to stabilization of the molecular complex.

The preceding orbital analysis of σ and π interactions between an ML_4 fragment and a H_2 molecule may be related to the classical view of coordination in an ML_5 d^8 complex.[24] Rossi and Hoffmann have rationalized the preferred site (axial or equatorial) for a determined ligand, according to its electronic properties, in a d^8 ML_5 complex with a trigonal-bipyramid geometry.[24] Two conclusions turn out to be of special relevance to the present study: (a) the best σ donor occupies an axial position; (b) the equatorial π interaction is stronger than the axial. Coordination of the H_2 molecule with a C_{2v} ML_4 system would lead to a trigonal bipyramid with an equatorial H_2 molecule, whereas coordination with a C_{3v} ML_4 system leads to a trigonal bipyramid with an axial H_2 molecule. Since phosphines are better σ donors than a H_2 molecule, they will likely occupy the axial positions, so the H_2 molecule will occupy an equatorial site. The present results do not allow us to compare the different relative stabilities of the complexes with H_2 in either position, because placement of H_2 in equatorial site leads to dihydride. Axial placement of the H_2 molecule in the experimental complex[11] can be justified by the presence of strong steric requirements that make this position of H_2 the only available.

Regarding the π interaction, the present results agree completely with the aforementioned paper[24] in that the π interaction is stronger in the equatorial position than in the axial one. For the H_2 molecule, such interaction consists of a back-donation to the σ^* orbital. An excess of back-donation leads to the dihydride; as happens in this complex for the placement of the H_2 molecule in the equatorial site. Analysis by Rossi and Hoffmann of the stronger π interactions in the equatorial site is thus completely adequate for the present case. The orbital that accounts for such interaction in the C_{2v} fragment is clearly antibonding with both equatorial phosphines. Thus, it has a higher energy than it does in the C_{3v} fragment and can overlap much better with a π-type orbital, since it is hybridized away from the other equatorial ligands (see Table III and Figure 3).

IV. Conclusions

Through a study on the $[Rh(PH_3)_4]^+ + H_2$ system, we have explained the experimental results of Bianchini et al.[11] on the stability of the molecular hydrogen complex $[Rh(PH_3)_4(H_2)]^+$ vs the dihydride $[Rh(PH_3)_4H_2]^+$ when the ligands have a pyramidal C_{3v} structure around the metal and on the opposite stability when they have a C_{2v} structure.

Generalization of these results to other d^8 ML_4 complexes might be partially questioned by an interesting work published recently by Sweany et al.,[25] where synthesis of a C_{2v} symmetry $[Co(CH_3)(CO)_3(H_2)]$ complex is reported, as a first step toward formation of the dihydride. In this case, presence of π-acceptor ligands retards back-donation as we have explained before, thus favoring the existence of the molecular hydrogen complex.

Therefore, we conclude that if the d^8 ML_4 complexes adopt a C_{3v} symmetry structure, their preferred way to coordinate H_2 is the η^2 one; otherwise, the dihydride is more stable. The reason for the so recent synthesis of this kind of molecular complex must be attributed to the intrinsic instability of the C_{3v} geometry with respect to the C_{2v} one. In the case of the complex prepared by Bianchini et al., this instability is compensated by the strong steric requirements of the ligands.

Further work will analyze the influence of analogous effects on the mechanism and transition-state nature of typical oxidative-addition reactions of either H–H bonds or C–H bonds.

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Registry No. $[Rh(PH_3)_4]^+$, 121176-09-8; $[Rh(PH_3)_4H_2]^+$, 121176-10-1; H_2, 1333-74-0.

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Platinum(III) in the REOA Mechanism of $PtCl_4^{2-}$ and $PtCl_6^{2-}$. A Pulse-Radiolysis Study

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In aqueous solutions $PtCl_4^{2-}$ is oxidized by OH to $PtCl_4OH^{2-}$ and $PtCl_6^{2-}$ reduced by e_{aq}^- or H to $PtCl_6^{3-}$. These Pt(III) species both react subsequently with H_2O to produce $PtCl_4(OH)_2^{3-}$ and H^+. All these processes are fast, whereas decay of $PtCl_4(OH)_2^{3-}$ by disproportionation is relatively slow. Kinetics of reactions and properties of intermediate species are described. The early stage of the reductive elimination/oxidative addition (REOA) mechanism of Pt(II) and Pt(IV) is proposed.

