

Chain processes in the photochemistry of Pt^{IV} halide complexes in aqueous solutions*

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The mechanisms of the photoaquation of PtCl₆²⁻ and PtBr₆²⁻ complexes were compared by the experimental results on stationary photolysis, nanosecond laser flash photolysis, and ultrafast pump-probe spectroscopy. The formation of the photoaquation product of the bromide complex, viz., PtBr₅(H₂O)⁻, was shown to proceed *via* the mechanism of heterolytic cleavage of the Pt–Br bond, and the platinum cation remained tetravalent in the course of the whole process. For the chloride complex, the Pt–Cl bond cleavage was found to be homolytic, and precursors of the photoaquation product, viz., PtCl₅(H₂O)⁻ complex, are intermediates of trivalent platinum sequentially transforming into each other. The reactions of these intermediates determine the chain character of the photoaquation process.

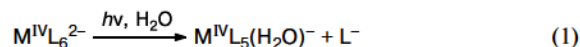
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In the XX century, halide complexes of platinum were considered as an object of photochemistry very significant from the fundamental point of view.^{1–3} This interest was caused by a combination of simplicity of the systems studied and variety of facts to be explained. Among these facts are many short-lived intermediates,^{4–8} rarely met chain photoaquation processes (in the case of complex PtCl₆²⁻),^{9,10} and a considerable diversity of photochemical properties of isoelectronic complexes PtCl₆²⁻ and PtBr₆²⁻.^{1,11} The photolysis mechanisms were proposed on the basis of stationary experiments,^{1,11,12} and the development of laser techniques made it possible to check the assumptions using time-resolved methods (laser flash photolysis in various time intervals).

In the XXI century, the photochemistry of halide complexes of Platinum Group metals obtained a new stimulus to development, which is due to two practical tasks: photocatalysis^{13–17} and photodynamic therapy (PDT) of malignant tumors.^{18,19} A fundamental problem in photocatalysis is the extension of the absorption spectrum of

titanium dioxide over the visible range. One of the methods to achieve this is the photochemical modification of the TiO₂ surface with platinum metals.^{13–17} Complexes PtCl₆²⁻ and PtCl₄ are used, in particular, for the modification. The application of the platinum complexes in PDT (see Refs 18 and 19) allows one to hope that a medicinal technology combining cytotoxicity of the platinum complexes and advantages of PDT (selectivity and reduced toxicity) would be developed. Therefore, mechanisms of photolysis of the complexes, beginning from the simplest one among which are hexahalide complexes, are necessary to be reliably known.

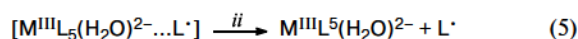
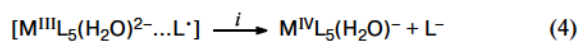
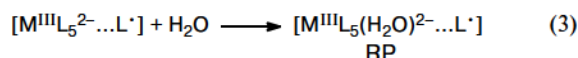
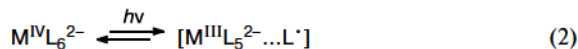
The photosolvation of complexes can proceed *via* two main mechanisms proposed in the 1960s. In the simplest case, the metal–ligand bond cleavage (1) in a complex of tetravalent metal with six ligands (M^{IV}L₆²⁻) is heterolytic.



An alternative to the heterolytic bond cleavage is Adamson's mechanism of radical pairs (2)–(5),¹² including redox stages. In this case, the formation of two intermediates is assumed. They are conventionally named the primary (reaction (2)) and secondary (reaction (3)) radi-

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cal pairs, although they are in fact anion—radical pairs. For platinum, whose trivalent state is unstable, the chain photoaquation process with the Pt^{III} complexes as chain mediators can occur in the case of the radical pair mechanism¹⁰



RP is secondary radical pair.

i is the backward electron transfer; *ii* is radical escape to the bulk.

Perhaps, the most disputable question in the photochemistry of the platinum(IV) hexahalide complexes is the problem of high differences in photochemical properties of the chloride and bromide complexes. The PtCl₆²⁻ and PtBr₆²⁻ anions are high-field complexes with the electronic configuration 5d⁶, and their electronic absorption spectra differ, in fact, only in the shift of absorption bands of the bromide complex to the visible region.^{1,11} In aqueous solutions both complexes undergo photoaquation with the formation (at the first stage) of complexes PtCl₅(H₂O)⁻ and PtBr₅(H₂O)⁻. However, the quantum yields of photoaquation with a change in the parameters of the process are quite different. For the PtBr₆²⁻ complex, the quantum yield (0.4)^{20–22} is independent of the exciting light wavelength and intensity, indicating the heterolytic mechanism (1). The quantum yield of photoaquation of PtCl₆²⁻ depends on the exciting light wavelength and intensity¹⁰ and can be either lower^{4,6,23} or substantially higher than unity if the experimental conditions change.^{10,23} This indicates chain processes, and correspondingly, a contribution of the homolytic mechanism (2)–(5), which is confirmed by the detection of Pt^{III} intermediates in flash radiolysis experiments.^{4,7}

When studying the photoaquation mechanisms of the PtCl₆²⁻ and PtBr₆²⁻ complexes, it was assumed¹¹ that their distinction is caused by the difference in rate constants of the reactions between the Pt^{III} and Pt^{IV} complexes responsible for chain development. However, no intermediate absorption belonging to Pt^{III} was observed in experiments on the laser flash photolysis of PtBr₆²⁻.²² It is most likely that the question about reasons for the difference in mechanisms cannot be answered without the application of ultrafast pump–probe kinetic spectroscopy to determine all stages of photolysis: from light quantum absorption to the formation of final products.

