$, Fig. 7). If the mechanism of photoaquation was determined only by the formation of the primary and secondary radical pairs $[PtBr_5^{2-}\ldots Br^\bullet]$ and $[PtBr_5(H_2O)^{2-}\ldots Br^\bullet]$, one should expect that the quantum yield of $Br_2^{\bullet-}$ formation is comparable with that of photoaquation. Therefore, if the secondary radical pair $[PtBr_5(H_2O)^{2-}\ldots Br^\bullet]$ is the source of a bromine atom, it could gain no more than 20% of photoaquation process.

In the case of a bromide anion attacking the $[PtBr_5(H_2O)^{2-}\ldots Br^\bullet]$ radical pair (reaction (15)) the yield of $Br_2^{\bullet-}$ depends on Br^- concentration according to the equation:

$$\varphi\left(Br_2^{\bullet-}\right) = \frac{k_{13}}{k_{13} + k_{-12}} \times \frac{k_{15}\,[Br^-]}{k_{14} + k_{15}\,[Br^-]} \tag{20}$$

This equation does not describe the S-type dependence of $Br_2^{\bullet-}$ quantum yield via Br^- concentration. Moreover, the S-type dependence could not be described even though to take into account the dependence of the rate constant k_{15} on the ionic strength μ for the reaction of two negatively charged ions ($z_1 \times z_2 = 2$), which is described by Davies [28–30].

$$k_{15} = k_{15}(\mu = 0) \times e^{2.3 \times 0.51 \times z_1 z_2 \left(\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.3\mu\right)} \tag{21}$$

Fig. 7 shows the result of such an extrapolation (curve 3, which is obtained using $k_{15}/k_{14} = 10$ and $k_{-12}/k_{13} = 12$).

For the mechanism of the intersphere electron transfer including the formation of the $[PtBr_6^{3-}\ldots Br^\bullet]$ radical pair, S-type dependence could be explained by the participation of the two free bromide anions in the process of $Br_2^{\bullet-}$ formation. The first Br^- anion attacks the light-excited complex (reaction (16)), and the second Br^- anion accepts a bromine atom from the radical pair (reaction (18)). In this case, the yield of $Br_2^{\bullet-}$ as a function of Br^- concentration is initially quadratic and flattens out when all the bromine atoms are captured (Eq. (22)).

$$\varphi\left(Br_2^{\bullet-}\right) = \frac{k_{16}\,[Br^-]}{k_{-10} + k_{10} + k_{16}\,[Br^-]} \times \frac{k_{18}\,[Br^-]}{k_{17} + k_{18}\,[Br^-]} \tag{22}$$

In Eq. (22), the rate constants k_{16} and k_{18} depend on the ionic strength μ via Eq. (21). Fig. 7 (curve 4) shows the result of simulation using Eq. (22), which is satisfactorily coincident with the S-type curve. This simulation was performed using reduced values of the electric charges of the excited $(PtBr_6^{2-})^*$ complex (−0.7 instead of −2) and the $[PtBr_6^{3-}\ldots Br^\bullet]$ radical pair (−1 instead of −3). The reason of this effect is probably that the electric charge is distributed over the large surface, and the bromide anion effectively interacts with a part of the total charge. Another reason to decrease the electric charge could be the inexactness of the Davies equation (21) at very high values of ionic strength (4 M).

The best values of the rate constants ratios obtained by calculations are $k_{16}/k_{-10} \approx 0.1$ and $k_{18}/k_{-10} \approx 0.1$ (at zero ionic strength of the solution). Therefore, if the lifetime of the excited state $(PtBr_6^{2-})^*$ is ca. 10 ps ($k_{-10} \approx 10^{11}\ s^{-1}$), one can estimate the values of k_{16} and k_{18}, which gives $k_{16} \sim k_{18} \sim 2.5 \times 10^9\ M^{-1}\ s^{-1}$. This value is close to the rate constant of the diffusion-controlled reaction.

