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Photolysis of $[\mathrm{PtBr_6}]^{2-}$ complex in frozen methanol matrix

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Photochemistry of the $[\mathrm{PtBr_6}]^{2-}$ complex in the low-temperature methanol matrix (77 K) was studied by low-temperature spectrophotometry and ESR spectroscopy. The $[\mathrm{PtBr_4}]^{2-}$ complex is the main photolysis product. The mechanism of two-electron reduction of the platinum(IV) ion is proposed. The primary photochemical process is electron transfer from the solvent molecule to the photoexcited initial complex to form the intermediate radical complex ($[\mathrm{PtBr_6}]^{3-}\ldots{}^\bullet\mathrm{CH_2OH}$). The transfer of the second electron in the radical complex produces the final reaction products.

Key words: photochemistry, platinum(IV) halide complexes, frozen alcohol matrices, optical absorption spectra, ESR spectroscopy.

Platinum(IV) halide complexes demonstrate high photochemical activity.[1] The photochemistry of the $[\mathrm{PtBr_6}]^{2-}$ complex has been studied by stationary methods in both aqueous solutions[2—7] and organic solvents and frozen matrices.[8—10] It has been established[1] that the main photochemical process in an aqueous medium is photoaquation with a quantum yield of 0.4. In acetonitrile the $\mathrm{Br^-}$ ion is also photosubstituted by the solvent molecule.[8] The process is more complicated in alcohol solutions and depends on the concentration of dissolved oxygen. The final photolysis product in a deaerated methanol solution is the $\mathrm{Pt^{II}}$—$[\mathrm{PtBr_4}]^{2-}$ complex, which is formed by reactions of intermediate $\mathrm{Pt^{III}}$ complexes with the hydroxymethyl radical

$$[\mathrm{PtBr_6}]^{2-} \xrightarrow{h\nu} ([\mathrm{PtBr_6}]^{2-})^* \xrightarrow{\mathrm{MeOH}} [\mathrm{PtBr_5}]^{2-} + {}^\bullet\mathrm{CH_2OH} + \mathrm{Br^-} + \mathrm{H^+}, \qquad (1)$$

$$[\mathrm{PtBr_5}]^{2-} \longrightarrow [\mathrm{PtBr_4}]^{-} + \mathrm{Br^-}, \qquad (2)$$

$$[\mathrm{PtBr_4}]^{-} + \mathrm{MeOH} \longrightarrow [\mathrm{PtBr_4}]^{2-} + {}^\bullet\mathrm{CH_2OH} + \mathrm{H^+}, \qquad (3)$$

$$[\mathrm{PtBr_6}]^{2-} + {}^\bullet\mathrm{CH_2OH} \longrightarrow \mathrm{CH_2O} + [\mathrm{PtBr_5}]^{2-} + \mathrm{Br^-} + \mathrm{H^+}, \qquad (4)$$

$$2\,{}^\bullet\mathrm{CH_2OH} \longrightarrow (\mathrm{CH_2OH})_2. \qquad (5)$$

The reaction mechanism and the nature of the final photolysis product change in solutions containing dissolved oxygen.[9] Photosolvation is initiated instead of the photoreduction of $[\mathrm{PtBr_6}]^{2-}$, and its final product is the $\mathrm{PtBr_5(MeOH)^-}$ complex. This compound is assumed to be formed by the oxidation of the intermediate $\mathrm{Pt^{III}}$ complex with the peroxide radical

$${}^\bullet\mathrm{CH_2OH} + \mathrm{O_2} \longrightarrow {}^\bullet\mathrm{OOCH_2OH}, \qquad (6)$$

$$[\mathrm{PtBr_5}]^{2-} + {}^\bullet\mathrm{OOCH_2OH} \longrightarrow \mathrm{PtBr_5(MeOH)^-} + \mathrm{O_2CH_2OH^-}. \qquad (7)$$

The mechanism including reactions (1)—(7) was confirmed by the ESR detection of the ${}^\bullet\mathrm{CH_2OH}$ radicals during photolysis of the $[\mathrm{PtBr_6}]^{2-}$ complex in a low-temperature methanol matrix (77 K).[10] However, these results[10] are qualitative because the yield of the radicals relatively to the amount of the photoreduced complexes was not measured, and it is not clear whether the radicals are formed only by photolysis of the platinum complex or not.