In the recent years, methods of femtosecond spectroscopy were applied to the study of the photochemistry of some platinum metals halide complexes (PtBr₆²⁻,^{8,24,25} PtCl₆²⁻,⁸ IrCl₆²⁻,^{26,27} IrBr₆²⁻ (see Ref. 28)). In this work, the photoaquation processes of the PtBr₆²⁻ and PtCl₆²⁻ are compared using the data on stationary photolysis, laser flash photolysis in the nanosecond time interval, and ultrafast pump–probe kinetic spectroscopy.

Experimental

Solutions of the PtBr₆²⁻ complex were prepared from salt Na₂PtBr₆·H₂O synthesized according to an earlier described procedure.²⁹ Salt Na₂PtCl₆ (Aldrich) was used as a source of PtCl₆²⁻ ions. Deionized water was used to prepare solutions. Optical absorption spectra were recorded on an Agilent 8453 spectrophotometer (Agilent Technologies). Stationary photolysis was carried out with a high-pressure mercury lamp with a set of glass filters to pick out radiation with the required wavelength. Photoaquation quantum yields were measured with a ferrioxalate actinometer using the express procedure.³⁰

Experiments on nanosecond laser flash photolysis were carried out using an earlier described³¹ technique with the excitation with an XeCl laser (308 nm, pulse duration 15 ns, pulse energy up to 20 mJ). The resolution time of the technique was 50 ns.

Experiments on ultrafast kinetic spectroscopy were carried out on a system described in detail earlier.³² The samples were irradiated with the second-harmonic radiation of a generator–amplifier system based on a titanium–sapphire laser (CDP Ltd., Moscow, pulse duration ~60 fs at the wavelength ~400–420 nm, energy 20–25 mJ in a pulse, pulse repetition frequency 10 Hz, beam diameter 0.4–0.5 mm). A portion of the exciting laser beam was focused into a cell with water to generate the probing radiation (continuum). One time-resolved spectrum was obtained by averaging 200 exciting pulses. A rotating cell with an optical thickness of 1 mm was used for spectra recording. Rotation made it possible to provide a uniform irradiation of the sample and to prevent undesirable thermal effects related to heating of the sample with an exciting pulse. The degree of photodegradation of the sample within the time of performing experiment did not exceed 5%. The time-resolved spectra were recorded with a time delay multiple to 100 fs, during the first 3 ps after an exciting pulse, and further with an exponentially increasing delay. As a rule, 60–70 spectra with a maximum delay of 100 ps were obtained for each spectrum. Experimental data were approximated using the procedure of processing of an array of kinetic curves by one set of parameters (global fit). The processing program made it possible to correct the dispersion of the group velocity (chirp correction) and to calculate the apparatus function of the system. The resulting time resolution was 150–200 fs.

Results and Discussion

Electronic absorption spectra and stationary photolysis of the PtCl₆²⁻ and PtBr₆²⁻ complexes. Platinum(IV) forms stable and kinetically inert complexes with many ligands. The absorption spectra of the PtCl₆²⁻ and PtBr₆²⁻ com-

plexes in water are shown in Fig. 1, *a* and *b*, respectively. The spectra of both complexes coincide with those known from the literature^{9,21} and contain partially overlapped ligand-to-metal charge-transfer (LMCT) bands and d–d-bands. For the PtCl_6^{2-} complex, the most intense band with a maximum at 202 nm is attributed to the transition from the σ -orbitals of the ligands to the vacant σ^* -orbitals, which are predominantly localized on the central ion.^{33,34} The corresponding LMCT band in the spectrum of complex PtBr_6^{2-} has a maximum at 226 nm.³⁵ The absorption band of PtCl_6^{2-} with a maximum at 262 nm and the absorption of PtBr_6^{2-} at 290–450 nm correspond to transitions from the π -orbitals of the ligands to the e_g^* -orbitals of the central ion.^{25,33} The shoulder at 355 nm in the spectrum of PtCl_6^{2-} and the absorption at 450–550 nm in the spectrum of PtBr_6^{2-} belong to the d–d-bands of the platinum ion.^{25,33–35} For the PtBr_6^{2-} complex, a partial overlapping of the LMCT- and d–d-bands is observed at 300–450 nm.^{25,35}

The irradiation of aqueous solutions of complexes PtCl_6^{2-} and PtBr_6^{2-} in the visible and near-UV regions results in photoaquation.^{10,20} The characteristic spectral changes in the course of photolysis at the wavelength 313 nm are shown in Fig. 1. In both cases, the isosbestic points are retained, which characterizes the transition of the initial complex to one absorbing product. The addition of free halogen ions to the irradiated solution initiates the recovery processes of the initial spectra, indicating in favor of photoaquation. The products of the first photolysis stage are complexes $\text{PtCl}_5(\text{H}_2\text{O})^-$ and $\text{PtBr}_5(\text{H}_2\text{O})^-$. The isosbestic points disappear for deep photolysis, *i.e.*, the further photoaquation occurs.

