

## Photochemistry of the $\text{PtCl}_6^{2-}$ complex in acidic aqueous solutions

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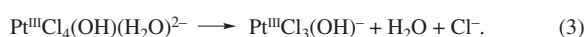
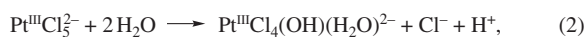
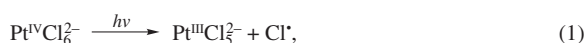
DOI: 10.1016/j.mencom.2016.01.014

The  $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$  complex in acidic aqueous solutions is the subject of photoaquation; the dependence of quantum yield upon acid concentration is the curve with the maximum.

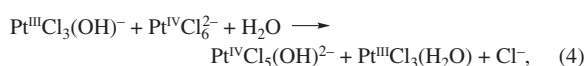
The photochemical activity of hexachloroplatinate(IV) is well known.<sup>1</sup> The four-electron photoreduction of  $\text{Pt}^{\text{IV}}$  to  $\text{Pt}^{\text{0}}$  in water–methanol mixtures<sup>2</sup> is used for producing platinum nanoparticles.<sup>3</sup> In photocatalysis, the photochemical modification of  $\text{TiO}_2$ <sup>4</sup> and  $\text{CdS}$ <sup>5</sup> surfaces by platinum metal complexes allows one to shift the absorption spectra of semiconductors to the visible spectral range.

The photochemistry of the hexahalide complexes of platinum group metals was recently reviewed.<sup>6</sup> The only photochemical reaction of aqueous  $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$  solutions is photoaquation.<sup>7–12</sup> The homolytic cleavage of the Pt–Cl bond followed by chlorine atom escape into the bulk of solution [reaction (1)] was considered as the primary photochemical process. In this case, the photoaquation can follow the chain mechanism. The analysis of both experimental data<sup>7–12</sup> and the results of quantum-chemical calculations<sup>13–15</sup> allowed us to conclude that the chain carrier was the planar complex  $\text{Pt}^{\text{III}}(\text{Cl})_{4-n}\text{X}_n$  ( $n = 1–3$ ;  $\text{X} = \text{OH}^-$ ,  $\text{H}_2\text{O}$ ). Intermediates identified as  $\text{Pt}^{\text{III}}\text{Cl}_4(\text{OH})(\text{H}_2\text{O})^{2-}$  and  $\text{Pt}^{\text{III}}\text{Cl}_{4-n}\text{X}_n$  ( $n = 1–3$ ;  $\text{X} = \text{OH}^-$ ,  $\text{H}_2\text{O}$ ) were recorded by means of laser flash photolysis.<sup>6,12</sup> The chain process with the  $\text{Pt}^{\text{III}}\text{Cl}_3(\text{OH})^-$  complex as a chain carrier is described by equations (2)–(7). In the solutions with close to neutral pH values, the equilibria of reactions (5) and (6) are shifted toward the  $\text{Pt}^{\text{III}}\text{Cl}_3(\text{OH})^-$  and  $\text{Pt}^{\text{IV}}\text{Cl}_5(\text{OH})^{2-}$  complexes. A quasi-stationary concentration of the  $\text{Pt}^{\text{III}}\text{Cl}_3(\text{OH})^-$  intermediates is established for  $\sim 20 \mu\text{s}$ .<sup>15</sup>

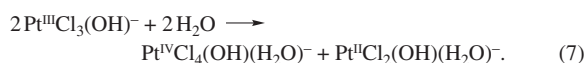
### Chain initiation



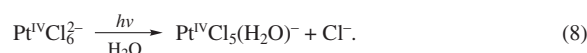
### Chain propagation



### Chain termination



In addition to the chain process, the direct (non-chain) mechanism is also possible. In the direct process, the heterolytic Pt–Cl bond cleavage occurs:<sup>14</sup>



The coexistence of the direct and chain mechanisms of photoaquation is a unique feature of the photochemistry of  $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$ . Only direct photoaquation was observed for  $\text{Pt}^{\text{IV}}\text{Br}_6^{2-}$  and  $\text{Pt}^{\text{IV}}(\text{SCN})_6^{2-}$  complexes.<sup>16,17</sup>