The mechanism of photoreduction of the $[\mathrm{PtCl_6}]^{2-}$ complexes in liquid and frozen alcohol solutions was studied[11—13] by laser nanosecond flash photolysis. It was shown[11] that the primary photoprocess of electron transfer from the solvent molecule affords a complex of the ${}^\bullet\mathrm{CH_2OH}$ radical with the intermediate platinum(III) compound

$$[\mathrm{PtCl_6}]^{2-} \xrightarrow{h\nu} ([\mathrm{PtCl_6}]^{2-})^* \xrightarrow{\mathrm{MeOH}} [\mathrm{PtCl_6}]^{3-}\ldots{}^\bullet\mathrm{CH_2OH} + \mathrm{H^+}. \qquad (8)$$

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The $[PtCl_6]^{3-}$...$R^{\cdot}CHOH$ radical complexes are unstable even at 77 K. The electron transfer from the radical to the central ion produces the final photolysis product $[PtCl_4]^{2-}$,

$$[PtCl_6]^{3-}...{}^{\cdot}CH_2OH \longrightarrow$$
$$\longrightarrow [PtCl_4]^{2-} + CH_2O + 2\,Cl^- + H^+. \qquad (9)$$

Reaction (9) decreases the relative yield of the radicals during the photolysis of $[PtCl_6]^{2-}$ in the matrix to <1% of the number of the consumed complexes. In fact, ESR detects only a minor amount of the radicals that did not form the radical complex with the platinum ion. In cooled alcohol solutions (170—240 K), the $[PtCl_6]^{3-}$...${}^{\cdot}CH_2OH$ radical complexes disappear due to the dissociation and formation of the secondary radical complex $[PtCl_6]^{3-}$...${}^{\cdot}OOCH_2OH$ in the reaction with O_2.[11] At room temperature dissociation predominates

$$[PtCl_6]^{3-}...{}^{\cdot}CH_2OH \longrightarrow [PtCl_6]^{3-} + {}^{\cdot}CH_2OH, \qquad (10)$$

$$[PtCl_6]^{3-}...{}^{\cdot}CH_2OH + O_2 \longrightarrow$$
$$\longrightarrow [PtCl_6]^{3-}...{}^{\cdot}OOCH_2OH. \qquad (11)$$

Since the structure and electronic and photochemical parameters of the $[PtCl_6]^{2-}$ and $[PtBr_6]^{2-}$ complexes are close, the formation of the radical complexes in the primary photochemical processes can be assumed to occur also in the case of the bromide complex. The purpose of this work is to reveal the detailed mechanism of photoreduction of the $[PtBr_6]^{2-}$ complex in organic media and to study the photolysis of $[PtBr_6]^{2-}$ in the frozen methanol matrix.

Experimental

Solutions of the $[PtBr_6]^{2-}$ complex were prepared from the $Na_2PtBr_6 \cdot H_2O$ salt synthesized according to a known procedure.[14] Solutions of the $[PtBr_4]^{2-}$ complex were prepared from the $K_2PtBr_4 \cdot 2H_2O$ salt synthesized as described previously.[14] The source of free Br^- ions was NaBr (Aldrich). Methanol (Merck, spectroscopic purity) was used without additional purification. Nitrogen was passed through the solution for 20 min to remove dissolved oxygen.

Optical absorption spectra were recorded on Specord UV—Vis (Carl Zeiss) and HP 8354 (Hewlett—Packard) spectrophotometers. Stationary photolysis was carried out using an excimer laser (XeCl, 308 nm) or a high-pressure mercury lamp with a set of glass filters. A deaerated methanol solution of the $[IrCl_6]^{2-}$ complex was used as standard for measuring the quantum yield of phototransformations.[15]

ESR spectra were recorded on an ESR-300 spectrometer (Bruker). The concentrations of radicals in samples were determined by the integration of the ESR spectra and calibration by a standard containing Cu^{2+} ions ($CuCl_2 \cdot 2H_2O$ single crystal). Low-temperature experiments were carried out at 77 K in MeOH mixtures with 5% water (to obtain transparent glass). The vitrifying H_2O + 4 *M* $Mg(ClO_4)_2$ matrix was used for recording the spectrum of the $[PtBr_4]^{2-}$ complex at 77 K. When the ratio of concentrations of species determined from the optical and ESR spectra was needed, the spectra were recorded for the same sample. For this purpose, special planar quartz cells were used (low-temperature photochemical experiments have been described in detail previously).[16]

Results and Discussion

Electronic absorption spectrum of $[PtBr_6]^{2-}$. The optical absorption spectra of the $[PtBr_6]^{2-}$ complex in MeOH at 298 K and in the frozen matrix (MeOH with 5% water) at 77 K are presented in Fig. 1. The spectrum recorded at room temperature coincides with that in the published work.[6] The most intense charge transfer band with a maximum at 226 nm corresponds to the electron transfer from the σ-orbitals localized on the ligands to the vacant σ*-orbitals localized on the metal ion. The less intense charge transfer bands (290—450 nm) correspond to transitions from the π-orbitals of the ligands. They overlap in