As mentioned above, the quantum yield of the first stage of photoaquation of complex PtBr_6^{2-} is independent of the exciting radiation wavelength and intensity, and concentration of the initial complex, being ~ 0.4 . The quantum yield of photolysis of PtCl_6^{2-} depends on the wavelength and intensity of the exciting light and concentration of the initial complex.

We measured the quantum yield of PtCl_6^{2-} photoaquation upon the excitation at 254 nm at different concentrations of the initial complex. The initial pH value of the solutions was 6.8. The measurements in the concentration range from 10^{-5} to 10^{-4} mol L⁻¹ were carried out in a cell with an optical path lengths of 1 cm, and a cell with the optical path length 1 mm was used for a range of 10^{-4} – 10^{-3} mol L⁻¹. When measuring the quantum yields that depend on the exciting light intensity, it is necessary to provide a constant density of the absorbed light power. In experiments (Fig. 2) the power density was $1.4 \cdot 10^{-7}$ Einstein L⁻¹ s⁻¹. In the case when the photoaquation of the complex is the chain process, the dependence of the quantum yield for excitation with the light with the wavelength λ (φ_λ) on the concentration of the complex (*c*) is described by the formula¹⁰

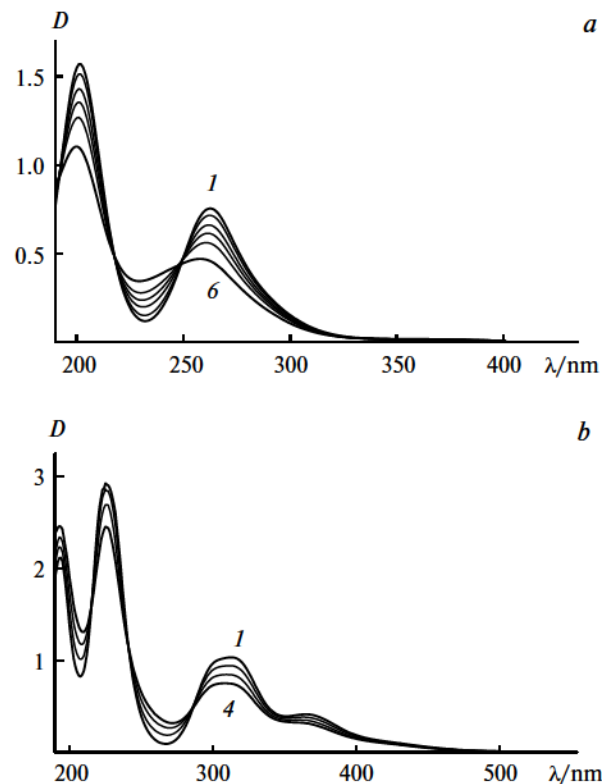


Fig. 1. Spectral changes in the course of stationary photolysis (313 nm) of aqueous solutions of the PtCl_6^{2-} and PtBr_6^{2-} complexes at the first stages (cell 1 cm, natural oxygen content): (a) complex PtCl_6^{2-} ($3.2 \cdot 10^{-5}$ mol L⁻¹, irradiation time 0 (1), 11 (2), 30 (3), 50 (4), 75 (5), and 133 s (6); (b) complex PtBr_6^{2-} ($5.5 \cdot 10^{-5}$ mol L⁻¹), irradiation time 0 (1), 4 (2), 9 (3), and 14 s (4).

$$\varphi_\lambda = \varphi_\lambda^0 \left(1 + k_p c / \sqrt{k_d \varphi_\lambda^0 I_0} \right), \quad (1)$$

where φ_λ^0 is the quantum yield at $c \rightarrow 0$, I_0 is the density of the absorbed light power (Einstein L⁻¹ s⁻¹), and k_p and k_d are the apparent rate constants for chain propagation and termination, respectively. The linear dependence in Fig. 2 indicates the chain character of the process. The cut section and the slope ratio of the line in Fig. 2 are equal to 0.24 ± 0.02 and $(1.9 \pm 0.1) \cdot 10^3$ L mol⁻¹, respectively. The cut section, being the limiting value of the photoaquation quantum yield when the concentration of the complex tends to zero, turned out to be halved than that in Ref. 10. In our case, the slope ratio of the dependence of $\varphi_{254 \text{ nm}}$ on the PtCl_6^{2-} concentration is approximately an order of magnitude lower than the published value¹⁰ (at comparable densities of the exciting light powers). It is impossible to determine a reason for the overestimated values of quantum yield measured earlier,¹⁰ because the experiment was not described in detail.¹⁰ Note that the pH of the medium is a substantial parameter affecting the quantum yield.