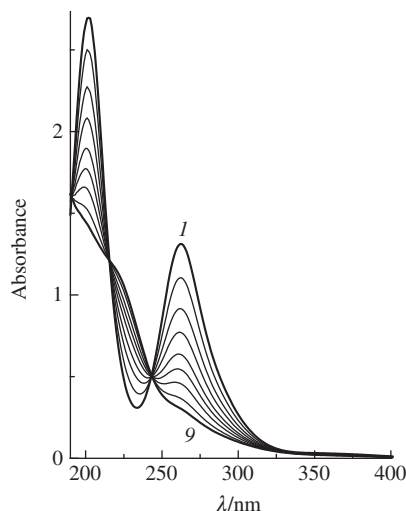
The quantum yield of  $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$  photoaquation ( $\varphi_{\text{aq}}$ ) depends on the concentration of the initial complex, irradiation wavelength and light intensity.<sup>10</sup> Depending on the experimental conditions, the quantum yield could be either lower<sup>9,12</sup> or sufficiently higher than unity.<sup>8,10,15</sup> The pH of solution is a factor affecting the quantum yield. The effect of acidity could be due to changes in the rate constants of elementary stages in reaction scheme (1)–(7) caused by the protonation/deprotonation of  $\text{Pt}^{\text{III}}$  intermediates. The acceleration of  $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$  photolysis in acidic solutions was reported;<sup>10</sup> however, systematic measurements were not performed. Here, we present quantitative data on the photochemistry of the  $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$  complex in acidic aqueous solutions.<sup>†</sup>

The electronic absorption spectrum of the  $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$  complex in aqueous solutions (curve 1 in Figure 1) contains two charge transfer bands at 202 and 262 nm with molar absorption coefficients of 49400 and 24000  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ , respectively. The analysis of the spectrum was performed elsewhere.<sup>19</sup> The most intense band at 202 nm belongs to a transition from the ligand  $\sigma$ -orbital to the vacant  $\sigma^*$  orbitals presumably localized at the central ion. The band at 262 nm corresponds to transitions from the  $\pi$  orbitals of ligands to the  $e_g^*$  orbitals of the central ion. The shoulder in the region of 355 nm is attributed to the  $d-d$  transitions of the platinum ion.

Changes in the UV spectra caused by the stationary photolysis (313 nm) of  $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$  0.1 M  $\text{HClO}_4$  are shown in Figure 1. Conservation of isosbestic points (at 215 and 243 nm) testifies that a single photolysis product is formed. The addition of free  $\text{Cl}^-$  ions to the irradiated solution results in the almost complete restoration of the initial spectrum of  $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$ , which is indicative of photoaquation. The penta(chloro)aquaplatinate ion  $\text{Pt}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})^-$  demonstrates acidic properties (reaction 6,  $\text{p}K_{\text{a}} = 3.8^{20}$ ).

<sup>†</sup> Commercial  $\text{Na}_2\text{PtCl}_6$  (Aldrich) was a source of  $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$  ions. Deionized water and chemically pure perchloric acid were used.

The UV absorption spectra were recorded using Agilent 8453 and Varian CARY 50 spectrophotometers. Stationary photolysis was performed using a high-pressure mercury lamp with a set of glass filters. To calculate the quantum yields, the light intensity was determined by either chemical actinometry (using a ferrioxalate method<sup>18</sup>) or instrumental measurements [using a SOLO 2 laser power and energy meter with a PH100-SiUV photodiode measuring unit (Gentec EO, Canada)].

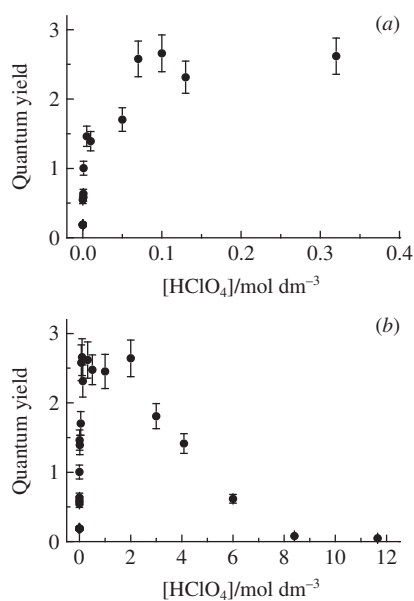


**Figure 1** Changes in the UV spectra caused by the stationary photolysis (313 nm) of the  $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$  complex in 0.1 M  $\text{HClO}_4$ ; 1 cm cell; initial concentration,  $5.6 \times 10^{-5}$  M. Curves 1–9 correspond to irradiation for 0, 4, 9, 13, 19, 24, 30, 42 and 55 s, respectively.

When  $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$  (about  $10^{-5}$  M) is photolysed in solution with nearly neutral pH, the  $\text{Pt}^{\text{IV}}\text{Cl}_5(\text{OH})^{2-}$  complex is the main photoproduct at a reaction depth of about 10%. When photolysis is performed in acidic solutions, the  $\text{Pt}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})^-$  complex is formed; its absorption spectrum was published.<sup>8</sup> The molar absorption coefficient of  $\text{Pt}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})^-$  at 262 nm ( $\varepsilon_{262}$ ) is  $12500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . The UV spectra of the  $\text{Pt}^{\text{IV}}\text{Cl}_5(\text{OH})^{2-}$  and  $\text{Pt}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})^-$  complexes have no significant difference. The value<sup>3</sup> of  $\Delta\varepsilon_{262} = 12000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  was used to calculate the quantum yields of  $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$  photoaquation.

