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# Full Articles

## Photochemistry of $PtBr_6^{2-}$ in aqueous solution

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Photochemistry of the $PtBr_6^{2-}$ complex in aqueous solution was studied by steady-state and laser flash photolysis (308 nm). The multistep photoaquation of the complex occurs in the nano- and microsecond time intervals without the formation of intermediate platinum(III) complexes.

**Key words:** platinum(IV), halide complexes, aqueous solutions, photochemistry, optical absorption spectra, laser flash photolysis, primary photochemical processes.

Halide complexes $MX_6^{2-}$ of heavy noble metals (Pt, Ir, and Os) are characterized by intense charge-transfer bands in the visible and UV spectral regions.[1] The existence of this absorption is usually accompanied by the high photochemical activity,[2] whose nature and mechanisms remain unknown for many complexes. The $PtBr_6^{2-}$ complex is not exception: its photochemistry in aqueous solution has been studied during the 50 years[2—8]; however, the mechanism of phototransformations remains unclear. Contradictions concern the interpretation of the experimental data and also their real content.

The quantum yield of the photoinduced ligand exchange in a $PtBr_6^{2-}$—$Br^-$ system has been found[3] to greatly exceed unity. To explain this fact, the chain mechanism was proposed and also used for the explanation of the high quantum yield of chloride ion exchange in a $PtCl_6^{2-}$—$Cl^-$ system.[9] It was assumed that the primary photolysis step was the homolytic cleavage of the Pt—Br bond to form the intermediate $Pt^{III}$ complex and bromine atom

$$PtBr_6^{2-} \xrightarrow{h\nu} PtBr_5^{2-} + Br^{\bullet}. \qquad (1)$$

No intermediate absorption that could be ascribed to the bromine atom, $Pt^{III}$ complexes, or products of their secondary reactions has been observed later[4] in experiments on lamp flash photolysis (time resolution ~30 μs) of aqueous solutions of $PtBr_6^{2-}$. The final photolysis products at times longer than several tens of microseconds were aquated $Pt^{IV}$ complexes. The two-electron photoreduction of $PtBr_6^{2-}$ with the escape of a $Br_2$ molecule from the coordination sphere and the formation of the

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platinum(II) complex $PtBr_4^{2-}$ was proposed**4** as the primary process

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

In opinion of the authors,**4** the $PtBr_4^{2-}$ complex is formed in the nonequilibrium (nonplanar) geometry and can serve as a chain carrier in the ligand exchange reaction. In this case, the step responsible for chain termination is the backward reaction of the $Pt^{II}$ complexes with $Br_2$, returning them to the $Pt^{IV}$ complexes. The formation of the aquated $Pt^{IV}$ complexes was explained by the aquation of the $PtBr_4^{2-}$ complex.

According to the third scheme,**2,5—7** the cleavage of the Pt—Br bond is heterolytic and the $PtBr_5(H_2O)^-$ aquated complex is a primary product of the photochemical process

$$PtBr_6^{2-} \xrightarrow{h\nu\ (+H_2O)} PtBr_5(H_2O)^- + Br^-. \qquad (3)$$

The $PtBr_5(H_2O)^-$ complex undergoes further photoaquation to form the next $PtBr_4(H_2O)_2$ complex in this chain of phototransformations.**10** The quantum yield of the first step in a neutral medium is**6** 0.4±0.1 and independent of the wavelength of the exciting light. It was assumed that this indicated fast nonradiative transitions to the lowest excited (presumably triplet) state from which photoaquation occurs. The increase in the quantum yield of photolysis with a decrease in the pH of solutions was observed.**6**

A comparison of the available experimental data on the photoexchange of the ligands and photoaquation of the $PtBr_6^{2-}$ complex suggested**2** that the exchange, unlike the aquation, is a chain process caused by the presence of admixtures of molecules of the oxidation nature in the solutions.