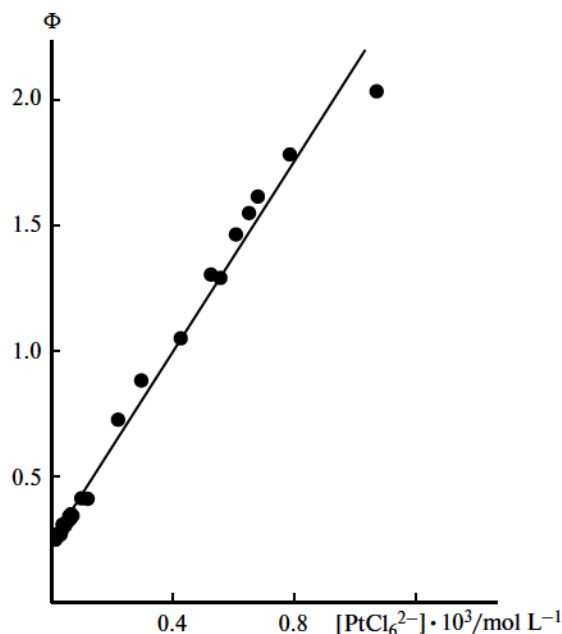


Fig. 2. Quantum yield of the photoaquation of PtCl_6^{2-} vs concentration of the complex (initial pH 6.8, irradiation at the wavelength 254 nm, power density of the absorbed radiation $1.4 \cdot 10^{-7}$ Einstein $\text{L}^{-1} \text{s}^{-1}$); points are experiment, and straight line is linear approximation.

Nanosecond laser flash photolysis of aqueous solutions of complexes PtCl_6^{2-} and PtBr_6^{2-} . The experimental results on laser flash photolysis (308 nm) of the complexes with a time resolution of 50 ns are presented in Fig. 3. The photolysis of complex PtBr_6^{2-} exhibits only a stepped decrease in the absorption at the band of the initial complex. The characteristic time of this change is shorter than the time resolution of the system. The spectrum of the stepped change in the absorbance exactly corresponds to the difference in the spectra of the PtBr_6^{2-} and $\text{PtBr}_5(\text{H}_2\text{O})^-$ complexes (see Fig. 3, *a*). Therefore, the characteristic time of formation of the photoaquation product is knowingly shorter than 50 ns. No Pt^{III} intermediates known from experiments on the pulse photolysis of the platinum bromide complexes³⁶ are observed in photochemical experiments. All these facts indicate in favor of the mechanism of the heterolytic Pt–Br bond cleavage in the initial complex.

In experiments on laser flash photolysis of aqueous solutions of the PtCl_6^{2-} complex (see Fig. 3, *b*), the successive formation of intermediates are observed in the visible (maxima of the absorption bands lie at 450 and 410 nm) and near-UV (350 nm) spectral ranges. The corresponding kinetic curves are presented in Fig. 4. The intermediates were identified^{7,8} using quantum chemical calculations.^{37–39} The intermediate absorbing at 450 nm (hereinafter, intermediate C) is a complex of trivalent platinum PtCl_4X_2 ($\text{X} = \text{OH}^-$, H_2O). The complex is formed

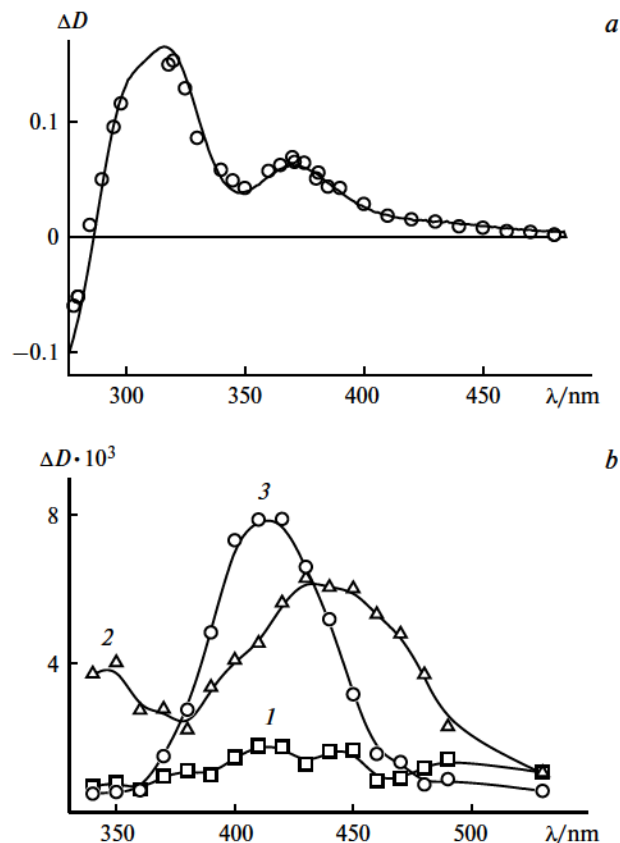


Fig. 3. Transient absorption spectra upon the laser flash photolysis (308 nm, cell 1 cm, natural oxygen content) of aqueous solutions of the PtBr_6^{2-} and PtCl_6^{2-} complexes: (*a*) PtBr_6^{2-} ($2.8 \cdot 10^{-5}$ mol L^{-1}), points are the transient absorption spectrum in 40 μs after a laser pulse, solid line is the difference between the spectra of the PtBr_6^{2-} complex and primary products of its photolysis combined with the experimental spectrum at the wavelength 370 nm; (*b*) PtCl_6^{2-} ($9.5 \cdot 10^{-5}$ mol L^{-1}), the spectra were recorded in 0 (*1*), 4 (*2*), and 49 μs (*3*) after a laser pulse.