The decrease of the quantum yield of $PtBr_6^{2-}$ photoaquation could be explained in the framework of the dissociative mechanism. After the Br^- escape from the coordination sphere of Pt(IV) and the formation of $\left(PtBr_5^{2-}\ldots Br^-\right)$ pair (reaction (10)) the competition between free bromide anions and water molecules for the penetration to the "empty" place in the coordination sphere is possible.

$$\left(PtBr_5^{2-}\ldots Br^-\right) \xrightarrow{Br^-} PtBr_6^{2-} + Br^- \tag{23}$$

Taking into account all the possible reactions, one can calculate the quantum yield of photoaquation in the presence of free Br^-

anions as

$$\varphi = \varphi_0 \frac{1}{(1+\varphi_0(k_{16}[Br^-]/k_{10}))(1+(k_{23}/k_{11})([Br^-]/[H_2O]))} \qquad (24)$$

where $\varphi_0 = \frac{k_{10}}{k_{-10}+k_{10}} = 0.39$ is the quantum yield in the absence of Br^-. In Eq. (24), the rate constants k_{16} and k_{23} depend on the ionic strength. One can satisfactorily fit the experimental data (curve 5 in Fig. 7) taking the values of k_{16} and k_{23} in Debye–Hückel approach $k_{16} = k_{16}(\mu = 0) \times e^{2.3\sqrt{\mu}}$ and $k_{23} = k_{23}(\mu = 0) \times e^{2.45\sqrt{\mu}}$. The best values of the rate constants ratios at zero ionic strength are $k_{16}/k_{10} \approx 0.007$ and $k_{23}/k_{11} \approx 5.5$. It remains unsolved why in this case the Debye–Hückel approximation gives the better result than Davies equation (Eq. (21)).

4. Conclusions

This work gives evidence that of the two possible mechanisms of $Br_2^{\bullet-}$ radical anion formation more reliable is the intersphere electron transfer from Br^- anion to the light-excited complex.

To study the details of fast processes followed by the excitation of $PtBr_6^{2-}$ complex, the experiments on the femtosecond kinetic spectroscopy are essential. The characteristic time of photoaquation obtained in the experiments on ultrafast kinetic spectroscopy is ca. 15 ps [8]. It should be noted that the work [8] does not demonstrate the sufficient changes of the observed kinetic curves caused by the addition of large (up to 4 M) amounts of free Br^- anions. That is no surprise, because the laser wavelength used for excitation was 420 nm, and available region of registration was 450–800 nm. In this spectral region the absorption of $Br_2^{\bullet-}$ radical anion is weak, therefore, it has not been observed in [8]. Of principal interest is to perform experiments on ultrafast kinetic spectroscopy of $PtBr_6^{2-}$ with a shorter excitation (266 nm) and a registration in the region of maximal absorption of $Br_2^{\bullet-}$ radical anion (366 nm) and (or) a bromine atom.