Three isosbestic points (215, 238, and 286 nm) were retained during the photolysis of $PtBr_6^{2-}$ in acidic (pH < 1) solutions.**8** Based on the analysis of the spectral changes, the authors concluded**8** that two bromide ions are substituted in the coordination sphere in one step for two water molecules with an quantum yield of 0.3.

$$PtBr_6^{2-} \xrightarrow{h\nu\ (+H_2O)} PtBr_4(H_2O)_2 + 2\,Br^-. \qquad (4)$$

Thus, different opinions were proposed concerning the mechanism of primary photoprocesses for $PtBr_6^{2-}$ in aqueous solutions. This fact pre-determined the statement of the problem of the present work in which we intended to answer the question about the existence of intermediate platinum(III) complexes using laser flash photolysis with nanosecond time resolution. These complexes have earlier been observed by the photolysis of $PtCl_6^{2-}$ in methanol**11—13** and in water.**14** This work continues our studies**15** on the photochemistry of the $PtBr_6^{2-}$ complex in organic and aqueous media.

## Experimental

Solutions of the $PtBr_6^{2-}$ and $PtBr_4^{2-}$ complexes were prepared from the $Na_2PtBr_6 \cdot H_2O$ and $K_2PtBr_4 \cdot 2H_2O$ salts, which have been synthesized previously according to an earlier described procedure.**16** The NaBr salt (Aldrich) was used as the source of free bromide ions. Solutions were prepared with deionized water. The samples were blown if necessary with argon for 20 min to remove oxygen from the solution.

Optical absorption spectra were recorded on an HP 8453 spectrophotometer with a diode matrix. Steady-state photolysis was carried out in a cell with a thickness of 1 cm using a high-pressure mercury lamp (DRSh-500) with a set of glass filters to isolate the line with $\lambda$ = 313 nm. The light intensity for the calculation of the quantum yield was measured using a ferrioxalate actinometer.**17** Experiments on laser flash photolysis were carried out on a setup**11** using a XeCl excimer laser (308 nm, 15 ns, 20 mJ) also in a 1-cm cell.

According to published data,**6,10** the $PtBr_6^{2-}$ complex in aqueous solutions undergoes the successive thermal aquation

$$PtBr_6^{2-} \rightleftarrows PtBr_5(H_2O)^- \rightleftarrows$$
$$\rightleftarrows PtBr_4(H_2O)_2 \rightleftarrows PtBr_3(H_2O)_3^+, \qquad (5)$$

changing the optical absorption spectrum without retention of the isosbestic points. However, these reactions proceed slowly: the characteristic time of changing the optical absorption spectrum is several hours. Therefore, all experiments were carried out with freshly prepared solutions. The aquation is accompanied by a change in the pH of the solution, because the $PtBr_5(H_2O)^-$ complex is a weak acid (p$K_a$ = 4.4).**10** Therefore, experiments on photolysis were carried out in a buffer aqueous solution at pH 6.86 (0.0315 *M* $KH_2PO_4$ and 0.0352 *M* $Na_2HPO_4$) and in 1 *M* $HClO_4$. The $PtBr_5(H_2O)^-$ complex in the buffer solution transforms into $PtBr_5(OH)^{2-}$, whereas in an acidic medium the complex does not dissociate.

## Results and Discussion

**Electronic absorption spectrum and thermal aquation of $PtBr_6^{2-}$.** The electronic configuration of the $Pt^{IV}$ atom is $5d^6$ and, hence, in the octahedral environment the highest occupied orbital is $t_{2g}^6$ and the major term of the $PtBr_6^{2-}$ complex is $^1A_{1g}$. Its optical absorption spectrum (Fig. 1, curve *1*) coincides with that described earlier.**1,7** The intense charge-transfer (CT) band with a maximum at 226 nm ($\varepsilon$ = 70000 L mol$^{-1}$ cm$^{-1}$) corresponds to the electron transfer from the $t_{1u}(\sigma)$ orbital localized on the ligands to the unoccupied $e_g(\sigma^*)$ orbital. Less intense charge-transfer bands at 310 and 365 nm ($\varepsilon$ = 17 800 and 7400 L mol$^{-1}$ cm$^{-1}$, respectively) correspond to the transitions from the $t_{1u}(\pi)$ and $t_{2u}(\pi)$ orbitals of the bromine atom to the $e_g(\sigma^*)$ orbital. These CT bands overlap with weak d—d-transitions to the singlet $^1T_{1g}$ (435 nm) and triplet $^3T_{1g}$ (525 nm) excited states.**1**