with a characteristic time of 1 μs (the precursor will be considered further). Then intermediate C within ~ 7 μs is transformed into intermediate D that absorbs at 410 nm and has the structure $\text{PtCl}_{4-n}\text{X}_n$ ($n = 1-3$; $\text{X} = \text{OH}^-$, H_2O). Thus, the quasi-stationary concentration of the $\text{Pt}^{\text{III}}\text{Cl}_3(\text{OH})^-$ intermediate is established within ~ 20 μs (see experimental data in Fig. 4, *a*). The characteristic time of formation of the photoaquation product, $\text{Pt}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})^-$ complex, exceeds 1 ms. The estimates of the concentration of the Pt^{III} intermediates showed⁷ that their number in the samples did not exceed 10% of the concentration of the disappeared PtCl_6^{2-} complexes. Finally, the absorption at 350 nm belongs to the dihaloid radical anion $\text{Cl}_2^{\cdot -}$.⁴⁰

The formation of the Pt^{III} intermediates in experiments on laser flash photolysis of PtCl_6^{2-} and the linear dependence of the quantum yield of photoaquation on the concentration of the complex can be explained in terms of the

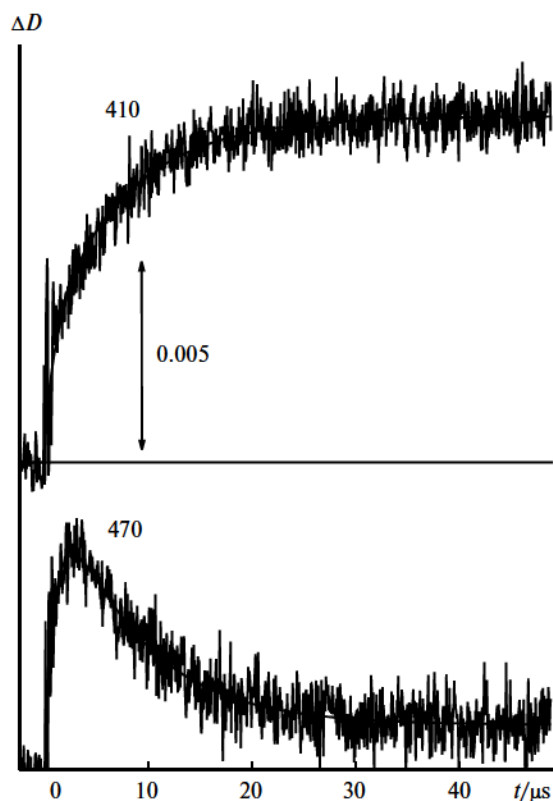
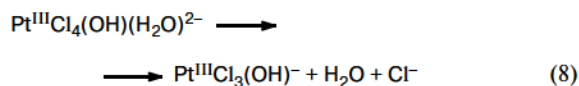
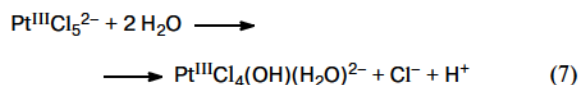
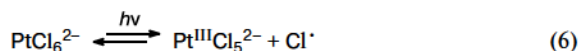


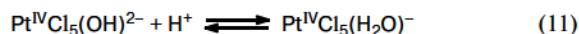
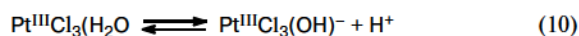
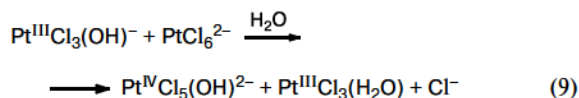
Fig. 4. Characteristic kinetic curves of changing the intermediate absorption upon the photoaquation of the PtCl_6^{2-} complex ($9.5 \cdot 10^{-5} \text{ mol L}^{-1}$): experiment (308 nm, cell 1 cm, natural oxygen content) and approximation by the biexponential functions (smooth lines); number at the curves are λ/nm .

chain mechanism of photolysis. A possible variant of the chain photochemical process with the $\text{Pt}^{\text{III}}\text{Cl}_3(\text{OH})^-$ complex as a chain mediator is presented below.

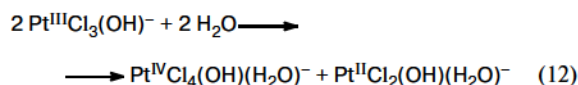
Chain generation



Chain propagation



Chain termination



If the rate-determining step of the chain propagation stage in the mechanism (6)–(12) is reaction (9), then the dependence of the quantum yield on the concentration of the initial complex PtCl_6^{2-} is described by Eq. (I) with $k_p = k_9$ and $k_d = k_{12}$.

Primary processes in the photochemistry of complexes PtCl_6^{2-} and PtBr_6^{2-} . Information about the primary photo-physical and photochemical processes for the PtBr_6^{2-} (see Ref. 24) and PtCl_6^{2-} (see Ref. 8) complexes was obtained by femtosecond kinetic spectroscopy. In both cases, the whole array of kinetic data is satisfactorily described by the triexponential function

$$\begin{aligned} \Delta D(\lambda, t) = A_1(\lambda) \exp(-t/\tau_1) + \\ + A_2(\lambda) \exp(-t/\tau_2) + A_3(\lambda) \exp(-t/\tau_3). \end{aligned} \quad (\text{II})$$

The transient absorption spectra detected at different time moments (immediately after a laser pulse, after the end of the first process, and after the end of the second process) are shown in Fig. 5.