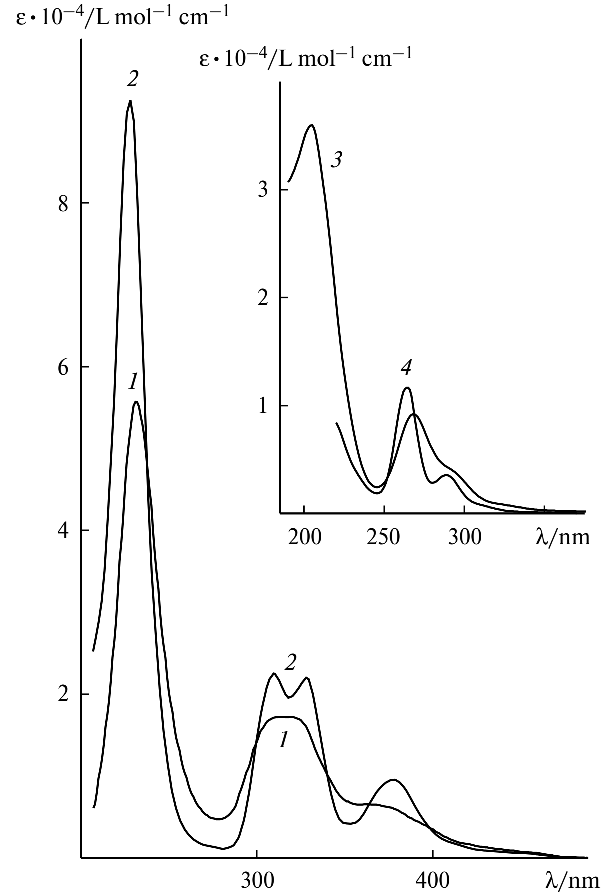


Fig. 1. Optical absorption spectra of the platinum bromide complexes: $[PtBr_6]^{2-}$ complex in MeOH at 298 (*1*) and 77 K (*2*), $[PtBr_4]^{2-}$ complex in water at 298 K (*3*) and in an aqueous 4 *M* solution of $Mg(ClO_4)_2$ at 77 K (*4*).

part with the d—d bands.[17] When the temperature decreases, the bands become narrower, and the molar absorption coefficients in the maxima of the absorption bands increase (see Fig. 1).

Change in optical spectra during photolysis of $[PtBr_6]^{2-}$. Changes in the optical absorption spectra of frozen $[PtBr_6]^{2-}$ solutions during stationary irradiation are shown in Fig. 2. New absorption bands with maxima at 209 and 270 nm appear during photolysis. Three isosbestic points at 218, 247, and 291 nm are retained to deep conversions. The quantum yield of consumption of the starting complex determined from the rate of disappearance of the band with a maximum at 377 nm is $3.7 \cdot 10^{-3}$ (accuracy ~20%). The quantum yield is independent of the concentration of the starting complex (10^{-4}—10^{-3} mol L^{-1}) and intensity of laser pulses (20—200 mJ cm^{-2}), which excluded two-quantum processes.

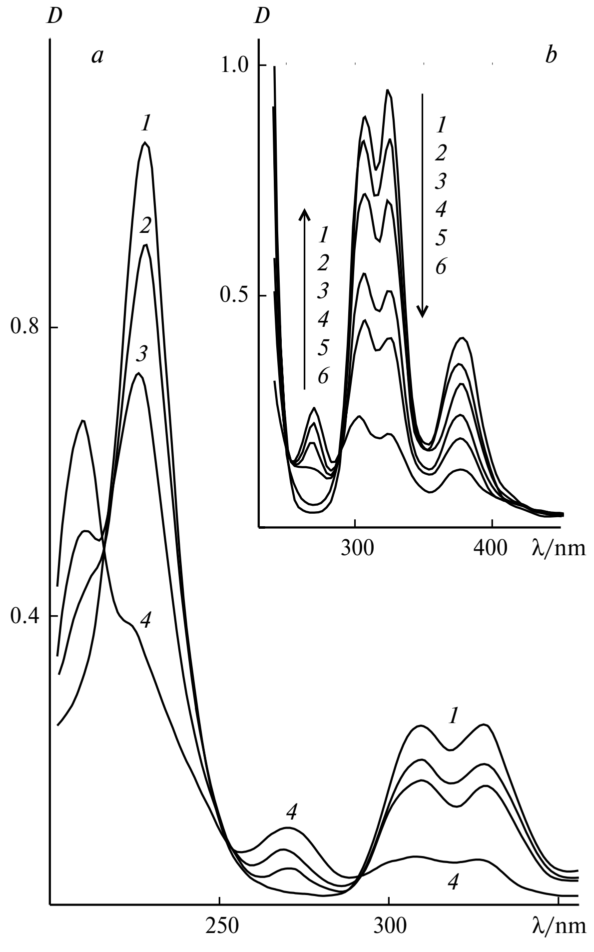
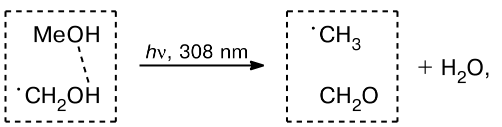