**Steady-state photolysis of $PtBr_6^{2-}$ under different conditions.** The change in the optical absorption spectrum

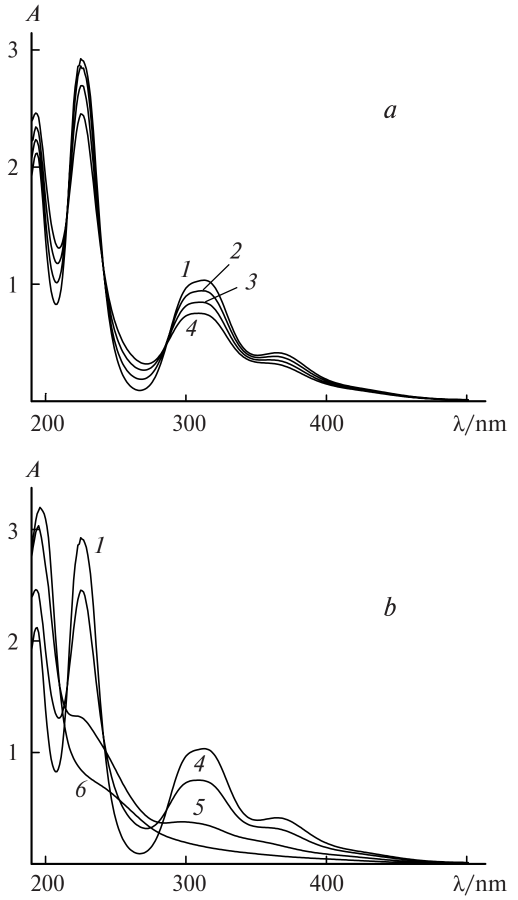

**Fig. 1.** Steady-state photolysis of the $PtBr_6^{2-}$ complex ($5.5 \cdot 10^{-5}$ mol $L^{-1}$) in an aqueous solution upon irradiation for 0 (*1*), 4 (*2*), 9 (*3*), 14 (*4*), 60 (*5*), and 240 s (*6*); *a* is the initial photolysis step (0—14 s), and *b* is more prolonged irradiation (0—240 s).

during the steady-state photolysis of $PtBr_6^{2-}$ in an aqueous solution is shown in Fig. 1. In the initial photolysis step (at the conversion <25%), three isosbestic points at 216, 242, and 287 nm are retained (see Fig. 1, *a*). Under more prolonged irradiation the isosbestic points disappear and a shoulder is formed in a region of 250 nm (see Fig. 1, *b*, curves *5* and *6*). The character of spectral changes during photolysis is independent of the presence of oxygen in the solution. For photolysis in a buffer solution (pH 6.86), the dynamics of spectral changes is analogous to the changes observed in an aqueous solution with a slight shift of the isosbestic points in the first step of the photoreaction (217, 245, and 291 nm).

For photolysis in an acidic solution, the pattern of spectral changes differs substantially (Fig. 2). The spectrum virtually stops changing after the decrease in the absorption band with a maximum at 313 nm by ~2 times (see Fig. 2, *b*). The isosbestic points at 214, 239, and 284 nm are retained within the whole irradiation process, which agrees with published data.[8]