Introduction

About 30 years ago Rich and Taube[1] observed that labile Pt(III) plays an important role in exchange reactions of $PtCl_6^{2-}$. Grinberg and Shagisultanova[2] determined that exchange of bromide in $PtBr_4^{2-}$ and $PtBr_6^{2-}$ is mediated by a redox process. Since then, the problem of the reductive elimination/oxidative addition mechanism (REOA) has been the subject of numerous studies, summarized by Mason,[3] Peloso,[4] and Elding and Gustafson.[5] The participation of Pt(III) as an intermediate was usually not discussed.

In general, within the REOA mechanism the processes involving Pt(II) are described as oxidative addition to the square plane and as the elimination of ligands from the reduced octahedron of Pt(IV). In both cases, the initial fast reaction is followed by subsequent ligand exchange, which may be less rapid.

The technique of pulse radiolysis is very suitable for studying redox reactions in aqueous solutions. Pt(III), a logical intermediate

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in redox processes in the Pt(II)–Pt(IV) system, has been observed in the pulse-radiolysis experiments[6-11] but not in work carried out using more conventional techniques. We noted only one work, by Halpern and Pribanić,[12] in which authors oxidizing Pt(II) with Ir(IV) found it necessary to acknowledge the Pt(III) concept and the evidence stemming out of pulse radiolysis.

One of the shortcomings of the hitherto collected evidence is that it has been obtained with the aid of spectrophotometric observations only. In this work we try to complement it with the observations of changes in conductivity when oxidizing $PtCl_4^{2-}$ or reducing $PtCl_6^{2-}$.

Experimental Section

Pulse-radiolysis experiments were performed with a Van de Graaff electron accelerator and previously described equipment for optical absorbance and conductivity measurements,[13] which could be made simultaneously. Electron pulses of 2.6 MeV and 1-μs duration were used for the irradiations. The dose per pulse was ca. 400 rad (ca. 2.5×10^{16} eV·g^{-1}) as measured by KCNS or tetranitromethane dosimetry. Optical observations were rechecked with 0.5-μs pulses of 10-MeV electrons from a 13/9 LAE accelerator.[14] Analytical grade reagents and 6-fold-distilled water were used. Solutions were saturated with Ar or N_2O by the conventional technique. In conductivity experiments the temperature (usually ca. 20 °C) was measured in the cell for each run; in calculations the following values of mobilities were used: H_3O^+ 350, OH^- 198.6, Cl^- 76.35 Ω^{-1} M^{-1} at 25 °C.[15] Appropriate temperature corrections applied.

Results

The radiolytic decomposition of water may be described by the general equation

$$H_2O \rightarrow e_{aq}^-, H, H_3O^+, OH^-, OH, H_2O_2, H_2 \qquad (1)$$

The last two products are virtually unreactive within a few milliseconds after the pulse and need not be considered. H and e_{aq}^- are known to reduce both Pt(II) and Pt(IV), whereas OH oxidizes Pt(II): these reactions are very fast.[6,7] H_3O^+ and OH^- are produced at concentrations too low[16] (ca. 10^{-6} M) to affect the platinum complex at either valency level, and they undergo rapid neutralization.[17]

To avoid disturbances in conductivity measurements caused by neutralization of e_{aq}^-, H_3O^+, and OH^-, solutions were either slightly acidic ($HClO_4$, pH ~ 5) or alkaline (NaOH, pH ~ 9). Under these conditions, neutralization was completed within the duration of the electron pulse.

Oxidation of $PtCl_4^{2-}$. Solutions of $PtCl_4^{2-}$ were always saturated with N_2O, in order to remove reducing e_{aq}^- and to transform it into oxidizing OH in the reaction

$$N_2O + e_{aq}^- \rightarrow N_2 + OH^- + OH \qquad (2)$$

Addition of $HClO_4$ or NaOH up to pH ~ 5 or pH ~ 9, respectively, did not affect the absorption spectrum of $PtCl_4^{2-}$. It was assumed that ligand-exchange processes could be neglected. Considering the primary yield of OH, $G_{OH} = 2.9$, and that of e_{aq}^-, $G_{e_{aq}^-} = 2.6$, the expected yield of oxidation was $G_{ox} = G_{OH} + G_{e_{aq}^-} = 5.5$ (ions per 100 eV of absorbed radiation energy).