Fig. 2. Change in the optical absorption spectrum during the photolysis of the $[PtBr_6]^{2-}$ complex in the frozen (77 K) methanol matrix: *a*, $[PtBr_6]^{2-} = 2.2 \cdot 10^{-3}$ mol L^{-1}, irradiation time 0 (*1*), 1 (*2*), 2 (*3*), and 8 min (*4*); *b*, $[PtBr_6]^{2-} = 8.6 \cdot 10^{-3}$ mol L^{-1}, irradiation time 0 (*1*), 0.1 (*2*), 0.25 (*3*), 0.4 (*4*), 0.7 (*5*), and 1.7 min (*6*). Irradiation by XeCl laser pulses (308 nm, 10 Hz), cell thickness 50 μ.

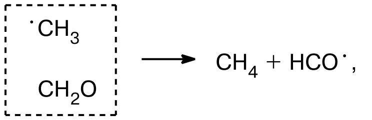
It can be assumed that new absorption bands (209 and 270 nm) belong to the Pt^{II}—$[PtBr_4]^{2-}$ complex. The spectrum of this complex in an aqueous solution at 298 K (see Fig. 1, curve *3*) coincides with those presented previously.[18,19] When the solution is frozen in the matrix containing 4 *M* $Mg(ClO_4)_2$ (see Fig. 1, curve *4*), the absorption bands become narrower with a minor shift of the absorption maximum to the UV region: the maximum of the band at 268 nm shifts to 265 nm. The optical spectrum of $[PtBr_4]^{2-}$ cannot be detected in the frozen methanol matrix. Dissolution of the $K_2PtBr_4 \cdot 2H_2O$ salt in alcohol is accompanied by decomposition and precipitation of metallic platinum.

One more species can give rise to the band with the maximum at 270 nm, namely, the $[Br_3]^-$ ion[20] that is formed by photoreduction of the Fe^{III} and Cu^{II} bromide complexes in alcohol solutions.[21,22] However, in the case of the $[PtBr_6]^{2-}$ complex, the appearance of the $[Br_3]^-$ ion is improbable, because its formation requires a sufficiently high concentration of the free Br^- ion.[22] In addition, the secondary photolysis of the $[Br_3]^-$ ion during prolonged irradiation should produce the $[Br_2]^{\bullet -}$ radical anion[22] with the characteristic optical and ESR spectra. No spectral evidence of $[Br_2]^{\bullet -}$ was detected in our experiments.

ESR spectra of photolysis products. The starting $[PtBr_6]^{2-}$ complex is not paramagnetic (electronic configuration is $5d^6$, total electron spin is zero). Photolysis of $[PtBr_6]^{2-}$ in the methanol matrix in the ESR spectrum produces a characteristic triplet (Fig. 3) belonging to the $^{\bullet}CH_2OH$ radical.[23] Prolonged irradiation results in the secondary photolysis of the $^{\bullet}CH_2OH$ radical and produces the $^{\bullet}CH_3$ and $HCO^{\bullet}$ radicals.[24] The methyl radicals disappear rapidly even at 77 K to form the $HCO^{\bullet}$ and $^{\bullet}CH_2OH$ radicals.[25,26] The ESR spectrum of the $HCO^{\bullet}$ radical is an asymmetrical doublet with the splitting ~130 G (see Fig. 3, curves *1* and *2*). The $HCO^{\bullet}$ radicals irradiated by the visible light are reduced to the $^{\bullet}CH_2OH$ radicals[24] (see Fig. 3, curve *3*). The mechanism of photolysis of the hydroxymethyl radicals is described by the equations[25—27]



$$\boxed{\begin{matrix} \text{MeOH} \\ {}^{\bullet}\text{CH}_2\text{OH} \end{matrix}} \xrightarrow{h\nu,\ 308\ \text{nm}} \boxed{\begin{matrix} {}^{\bullet}\text{CH}_3 \\ \text{CH}_2\text{O} \end{matrix}} + \text{H}_2\text{O}, \qquad (12)$$



$$\boxed{\begin{matrix} {}^{\bullet}\text{CH}_3 \\ \text{CH}_2\text{O} \end{matrix}} \longrightarrow \text{CH}_4 + \text{HCO}^{\bullet}, \qquad (13)$$