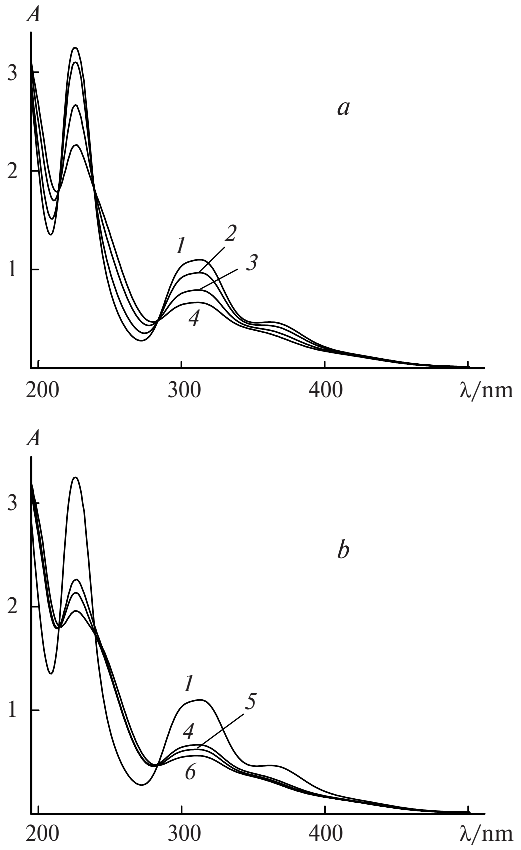

**Fig. 2.** Steady-state photolysis of the $PtBr_6^{2-}$ complex ($5.8 \cdot 10^{-5}$ mol $L^{-1}$) in 1 *M* $HClO_4$ upon irradiation for 0 (*1*), 4 (*2*), 12 (*3*), 23 (*4*), 35 (*5*), and 180 s (*6*); *a* is the initial photolysis step (0—23 s), and *b* is more prolonged irradiation (0—180 s).

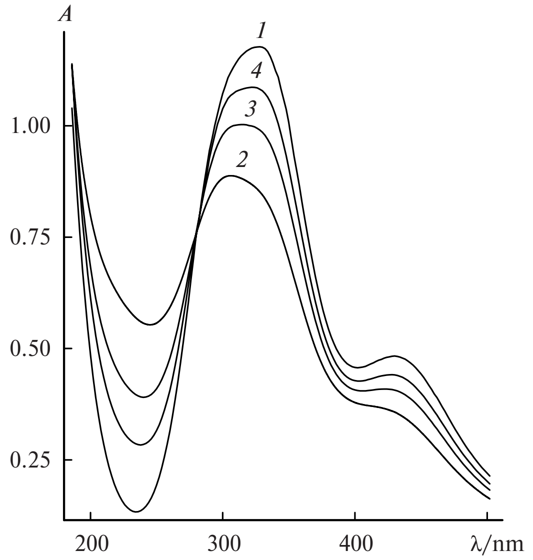

**Fig. 3.** Recovery of the spectrum of $PtBr_6^{2-}$ ($1.5 \cdot 10^{-4}$ mol $L^{-1}$) after photolysis in an aqueous solution containing 0.4 *M* NaBr: *1*, initial spectrum; *2*, after irradiation (2 min); *3* and *4*, spectra after storage in the dark for 12 and 93 min, respectively.

**Dark reactions after irradiation of $PtBr_6^{2-}$ solutions.** In all cases, the spectrum of the initial complex (Fig. 3) appears upon the addition of free bromide ion to the irradiated solution, which can occur if the aquated $Pt^{IV}$ complexes are photolysis products. Let us consider the reactions that occur using the photolysis of aqueous solutions of $PtBr_6^{2-}$ as an example (see Fig. 1). In the first step corresponding to the substitution of one $Br^-$ ion and the formation of the $PtBr_5(H_2O)^-$ complex three isosbestic points are retained (see Fig. 1, *a*). The further irradiation results in the formation of the $PtBr_4(H_2O)_2$ complex with the absorption, according to earlier**10** published data, at 250 nm (see Fig. 1, *b*, curve *5*). The very prolonged irradiation induces the photoaquation of the $PtBr_4(H_2O)_2$ complex accompanied by the disappearance of the absorption at 250 nm. Thus, the quantum yields of the photoaquation of $PtBr_6^{2-}$ and $PtBr_5(H_2O)^-$ are comparable in value, whereas the quantum yield of $PtBr_4(H_2O)_2$ is lower by an order of magnitude.

The kinetic curves demonstrating the appearance of the spectrum of $PtBr_6^{2-}$ in an irradiated aqueous solution after the addition of the $Br^-$ ion are presented in Fig. 4. The main contribution to the absorption at 313 and 365 nm is made by the $PtBr_6^{2-}$ complex, whereas the aquated complexes absorb at 268 nm to a greater extent. The reaction kinetics can be described by two exponential curves with the characteristic times 170±10 and 1200±200 s. Two steps correspond to the consecutive substitution of two water molecules in the coordination sphere for the bromide ions

$$PtBr_4(H_2O)_2 \longrightarrow PtBr_5(H_2O)^- \longrightarrow PtBr_6^{2-}.$$

The kinetics of water molecule substitution for the bromide ion in the $PtBr_5(H_2O)^-$ complex has been studied earlier**18,19** in an acidic medium (0.5 *M* $HClO_4$). The apparent rate constant of substitution ($k_{app}$) was found**18,19** to depend on the concentration of the bromide ions as follows:

$$k_{app} = k_1[Br^-] + k_2[Br^-]^2, \quad (6)$$

where $k_1 = 1.8 \cdot 10^{-3}$ L mol$^{-1}$ s$^{-1}$ and $k_2 = 4.5 \cdot 10^{-2}$ L$^2$ mol$^{-2}$ s$^{-1}$. The square dependence of $k_{app}$ on the $Br^-$ concentration was explained by the formation of an outer-sphere complex of the bromide ion with $Pt^{IV}$. At the concentration $[Br^-] \approx 1$ mol L$^{-1}$ the presented $k_1$ and $k_2$ values give the characteristic time of $H_2O$ substitution for $Br^-$ in the $PtBr_5(H_2O)^-$ complex in an acidic solution equal to ~20 s. It follows from the data in Fig. 4 that in a neutral aqueous solution the lifetime of $PtBr_5(H_2O)^-$ is by approximately two orders of magnitude higher (~1200 s). A comparison of these times indicates the catalytic effect of the $[H]^+$ ions in the reaction considered and shows its scale.

**UV spectra of aquation products.** The photolysis of $PtBr_6^{2-}$ in a buffer solution with pH 6.86 gives the $PtBr_5(OH)^{2-}$ complex as the primary photoaquation product, whose spectrum is presented in Fig. 5 (curve *2*, two bands with maxima at 268 and 343 nm and absorption coefficients $\varepsilon \approx 18000$ and 4600 L mol$^{-1}$ cm$^{-1}$, respectively). The initial regions of the kinetic curves measured as the dependence of the absorption on the irradiation duration (regions of retention of the isosbestic points) were used in calculation. According to published data,**6** we accepted that the absorption coefficient for $PtBr_5(OH)^{2-}$ at 313 nm is 7000 L mol$^{-1}$ cm$^{-1}$. It can be assumed for the photolysis of $PtBr_6^{2-}$ in an acidic solution (1 *M* $HClO_4$) that the primary photoaquation product is the $PtBr_5(H_2O)^-$ complex (see Fig. 5, curve *3*). We also accepted in the calculation that the absorption coefficient of $PtBr_5(H_2O)^-$ at 313 nm is 10 000 L mol$^{-1}$ cm$^{-1}$.**18**

The sharp retardation of the photochemical transformations in an acidic solution for the incomplete conver-

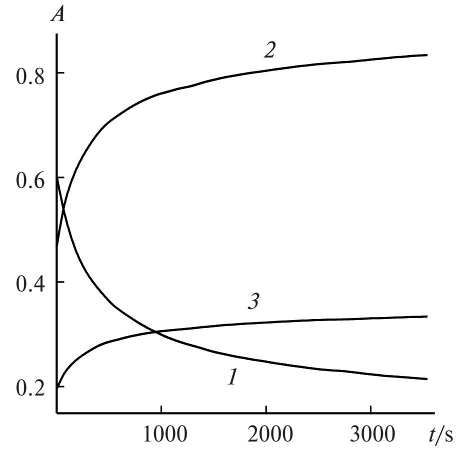

**Fig. 4.** Kinetics of changes in the absorbance at λ = 268 (*1*), 313 (*2*), and 365 nm (*3*) after photolysis of $PtBr_6^{2-}$ ($5.8 \cdot 10^{-5}$ mol L$^{-1}$) in an aqueous solution containing 1 *M* NaBr.

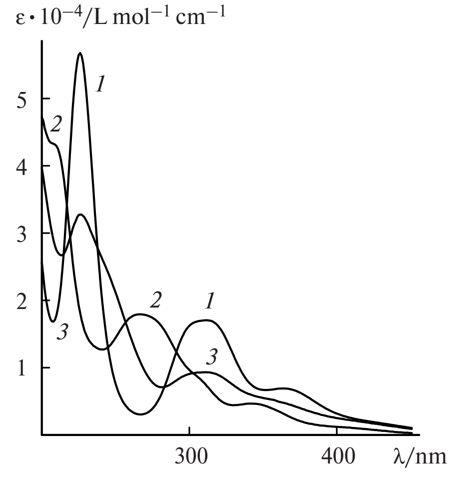

**Fig. 5.** Optical absorption spectra of the $PtBr_6^{2-}$ (*1*), $PtBr_5(OH)^{2-}$ (*2*), and $PtBr_5(H_2O)^-$ (*3*) complexes.