In the case of the bromide complex, all processes are terminated in ~ 50 ps. The characteristic times of three exponential processes (see Eq. (II)) are given in Table 1. The initial spectrum (see Fig. 5, *a*, curve 1) represents a broad band in the whole spectral range accessible for detection (460–780 nm). Then the spectrum narrows and a band with a broad maximum at 520–570 nm is formed (curve 2), which, in turn, is transformed into a band with a maximum in the region < 460 nm (curve 3). The latter curve disappears completely without the formation of a long-lived intermediate absorption.

Earlier²⁴ we have interpreted the observed spectral changes from the viewpoint of formation and subsequent reactions of the lowest excited state of the PtBr_6^{2-} complex, which was consistent with the quantum yield of photoaquation independent of the excitation wavelength. However, later it was shown²⁵ using the experimental data observed with a shorter time resolution and quantum chemical calculation that the lowest excited state of PtBr_6^{2-} is dissociative and the observed changes can be described from the viewpoint of the successive formation of the triplet and singlet states of the $\text{Pt}^{\text{IV}}\text{Br}_5^-$ complex. This interpretation also corresponds to the quantum yield of photoaquation independent of the excitation wavelength. The subsequent processes corresponding to different characteristic times are listed in Table 1. A detailed scheme of the reactions that mainly occur in the solvent cage is presented by reactions (13)–(18). It is noteworthy that the first characteristic time (400 fs) includes a whole set of successive processes: internal conversion, electronic

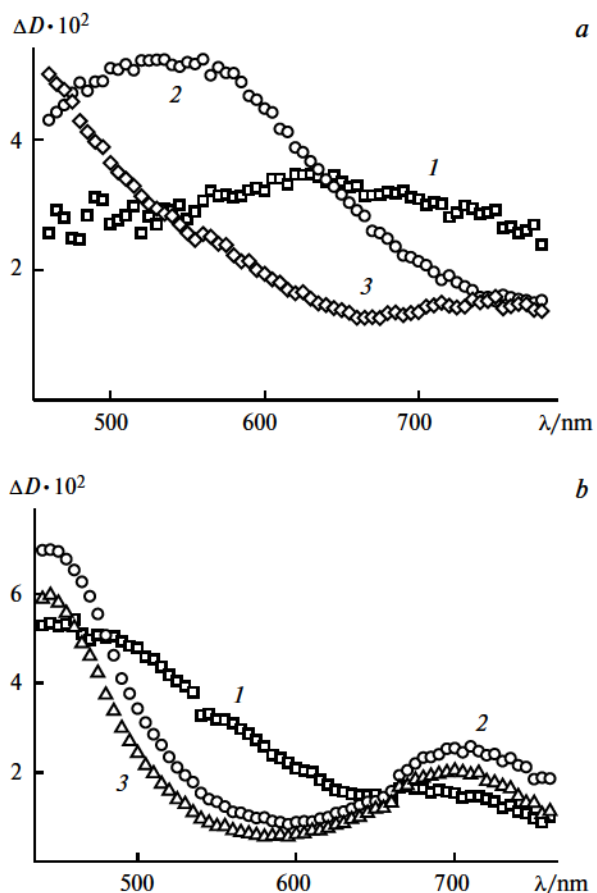
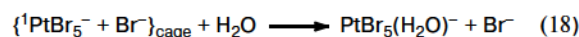
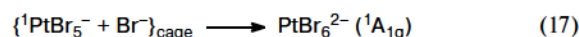
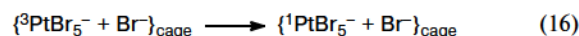
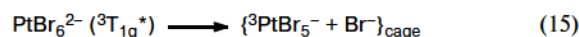
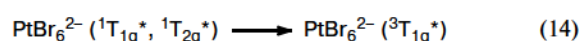
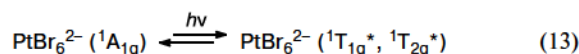


Fig. 5. Transient absorption spectra in experiments (cell 1 mm) on ultrafast pump-probe kinetic spectroscopy of the PtBr_6^{2-} (a, $\lambda_{\text{pump}} = 420$ nm, concentration $3.8 \cdot 10^{-3}$ mol L^{-1}) and PtCl_6^{2-} complexes (b, $\lambda_{\text{pump}} = 405$ nm, concentration 0.03 mol L^{-1}) and the results of experimental data processing by the triexponential function (II). Curves 1 are the initial spectra, curves 2 are the spectra after the end of the first process, and curves 3 are the spectra after the end of the second process.

transition to the low-lying dissociative excited state ${}^3\text{T}_{1g}$, loss of the ligand, and relaxation to the ground state of the ${}^3\text{Pt}^{\text{IV}}\text{Br}_5^-$ complex with the trigonal bipyramid structure. The second characteristic time (2.2 ps) corresponds to the intersystem crossing of the triplet state of the ${}^3\text{Pt}^{\text{IV}}\text{Br}_5^-$ intermediate, whereas the cage pair $\{\text{}^1\text{PtBr}_5^- + \text{Br}^-\}_{\text{cage}}$ is transformed into the initial complex PtBr_6^{2-} and aquated

complex $\text{PtBr}_5(\text{H}_2\text{O})^-$ within the third characteristic time (15 ps). Note that processes (13)–(18) contain vibrational relaxation and solvent relaxation. The situation where several physical and chemical processes having similar characteristic times are kinetically presented as one process is often met in femtosecond spectroscopy⁴¹:



Thus, the photoaquation of the PtBr_6^{2-} complex proceeds *via* the heterolytic mechanism: the platinum cation remains in the tetravalent state and the full time of formation of the final product does not exceed 50 ns.