$$^{\bullet}CH_3 + MeOH \longrightarrow CH_4 + {}^{\bullet}CH_2OH, \qquad (14)$$

$$^{\bullet}CH_2OH \xrightarrow{h\nu} H^{\bullet} + HCO^{\bullet}, \qquad (15)$$

$$H^{\bullet} + MeOH \longrightarrow H_2 + {}^{\bullet}CH_2OH. \qquad (16)$$

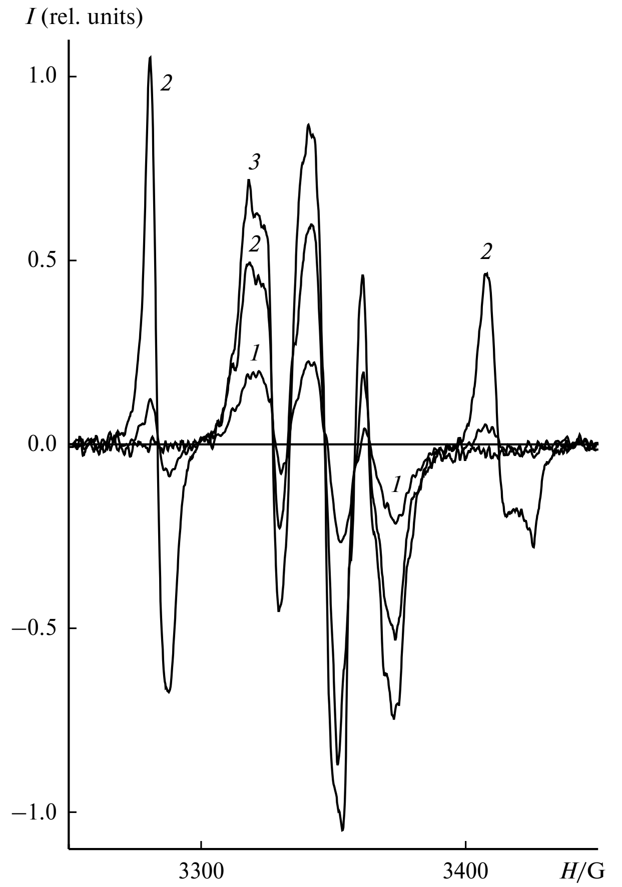


Fig. 3. Change in the ESR spectra during the photolysis of the $[PtBr_6]^{2-}$ complex ($1 \cdot 10^{-3}$ mol L^{-1}) in the methanol matrix: irradiation by XeCl laser pulses (308 nm, 10 Hz), 1000 (*1*) and 4000 pulses (*2*); result of the additional irradiation of the sample by the light from a DRSh-500 mercury lamp with $\lambda > 450$ nm to transform the $HCO^•$ radical into $^•CH_2OH$ (*3*).

The photochemical process is believed to involve the solvent molecule bound through the hydrogen bond to the $^•CH_2OH$ radical. The chain of transformations of the radicals upon light absorption by the $^•CH_2OH$ radical results in the photostimulated migration of the valence in the matrix bulk.[28]

When $[PtBr_6]^{2-}$ is photolyzed in the frozen methanol matrix, the ESR spectrum exhibits signals only from the organic radicals listed above with the g factors close to the g factor of the free electron (g_e). The signals characteristic of transition metal ions with the g factors, which differ strongly from g_e, were not detected. This fact contradicts the result of the work[10] reported the detection of the ESR signal with the g factor ~2.43, which appeared due to the photolysis of $[PtCl_6]^{2-}$ and $[PtBr_6]^{2-}$ in alcohol matrices and was ascribed to the intermediate Pt^{III} complexes.

Mechanism of $[PtBr_6]^{2-}$ photolysis. In order to determine the quantitative ratio between concentrations of various species during photolysis, the optical and ESR spectra were detected for the same sample. The changes in time in the concentrations of the starting complex, the $^•CH_2OH$ and $HCO^•$ radicals, the overall concentration of the radicals, and the absorbance at 270 nm during the photolysis of $[PtBr_6]^{2-}$ are shown in Fig. 4. The induction period confirms the formation of the $HCO^•$ radicals due to the secondary photochemical reaction, *viz*., photolysis of the $^•CH_2OH$ radicals. Such kinetic curves are typical of $^•CH_2OH$ accumulation regardless of the method of generation (for example, for γ-radiolysis of MeOH [24] or photolysis of transition metal complexes[29]).