sion (see Fig. 2) can be related to the fact that the $PtBr_4(H_2O)_2$ complex (product of the second photoaquation step) is rapidly transformed back into $PtBr_5(H_2O)^-$. It has already been shown that in an acidic medium the processes of water substitution for the bromide ion in the bromide $Pt^{IV}$ complex are substantially accelerated.

**Quantum yield of photolysis of $PtBr_6^{2-}$.** The same molar absorption coefficient for $PtBr_5(H_2O)^-$ at 313 nm was used when determining the quantum yield of the first step of $PtBr_6^{2-}$ photolysis as that used in the calculation of the UV spectrum. The quantum yield measured for an aqueous solution (0.39±0.05) coincides with the value earlier obtained[6] (0.4±0.1). In a buffer solution (pH 6.86) the quantum yield is slightly lower (0.29±0.05) and in an acidic solution (1 *M* $HClO_4$) it is substantially higher (0.60±0.06). In the latter case, the quantum yield is by 2 times higher than the presented[8] value (0.5 *M* $HClO_4$).

**Laser flash photolysis of aqueous solutions of $PtBr_6^{2-}$.** The experiments on laser flash photolysis of aqueous solutions of $PtBr_6^{2-}$ found no intermediate absorption. The kinetic curves demonstrated only an instant change in the absorption, indicating that all the processes occurred within the times <50 ns (time resolution of the setup). In a spectral range of 285—500 nm, the absorbance after a laser pulse decreases and an absorption signal appears at $\lambda < 285$ nm (Fig. 6). The difference spectrum of the $PtBr_6^{2-}$ complexes and the product of the first photolysis step in an aqueous solution are shown in Fig. 6 (see Fig. 1, *a*). The spectral curves obtained by steady-state irradiation and pulse photolysis coincide, indicating that the first photoaquation step occurred within the time <50 ns. For buffer solutions (pH 6.86) the absence of an intermediate absorption implies that the acid-base equilibrium between the $PtBr_5(H_2O)^-$ and $PtBr_5(OH)^{2-}$ complexes is achieved also rather rapidly.

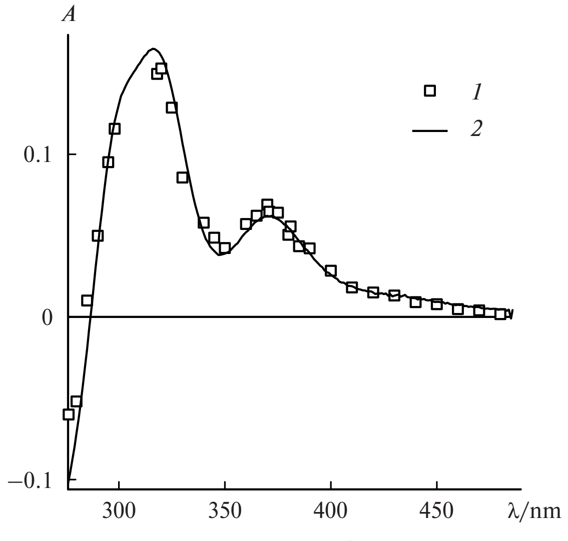

**Fig. 6.** Laser flash photolysis of $PtBr_6^{2-}$ ($2.8 \cdot 10^{-5}$ mol $L^{-1}$) in an aqueous solution: *1*, change in the absorbance of the sample after a pulse (50 ns); *2*, change in the absorbance during steady-state photolysis of an aqueous solution of $PtBr_6^{2-}$ (difference in spectra *1* and *2*, see Fig. 1).