The femtosecond photoexcitation of the PtCl_6^{2-} complex immediately after laser irradiation results in the formation of broad weakly structured band of intermediate absorption in a whole spectral range of 440–760 nm accessible for detection (see Fig. 5, b, curve 1). This band is transformed within 600 fs into two well formed bands with maxima at 445 and 710 nm (curve 2), which then somewhat narrow with the characteristic time ~ 10 ps. Thus formed intermediate absorption disappears with a characteristic time of 220 ps, which is an order of magnitude longer than the longest characteristic time for the bromide complex. Earlier⁵ the formation of a species with the absorption at 600 nm and a characteristic lifetime of ~ 200 ps was detected in experiment on the picosecond laser flash photolysis of PtCl_6^{2-} . Three values of characteristic time that describe the transformation of intermediate absorption for the PtCl_6^{2-} complex and their assumed interpretation are presented in Table 1. After the initial Franck–Condon state was formed, the fast (600 fs) electron transition occurs to form a species designated further

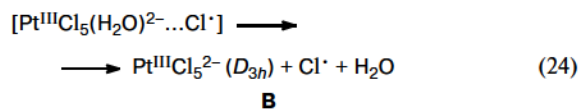
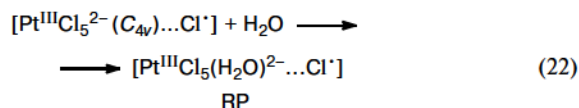
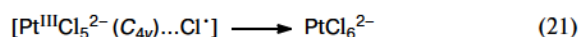
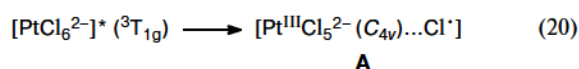
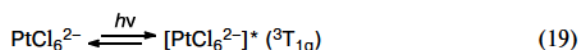
Table 1. Characteristic times and processes for the PtBr_6^{2-} and PtCl_6^{2-} complexes upon the femtosecond excitation in the region of visible d–d absorption bands (triexponential approximation; see Eq. (II))

Complex	τ_1/ps	Process	τ_2/ps	Process	τ_3/ps	Process
PtBr_6^{2-}	0.4	$(\text{PtBr}_6^{2-})^* \rightarrow \text{}^3\text{PtBr}_5^- + \text{Br}^-$	2.2	${}^3\text{PtBr}_5^- \rightarrow \text{}^1\text{PtBr}_5^-$	15	$\text{}^1\text{PtBr}_5^- \rightarrow \text{PtBr}_6^{2-} + \text{PtBr}_5(\text{H}_2\text{O})^-$
PtCl_6^{2-}	0.6	$(\text{PtCl}_6^{2-})^* \rightarrow [\text{PtCl}_5^{2-} \dots \text{Cl} \cdot]^*$	8.6	$[\text{PtCl}_5^{2-} \dots \text{Cl} \cdot]^* \rightarrow [\text{PtCl}_5^{2-} \dots \text{Cl} \cdot]$	220	$[\text{PtCl}_5^{2-} \dots \text{Cl} \cdot] \rightarrow \text{PtCl}_6^{2-} + [\text{Pt}^{\text{III}}\text{Cl}_5(\text{H}_2\text{O})^{2-} \dots \text{Cl} \cdot]$

as intermediate A (first process). The second process is the vibrational relaxation of intermediate A. The third process corresponds to the transition of intermediate A to the initial state of complex PtCl_6^{2-} and another species (intermediate B), whose formation starts a chain of consecutive transformations of intermediates of trivalent platinum. It is necessary to introduce intermediate B, which has no spectral manifestations in the spectral range accessible for measurements, into the scheme, because the decay time of intermediate A (220 ps) is several orders of magnitude shorter than the time of formation of intermediate C (1.2 μs).

We assume that intermediate A is Adamson's primary radical pair (see Eqs (2)–(5)) and intermediate B is complex $\text{Pt}^{\text{III}}\text{Cl}_5^{2-}$ with the trigonal bipyramid structure (D_{3h}). According to the quantum chemical calculations,³⁷ complex PtCl_5^{2-} with the square pyramid structure (C_{4v}) is characterized by two absorption bands in the visible spectral range, which is observed for intermediate A. The influence of the axial chlorine atom on the spectral properties should be weak for the case of a substantial elongation of the $\text{Pt}^{\text{III}}\text{—Cl}$ bond. According to the calculations,³⁷ the PtCl_5^{2-} complex with the D_{3h} structure should have only the absorption in the UV spectral range, which could not be detected in the described experiments.

Thus, we have a rather complicated scheme of the primary photophysical and photochemical processes preceding the formation of the initial intermediate of trivalent platinum, complex $\text{Pt}^{\text{III}}\text{Cl}_5^{2-}$ (D_{3h}), which begins the chain process of photoaquation of PtCl_6^{2-} (see reactions (6)–(12)). The processes that are manifested in femtosecond experiments are presented by Eqs (19)–(24).