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References

[1] V. Balzani, V. Carassiti, Photochemistry of Coordination Compounds, Academic Press, London–New York, 1970, pp. 259–261.
[2] S.A. Penkett, A.W. Adamson, Flash photolysis of cobalt(III) acidopentaammine and of $PtBr_6^{2-}$ complexes, J. Am. Chem. Soc. 87 (1965) 2514–2515.
[3] V. Balzani, V. Carassiti, F. Scandola, Electronic states in photochemistry of coordination compounds, Gazz. Chim. Ital. 96 (1966) 1213–1229.
[4] V. Balzani, M.F. Manfrin, L. Moggi, Photochemistry of coordination compounds. XVI. Hexabromoplatinate(IV) and hexaiodoplatinate(IV) ions, Inorg. Chem. 6 (1967) 354–358.
[5] V. Balzani, V. Carassiti, Photochemistry of some square-planar and octahedral platinum complexes, J. Phys. Chem. 72 (1968) 383–388.
[6] V.V. Vasil'ev, K.P. Balashev, G.A. Shagisultanova, Photosensitized reactions of hexabromoplatinate(IV) ion, Koord. Khim. 8 (1982) 1235–1240, in Russian.
[7] E.M. Glebov, V.F. Plyusnin, V.P. Grivin, A.B. Venediktov, S.V. Korenev, Photochemistry of $PtBr_6^{2-}$ in aqueous solutions, Russ. Chem. Bull. 56 (2007) 2357–2363.
[8] I.P. Pozdnyakov, E.M. Glebov, V.F. Plyusnin, N.V. Tkachenko, H. Lemmetyinen, Primary processes in photophysics and photochemistry of $PtBr_6^{2-}$ complex studied by femtosecond pump-probe spectroscopy, Chem. Phys. Lett. 442 (2007) 78–83.
[9] E.M. Glebov, V.F. Plyusnin, N.V. Tkachenko, H. Lemmetyinen, Laser flash photolysis of $IrCl_6^{2-}$ in aqueous solutions, Chem. Phys. 257 (2000) 79–89.
[10] E.M. Glebov, V.F. Plyusnin, V.P. Grivin, Yu.V. Ivanov, N.V. Tkachenko, H. Lemmetyinen, Mechanism of $Br_2^{\bullet-}$ and $Cl_2^{\bullet-}$ radical anions formation upon $IrCl_6^{2-}$ photoreduction in methanol solutions containing free Br^- and Cl^- ions, J. Photochem. Photobiol. A: Chem. 113 (1998) 103–112.
[11] I.I. Chernyaev (Ed.), Sintez kompleksnykh soedinenii metallov platinovoi gruppy [Synthesis of Complexes of Platinum Group Metals], Nauka, Moscow, 1964, p. 339 (in Russian).
[12] I.P. Pozdnyakov, V.F. Plyusnin, V.P. Grivin, D.Yu. Vorobyev, N.M. Bazhin, E. Vauthey, Photolysis of sulfosalicylic acid in aqueous solutions over a wide pH range, J. Photochem. Photobiol. A: Chem. 181 (2006) 37–43.
[13] C.M. Davidson, R.F. Jameson, Complexes formed between the platinum metals and halide ions. Part 3. Hydrolysis of haloplatinates – potentiometric and spectrophotometric studies, Trans. Faraday Soc. 61 (1965) 2462–2467.
[14] I.V. Znakovskaya, Yu.A. Sosedova, E.M. Glebov, V.P. Grivin, V.F. Plyusnin, Intermediates formed by laser flash photolysis of $PtCl_6^{2-}$ complex in aqueous solutions, Photochem. Photobiol. Sci. 4 (2005) 897–902.
[15] J.C. Scaiano, M. Barra, M. Krzywinski, R. Sinta, G. Calabrese, Laser flash-photolysis determination of absolute rate constants for reactions of bromine atoms in solution, J. Am. Chem. Soc. 115 (1993) 8340–8344.
[16] L.I. Elding, L. Gustafson, Platinum(IV) bromo aqua complexes. Acid hydrolysis equilibria and kinetics of bromide anation, Inorg. Chim. Acta 5 (1971) 643–649.
[17] L.I. Elding, L. Gustafson, Bromide anation kinetics for some platinum(IV) bromo aqua complexes, Inorg. Chim. Acta 22 (1977) 201–207.
[18] A.J. Frank, M. Graetzel, J.J. Kozak, Reduction of dimensionality in radical decay kinetics induced by micellar systems, J. Am. Chem. Soc. 98 (1976) 3317–3321.
[19] P. Morliere, L.K. Patterson, Evidence for Br_2^- reactions with Ni(III) macrocyclic complexes – Br_2^- as a possible reducing agent, Inorg. Chim. Acta 64 (1982) L183–L185.
[20] M. D'Angelantonio, M. Venturi, Q.G. Mulazzani, A re-examination of the decay kinetics of pulse radiolytically generated Br_2^- radicals in aqueous solutions, Radiat. Phys. Chem. 32 (1988) 319–324.
[21] G. Ferraudi, Magnetic field effects on the rates of $Cl_2^{\bullet-}$ and $Br_2^{\bullet-}$ reactions: the dependence of the rates of radical disproportionation and oxidation of Mn(II) complexes on field intensity, J. Phys. Chem. 97 (1993) 2793–2797.
[22] S.G. Entelis, R.P. Tiger, Kinetika reaktzii v rastvorakh. Kolitchestvenny uchet vliyaniya sredy (Kinetics of Reactions in Solutions. Qualitative account for the Medium Effects), Khimiya, Moscow, 1973, p. 34 (in Russian).
[23] W.B. Person, Electron affinities of some halogen molecules and the charge-transfer frequency, J. Chem. Phys. 38 (1963) 109–116.
[24] R.A. Lidin, L.L. Andreeva, V.A. Molochko, Spravochnik po Neorganicheskoi Khimii (Handbook in Inorganic Chemistry), Khimiya, Moscow, 1987, p. 152 (in Russian).
[25] A.J. Gordon, R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques and References, Wiley, New York, 1972, p. 132.
[26] L. Moggi, G. Varani, M.F. Manfrin, V. Balzani, Photochemical reactions of hexachloroiridate(IV) ion, Inorg. Chim. Acta 4 (1970) 335–341.
[27] P. Neta, R.E. Huie, A.B. Ross, Rate constants for reactions of inorganic radicals in aqueous solutions, J. Phys. Chem. Ref. Data 17 (1988) 1027–1284.
[28] C.W. Davies, Ion Association, Butterworths, London, 1962, pp. 37–53.
[29] B.J. Colston, V. Robinson, Use of metal ion indicators to determine complex stability constants; the method of competitive equilibration, Analyst 112 (1997) 1451–1455.
[30] M.S. Sun, D.K. Harriss, V.R. Magnuson, Activity corrections for ionic equilibria in aqueous solutions, Can. J. Chem. 58 (1980) 1253–1257.