**Discussion of reaction mechanism.** The steady-state measurements showed that the major process in the phototransformations of the $PtBr_6^{2-}$ complex in aqueous solutions is the successive aquation of the platinum complexes. Pulse experiments demonstrated that this process occurred more rapidly than several tens of nanoseconds involving no bimolecular reactions. If the intermediate products would escape into the solvent bulk, then the reactions of these species, finally resulting in aquation and proceeding with the diffusional rate constant, would occur within the time of an order of microseconds and could be detected ($\tau \sim (k_{\rm diff}C)^{-1} \sim 10^{-5}$—$10^{-4}$ s, where $C \sim 10^{-5}$—$10^{-6}$ L $mol^{-1}$ is the concentration of intermediate species after a laser pulse, and $k_{\rm diff} \approx 5 \cdot 10^9$ L $mol^{-1}$ $s^{-1}$ is the diffusion rate constant in water). Thus, all processes resulting in photoaquation are rapidly completed in the immediate vicinity of the excited complex.

Two mechanisms of the fast photoaquation of the $PtBr_6^{2-}$ complex can be proposed. If the complex initially excited to the charge-transfer state ($^1$CT, 308 nm) relaxes to the excited d—d state ($^3T_{1g}$), the heterolytic cleavage of the Pt—$Br^-$ bond can occur as the primary process followed by the aquation

$$PtBr_6^{2-}\ (^1A_{1g}) \xrightarrow{h\nu} (PtBr_6^{2-})^*\ (^1CT) \longrightarrow$$
$$\longrightarrow (PtBr_6^{2-})^*\ (^1T_{1g}), \qquad (7)$$

$$(PtBr_6^{2-})^*\ (^1T_{1g}) \longrightarrow (PtBr_6^{2-})^*\ (^3T_{1g}) \longrightarrow$$
$$\longrightarrow (PtBr_5^{-}\cdots Br^{-}), \qquad (8)$$

$$(PtBr_5^{-}\cdots Br^{-})\text{—}H_2O \longrightarrow PtBr_5(H_2O)^- + Br^-. \qquad (9)$$

In this case, the central platinum atom retains the tetravalent state during the whole process. The qualitative dependence of the terms of the $PtBr_6^{2-}$ complex on the Pt—Br distance is shown in Fig. 7. The terms with d—d-excitation ($^1T_{1g}$, $^3T_{1g}$) corresponding only to the angular redistribution of the electron density should have an energy minimum at distances close to the minimum distance for the ground $^1A_{1g}$ term. The charge-transfer (CT) states have energy minima at long distances because of a considerable radial shift of the electron density. For this reason, the absorption bands of d—d-transitions can be shifted to the long-wavelength region relative to the charge-transfer bands; however, the energy minimum for the lowest CT state can be either higher than the minimum of the $^3T_{1g}$ term (see Fig. 7, curve *1*) or substantially lower (curve *2*). The mechanism of photoaquation presented by reactions (7)—(9) relates to the case when the CT state is relatively high (curve *1*), the $^3T_{1g} \rightarrow$ CT crossing is impossible, and the photoaquation occurs from the $^3T_{1g}$ state. This mechanism coincides with the known

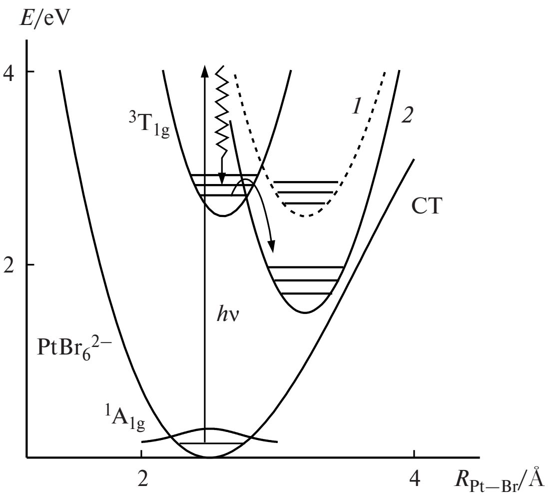

**Fig. 7.** Ground ($^1A_{1g}$) and lower-energy excited terms of the $PtBr_6^{2-}$ complex. Curves *1* and *2* correspond to two possible localizations of the lowest-energy charge-transfer (CT) state relative to the d—d-excited term ($^3T_{1g}$).

point of view[2,5—7] concerning the photochemical transformations of the $PtBr_6^{2-}$ complex in an aqueous solution and, most likely, this mechanism is most probable.