RP is secondary radical pair.

Thus, the scheme proposed for the photoaquation of complex PtCl_6^{2-} includes four main intermediates of trivalent platinum. The spectra of three of them (A, C, and D)

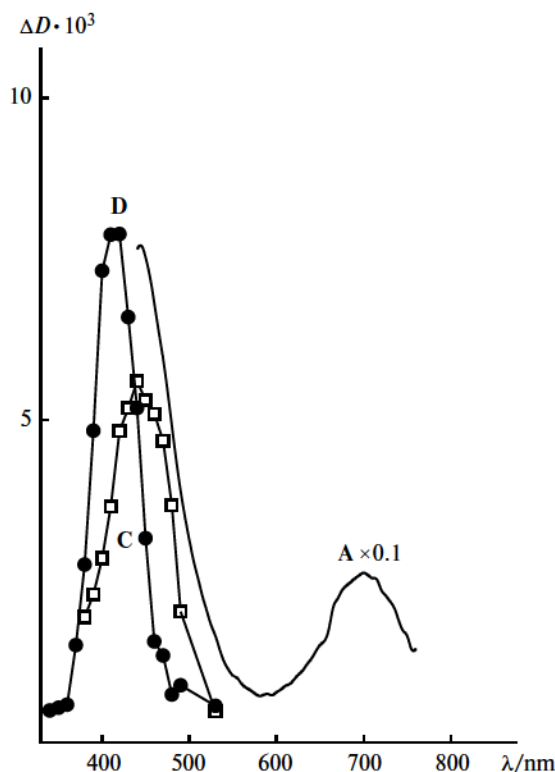


Fig. 6. Spectra of the intermediates formed upon the photolysis of aqueous solutions of the PtCl_6^{2-} complex. Intermediates C and D are the Pt^{III} complexes successively formed upon nanosecond laser flash photolysis (curves 2 and 3 in Fig. 3, b). Intermediate A is detected in femtosecond experiments (curve 3 in Fig. 5, b).

are shown in Fig. 6 (note that the figure does not reflect the real intensity of the absorption band of intermediate A with respect to intermediates C and D, since these species were detected under different experimental conditions). Intermediate B exhibits no pronounced absorption in the visible and near-UV spectral ranges. The characteristics of the intermediates and their assumed assignments are given in Table 2.

Table 2. Intermediate of PtCl_6^{2-} photolysis in aqueous solutions

Intermediate	λ_{max} /nm	τ_{form}	τ_{dec}	Structure
A	445, 700	600 fs	220 ps	$[\text{Pt}^{\text{III}}\text{Cl}_5^{2-} (C_{4v}) \dots \text{Cl}^\cdot]$
B	—	<100 ns	1.2 μs	$\text{Pt}^{\text{III}}\text{Cl}_5^{2-} (D_{3h})$
C	440–450	1.2 μs	7 μs	$\text{Pt}^{\text{III}}\text{Cl}_4\text{X}_2$ (X = OH^- , H_2O)
D	410	7 μs	> 1 μs	$\text{Pt}^{\text{III}}\text{Cl}_{4-n}\text{X}_n$ (n = 1–3; X = OH^- , H_2O)

Note: λ_{max} is the position of absorption band maxima, τ_{form} is the time of formation, and τ_{dec} is the decay time.

The interpretation proposed for the intermediate Pt^{III} compounds makes it possible to explain the whole massive of the data on the photochemistry of aqueous solutions of PtCl₆²⁻, namely:

(1) spectrally detected formation of three intermediates: one in the picosecond (A) and two in the microsecond (C, D) time intervals;

(2) necessity to introduce intermediate B that does not absorb in the visible and near-UV spectral range to concord the kinetic data in the pico- and microsecond ranges;

(3) formation of relatively long-lived intermediate (D) capable of providing the occurrence of the chain reaction;

(4) non-contradictory spectral characteristics of the assumed Pt^{III} intermediates and results of the earlier^{5,6,37–39} quantum chemical calculations.

Summarizing the data on the photochemistry of aqueous solutions of complexes PtBr₆²⁻ and PtCl₆²⁻, we can state that the distinction in their photochemical behavior is due to different natures of the primary intermediates. For the bromide complex, this is the ion pair {³Pt^{IV}Br₅⁻ + Br⁻}_{cage} in which the platinum cation remains to be in the tetravalent state. For the chloride complex, the primary photolysis product is intermediate A, being a species in which the platinum cation is in the trivalent state, presumably, Adamson's primary radical pair [Pt^{III}Cl₅²⁻ (C_{4v})...Cl[•]]. The formation of short-lived intermediate A is the starting point of processes of the successive formation of longer-lived Pt^{III} complexes, viz., intermediates B–D.

It should be mentioned that the intermediate Pt^{III} compounds were identified on the basis of results of the quantum chemical calculations performed^{37–39} in the 1980s by the X_α method. Since that time, quantum chemistry developed significantly. It seems of interest to calculate the structures and electronic absorption spectra of the Pt^{III} complexes by current methods, including calculations for Adamson's radical pairs that were not carried out previously. The coincidence of the results of these calculations with the experimentally obtained spectral characteristics of the Pt^{III} intermediates could be a decisive argument in favor of the proposed photolysis mechanism.

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