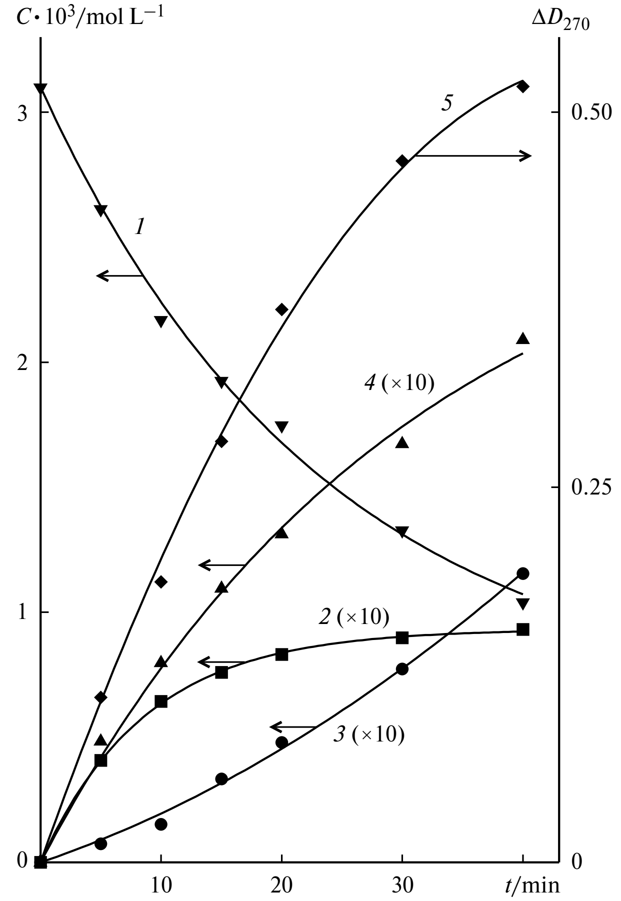


Fig. 4. Change in concentrations of various species during the photolysis of the $[PtBr_6]^{2-}$ complex ($3.1 \cdot 10^{-3}$ mol L^{-1}) in the methanol matrix: starting $[PtBr_6]^{2-}$ complex (*1*), radicals $^•CH_2OH$ (*2*) and $HCO^•$ (*3*), overall concentration of the radicals (*4*), and the change in the absorbance at 270 nm (*5*). Irradiation by XeCl laser pulses (308 nm, 10 Hz), cell thickness 0.24 mm.

As seen in Fig. 5, the overall concentration of the radicals is at most 10% of the amount of the reacted $[PtBr_6]^{2-}$ complexes. The $^•CH_2OH$ and $HCO^•$ radicals are stable in the methanol matrix at 77 K. Therefore, the low yield of these radicals can be due to two reasons. First, after an electron was transferred from the MeOH molecules to the excited complex, the radicals disappeared in the secondary dark processes. Second, the lines of the

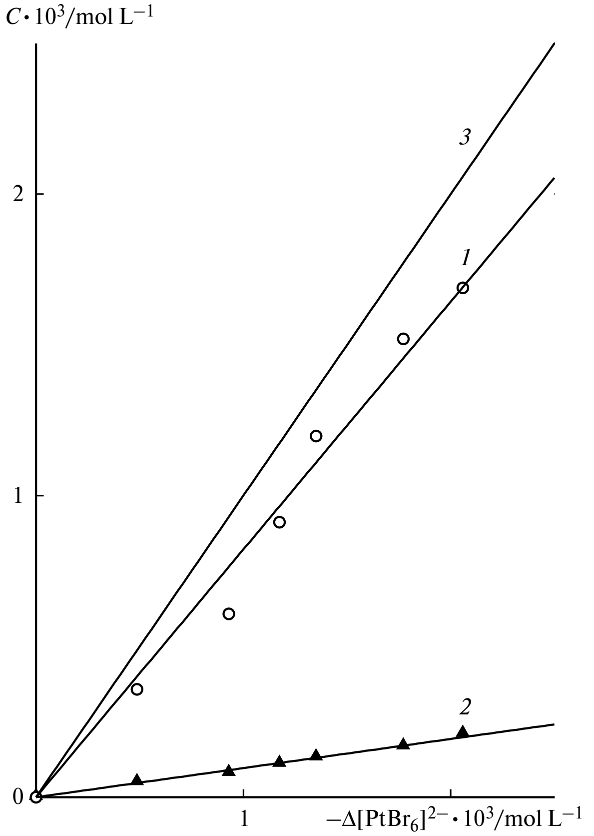


Fig. 5. Change in the relative yield of the $[PtBr_4]^{2-}$ complex (*1*) and overall concentration of the $^{\bullet}CH_2OH$ and $HCO^{\bullet}$ radicals (*2*) at different numbers of the reacted $[PtBr_6]^{2-}$ complexes; line *3* corresponds to 100% yield. The results were obtained by processing of the data in Fig. 4.

radicals are strongly broadened due to the dipole-dipole interaction with the paramagnetic Pt^{III} ion and are not observed in the ESR spectrum. A choice between two reasons can be made by the synchronous measurements of the optical and ESR spectra for the same sample. The increase in the intensity of the absorption band of the $[PtBr_4]^{2-}$ complex with a maximum at 270 nm makes it possible to calculate its relative yield. As shown in Fig. 5, the relative yield of the $[PtBr_4]^{2-}$ complex upon photolysis is 80—85% (calculated under assumption that the molar absorption coefficients of these complexes are equal in the methanol and aqueous matrices). When the mechanism of line broadening of the radicals is operative, the yield of $[PtBr_4]^{2-}$ would be much lower. Hence, the radicals disappear in the secondary dark processes involving the intermediate Pt^{III} complexes.