However, it cannot completely be excluded that the lowest in energy CT state has a deeper minimum compared to the $^3T_{1g}$ term (see Fig. 7, curve *2*). Then the $^3T_{1g} \rightarrow$ CT crossing is probable, and the photochemical reactions can start from the CT state

$$(PtBr_6^{2-})^* \, (^3T_{1g}) \longrightarrow (PtBr_6^{2-})^* \, (CT). \qquad (10)$$

In this case, the homolytic bond cleavage can occur to form a primary radical pair

$$(PtBr_6^{2-})^* \, (CT) \longrightarrow (PtBr_5^{2-}\cdots Br^{\bullet}), \qquad (11)$$

which can rapidly be transformed into a secondary radical pair

$$(PtBr_5^{2-}\cdots Br^{\bullet})\text{—}H_2O \longrightarrow [PtBr_5(H_2O)^{2-}\cdots Br^{\bullet}]. \qquad (12)$$

If the bromine atom from the secondary radical pair would escape into the solvent bulk, then in pulse experiments, according to the above estimates, the appearance of absorption of the intermediate platinum(III) complex $PtBr_5(H_2O)^{2-}$ could be expected in the microsecond time interval. The absence of this absorption can be caused by the fast back electron transfer

$$[PtBr_5(H_2O)^{2-}\cdots Br^{\bullet}] \longrightarrow [PtBr_5(H_2O)^{-}\cdots Br^{-}] \longrightarrow$$
$$\longrightarrow PtBr_5(H_2O)^{-} + Br^{-}. \qquad (13)$$

The back electron transfer competes with the diffusion separation of the secondary radical pair, whose lifetime is $\tau_{dif} = R^2/D \approx 0.4$ ns,[20] where $R \approx 6.5$ Å is the overall radius of the partners ($PtBr_5(H_2O)^{2-}$ complex and $Br^{\bullet}$ atom), $D \approx 10^{-5}$ cm$^2$ s$^{-1}$ is the overall diffusion coefficient. Thus, to suppress the diffusional separation of the pair, the back electron transfer should occur more rapidly than within ~40 ps.

The second mechanism is based on the concepts[3,21] developed for photochemical processes involving the $CoX(H_2O)_5^{2+}$ halide complexes. In the both possible mechanisms, the $PtBr_5(H_2O)^-$ and $Br^-$ ions are rapidly formed final species and, hence, these processes cannot be differentiated in nanosecond pulse experiments.

Both the heterolytic and homolytic cleavages of the Pt—Cl bond to form intermediate platinum(III) complexes can contribute to the photoaquation of the chloride $PtCl_6^{2-}$ complex. Under certain conditions, this results in the development of chain processes and the appearance of a dependence of the photolysis quantum yield on the concentration of the initial complex.[22—24] When the second mechanism is observed, the difference in the photoaquation processes of the $PtBr_6^{2-}$ and $PtCl_6^{2-}$ complexes can be determined by different rate constants of the back electron transfer in the secondary radical pair. It has earlier been proposed[25] that these differences are caused by a great difference in the rate constants of the reactions of the chloride and bromide $Pt^{III}$ and $Pt^{IV}$ complexes, which could be responsible for chain propagation. However, in the present work, for the flash photolysis of $PtBr_6^{2-}$ in the nanosecond time interval no spectral manifestations of the $Pt^{III}$ complexes were found (unlike the photolysis of aqueous solutions of $PtCl_6^{2-}$).[14]

Thus, experiments with pico- or femtosecond time resolution are necessary to perform for detailed investigation of the processes that occur upon the excitation of the $PtBr_6^{2-}$ complex. The second direction of possible studies is accepting of the bromine atom that can exist in the second radical pair. However, if this pair lives within ~40 ps due to the back electron transfer, the necessary concentrations of the acceptor can achieve inappropriately high values (>5 mol L$^{-1}$). For the $IrCl_6^{2-}$ complex, the use of the free $Cl^-$ ion in a concentration of ~1 mol L$^{-1}$ as an acceptor of the chlorine atom made it possible to estimate the back electron transfer (~100 ps),[26] which did not completely suppress the diffusional separation of the secondary radical pair. For this reason, both the photoaquation and photoreduction processes were detected for the $IrCl_6^{2-}$ complex.

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