The dependence of the quantum yield (313 nm) of  $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$  photoaquation on the concentration of  $\text{HClO}_4$  at an initial complex concentration of  $6 \times 10^{-5}$  M is shown in Figure 2. The quantum yield increased with the concentration of  $\text{H}^+$  in a range of 0–0.1 M [Figure 2(a)]. At pH 3, the quantum yield reached unity and at  $[\text{H}^+] = 0.07\text{--}2$  M it was 2.5. A further increase in the acid concentration (3–12 M) resulted in a drop in the quantum yield [to 0.05 at 11.7 M of acid, Figure 2(b)].

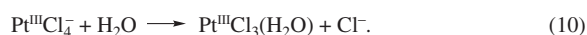
A hypothesis for explaining the dependence of Figure 2 was based on the ionic strength effect on the quantum yield of



**Figure 2** Dependence of the quantum yield of  $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$  photolysis (313 nm) in aqueous  $\text{HClO}_4$  solutions on acid concentration. Initial concentration of  $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$ ,  $5.6 \times 10^{-5}$  M. Acid concentrations: (a) 0–0.4 M and (b) 0–12 M.

photoaquation. To test this hypothesis, we performed experiments with the samples containing  $\text{LiClO}_4$  instead of perchloric acid and found that the presence of 0–1 M  $\text{LiClO}_4$  in the solutions of  $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$  with an initial concentration of  $5.5 \times 10^{-5}$  M did not change the quantum yield (its value remained intact 0.19, as in the absence of the salt). Therefore, the pH effect on the quantum yield of photoaquation is definitely caused by the existence of protons in solution.

The effect of  $\text{H}^+$  on the mechanism of  $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$  photoaquation was explained by the protonation of the complex considered as the main chain carrier. Its general formula is  $\text{Pt}^{\text{III}}(\text{Cl}^-)_{4-n}\text{X}_n$  ( $n = 1\text{--}3$ ;  $\text{X} = \text{OH}^-$ ,  $\text{H}_2\text{O}$ ).<sup>6,12</sup> In the acidic solutions, the equilibrium in reaction (5) is shifted to the left, and the electrically neutral  $\text{Pt}^{\text{III}}\text{Cl}_3(\text{H}_2\text{O})$  complex becomes chain carrier instead of negatively charged  $\text{Pt}^{\text{III}}\text{Cl}_3(\text{OH})^-$  complex. The spectra of these intermediates are practically indistinguishable.<sup>13</sup> In the photolysis mechanism, chain propagation reaction (4) should be replaced by the following reactions:

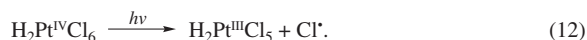


To explain the increasing branch of the dependence (Figure 2), one should propose that the increase in the concentration of protons ( $\text{HClO}_4$  concentrations of 0–2 M) results in a transition from chain propagation reaction (4) to ion–molecule reaction (9), whose rate constant should be definitely higher. However, ionic chain termination reaction (7) is replaced by reaction (11), in which neutral complexes are involved.



The chain length, which is a ratio between the rates of chain propagation and chain termination, for neutral or acidic solutions is  $\lambda_1 = k_4[\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}]/k_7[\text{Pt}^{\text{III}}\text{Cl}_3(\text{OH})^-]$  or  $\lambda_2 = k_9[\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}]/k_{11}[\text{Pt}^{\text{III}}\text{Cl}_3(\text{H}_2\text{O})]$ , respectively. From electrostatic considerations, one should expect that  $k_9/k_{11} > k_4/k_7$ , which explains the increase in the quantum yield.

The drop of the quantum yield at the high concentrations of  $\text{HClO}_4$  (3–12 M, Figure 2) cannot be explained based on simple electrostatic considerations. The effect is most likely caused by a decrease in the rate of chain initiation due to the protonation of the initial complex with the formation of its molecular form  $\text{H}_2\text{Pt}^{\text{IV}}\text{Cl}_6$ . At high acid concentrations, primary process (10) should be replaced by the reaction



It is possible to assume that the  $\text{H}_2\text{Pt}^{\text{III}}\text{Cl}_5$  intermediate cannot effectively react with water [similarly to reactions (2), (3)]. As a result, the formation of labile flat  $\text{Pt}^{\text{III}}$  complexes is suppressed, and the chain process cannot develop.

Thus, we found that the dependence of hexachloroplatinate(IV) photoaquation on acid concentration in acidic aqueous solutions passes through a maximum and proposed a qualitative explanation of this dependence.

This work was supported by the Russian Science Foundation (grant no. 15-13-10012).

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Received: 7th August 2015; Com. 15/4702