The low relative yields of the radicals in the photolysis of both $[PtCl_6]^{2-}$ **11** and $[PtBr_6]^{2-}$ in the methanol matrix suggest that the same primary photochemical and secondary dark processes occur in both cases. The final variant of the photochemical reaction is the $[PtBr_4]^{2-}$ complex ($[PtCl_4]^{2-}$ in the case of the chloride complex**11**), which appears due to the two-electron reduction of the starting $[PtBr_6]^{2-}$ complex. An alcohol molecule acts as the reducing agent. The primary photochemical process is electron transfer from the MeOH molecule to the excited complex. By analogy to the photochemistry of $[PtCl_6]^{2-}$, we can assume that the radical, which is formed on the direct contact with the photoreduced complex, forms a radical complex with the latter

$$[PtBr_6]^{2-} \xrightarrow{h\nu} ([PtBr_6]^{2-})^* \xrightarrow{MeOH} [PtBr_6]^{3-}\ldots{}^{\bullet}CH_2OH + H^+. \quad (17)$$

Radical complexes are intermediates in photochemical processes involving many transition metals.**11,29—34** For the metal ions, which have two neighboring stable valent states (for example, Cu^{II} and Cu^{I}), the radical complexes are stabilized in a frozen matrix. For example, the $[CuCl_4]^{3-}\ldots{}^{\bullet}CH_2OH$ and $[IrCl_6]^{3-}\ldots{}^{\bullet}CH_2OH$ radical complexes formed upon the photolysis of the $[CuCl_4]^{2-}$ and $[IrCl_6]^{2-}$ complexes are stable in methanol matrices and exhibit pronounced optical and ESR spectra.**29,32—34** When the temperature increases, the radical complexes dissociate with the escape of the radical to the matrix bulk. At room temperature dissociation takes several nanoseconds.

For platinum, which has two stable valent states (Pt^{IV} and Pt^{II}) separated by the intermediate unstable Pt^{III} state, the radical complexes are not stabilized even in the frozen matrix. They disappear in the dark transfer of the second electron from the radical to the Pt^{III} ion.**11** At room temperature, dissociation competes successfully with this dark reaction and provides the escape of the radical into the solvent bulk also within several tens of nanoseconds.

Thus, the radical $[PtBr_6]^{3-}\ldots{}^{\bullet}CH_2OH$ complex disappears in the methanol matrix, most likely, during recording of optical and ESR spectra (tens of seconds). The second electron, necessary for the formation of the final $[PtBr_4]^{2-}$ complex, is transferred to the Pt atom from the $^{\bullet}CH_2OH$ radical

$$[PtBr_6]^{3-}\ldots{}^{\bullet}CH_2OH \longrightarrow [PtBr_4]^{2-} + CH_2O + 2\,Br^- + H^+. \quad (18)$$

The $[PtBr_6]^{3-}\ldots{}^{\bullet}CH_2OH$ radical complex can exhibit an absorption band in the UV region (at 308 nm). Therefore, reaction (18) can also be initiated photochemically. In this case, the increase in the absorbance of the absorption band of the $[PtBr_4]^{2-}$ complex with a maximum at 270 nm should be accompanied by an induction period necessary for the accumulation of the primary radical complex. The kinetic curves in Figs. 4 and 5 show that the induction period is absent from the accumulation of $[PtBr_4]^{2-}$. This induction period is observed under the condition $\varepsilon_R\varphi_R \gg \varepsilon_C\varphi_C$, where $\varepsilon_R\varphi_R$ and $\varepsilon_C\varphi_C$ are the products of the molar absorption coefficients by the quantum yields at the excitation wavelength (308 nm) for the radical ($[PtBr_6]^{3-}...{}^{\bullet}CH_2OH$) and initial ($[PtBr_6]^{2-}$) complexes, respectively. For $[PtBr_6]^{2-}$, $\varepsilon_C\phi_C \approx 10^2$ L mol^{-1} cm^{-1}. Therefore, for the radical complex $\varepsilon_R\phi_R$ should be >> 10^2 L mol^{-1} cm^{-1}. At the highest quantum yield $\phi_R \approx 1$, this correlation is transformed into $\varepsilon_R >> 10^2$ L mol^{-1} cm^{-1}. At the molar absorption coefficient $\varepsilon_R \geq 10^3$ L mol^{-1} cm^{-1} corresponding to this condition, the isosbestic points should shift during photolysis, reflecting successively the steps $[PtBr_6]^{2-} \rightarrow$ $\rightarrow [PtBr_6]^{3-}...{}^{\bullet}CH_2OH \rightarrow [PtBr_4]^{2-}$. However, during irradiation three isosbestic points (see Fig. 2) corresponding to the transition $[PtBr_6]^{2-} \rightarrow [PtBr_4]^{2-}$ are retained in the whole time interval. In addition, the ESR spectrum does not manifest any properties of signals of the intermediate Pt^{III} complexes. Thus, the character and dynamics of changes in the optical and ESR spectra indicate that reaction (18) is most likely the dark process.

A minor amount of the ${}^{\bullet}CH_2OH$ radicals (~10% of the reacted $[PtBr_6]^{2-}$) is stabilized in the matrix and appears in the ESR spectrum

$$[PtBr_6]^{2-} \xrightarrow{h\nu} ([PtBr_6]^{2-})^* \xrightarrow{MeOH}$$
$$\longrightarrow [PtBr_6]^{3-} + {}^{\bullet}CH_2OH + H^+. \qquad (19)$$

These radicals can appear when an electron is transferred from the MeOH molecules in the second (neighboring to the Br$^-$ ligand) or third coordination spheres. In this case, the radical does not contact with the Pt atom, is not mobile, and cannot form a radical complex. The spin echo study[35,36] of the spatial distribution of the radicals formed during the photolysis of the $FeCl_3$ complex in the frozen methanol and isopropanol matrices shows that ~30% radicals appeared in the primary photochemical reaction are stabilized at the distance >14 Å from the Fe^{II} complex corresponding to the species in the third coordination sphere. Photostimulated valence migration can be another reason for the stabilization of some ${}^{\bullet}CH_2OH$ radicals at a considerable distance from the parent ion.[28]

According to the scheme of photolysis (17)—(19), the amount of the intermediate Pt^{III} complexes should coincide with that of the ${}^{\bullet}CH_2OH$ radicals detected by ESR. However, as already mentioned, we found no signals, which could be assigned to the $[PtBr_6]^{3-}$ complex, in a wide interval of magnetic fields. The detection of the ESR signals from some Pt^{III} complexes formed in radiation chemical processes has previously[37—39] been reported. They are characterized[38,39] by high $\Delta g = (g_{\perp} - g_{\|}) \approx$ 0.4—1.0, which is related to a considerable constant of spin-orbital interaction for the Pt atoms. Thus, the ESR signal of the intermediate Pt^{III} complexes in the frozen matrices is wide ($\Delta H \geq 10^3$ G) and, hence, its amplitude is small. The bromide complexes should be characterized by a noticeable hyperfine splitting on the Br nuclei (spin 3/2), which additionally decreases the line amplitudes. The short relaxation time of the paramagnetic ions also contributes to the broadening ($\Delta H \approx 10^2$ G for Pt^{III} in the single crystal[38]) and to the decrease in the line amplitudes. Therefore, the signal from Pt^{III} was not detected during γ-irradiation of the $[PtCl_6]^{2-}$ and $[PtBr_6]^{2-}$ complexes in frozen solutions even for radiation-chemical accumulation when high concentrations of intermediate species can be accumulated at high radiation doses.[37]

The second reason for which the signal from Pt^{III} can be nonmanifested in the ESR spectra is the disappearance of the $[PtBr_6]^{3-}$ complex in dark processes. One of these reactions, most likely, is electron transfer from the alcohol molecules in the second coordination sphere of this complex

$$[PtBr_6]^{3-} + MeOH \longrightarrow$$
$$\longrightarrow [PtBr_4]^{2-} + {}^{\bullet}CH_2OH + H^+ + 2\,Br^-. \qquad (20)$$

The laser flash photolysis of alcohol solutions of $[PtCl_6]^{2-}$ showed the transformation Pt^{IV} → Pt^{III} in the primary photochemical step. The formation of the final $[PtCl_4]^{2-}$ complex, *i.e.*, the step Pt^{III} → Pt^{II}, is a dark process and is related to electron transfer from the solvent molecules to the Pt^{III} ion ($[PtCl_4]^-$).[11—13] It is most likely that for the bromide complex $[PtBr_4]^{2-}$ can be formed due to reaction (20) or a similar reaction involving the $[PtBr_5]^{2-}$ and $[PtBr_4]^-$ complexes. When the solution is frozen, the rates of these processes should decrease. However, they can be manifested in stationary measurements (with duration of tens of seconds).

Thus, the detection of the optical and ESR spectra for the same sample during the photolysis of $[PtBr_6]^{2-}$ in the methanol matrix made it possible to measure the relative yields of the intermediate radical species. The results obtained show that the final product ($[PtBr_4]^{2-}$) is formed by two-electron transfer from the solvent molecules even in a low-temperature matrix. The transfer of the first electron is photoinitiated, and the second electron is transferred under dark conditions. The further detailed study of the spectroscopic parameters and kinetics of formation of the intermediate Pt^{III} complexes in matrices and solutions will be carried out by laser flash photolysis elsewhere.

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