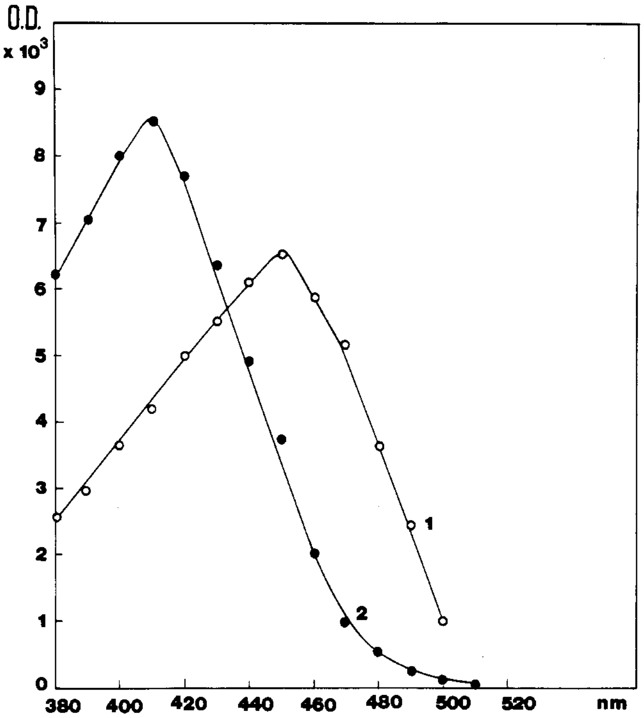

Figure 1. Absorption spectra of products arising from pulse irradiation of ca. 1×10^{-4} M $PtCl_4^{2-}$, N_2O-saturated solutions at pH = 4.96 or 8.83 (dose per pulse 2.54×10^{16} eV·g^{-1}; OD per 1-cm analytical light beam pass): (1) end of pulse absorption; (2) absorption 70 μs after pulse.

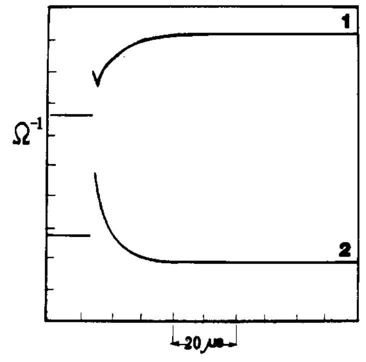

Figure 2. Change in conductivity signal upon pulse radiolysis of ca. 1×10^{-4} M K_2PtCl_4, N_2O-saturated solutions (dose per pulse 2.54×10^{16} eV·g^{-1}): (1) pH = 4.96; (2) pH = 8.83.

The transient absorption spectrum observed in ca. 1×10^{-4} M $PtCl_4^{2-}$ solution is shown in Figure 1. It has been established previously that, in neutral aqueous solutions, oxidation of $PtCl_4^{2-}$ produces a transient absorption peak at 450 nm, which transforms itself in a first-order reaction into an absorption at 410 nm, with a single isosbestic point at 430 nm.[6] This phenomenon could not be observed in 10^{-2} M H_2SO_4 or 10^{-2} M KOH solutions.[6] Four independent sets of experiments, where pH, [$PtCl_4^{2-}$], and dose were varied, gave the same absorptions, kinetics, and isosbestic points as those observed in the neutral solution. The extinction coefficients of peak absorptions have been calculated as $\epsilon^{450} = 2780 \pm 160$ M^{-1} cm^{-1} and $\epsilon^{410} = 3690 \pm 160$ M^{-1} cm^{-1}, the former at the end of the pulse and the latter 70 μs after the pulse. Both values are in very good agreement with those determined previously in neutral solutions.[6,7]

Observations of the transient absorption spectra of irradiated $PtCl_4^{2-}$ in solutions with pH ~ 5 and pH ~ 9 suggest that the same reactions are induced at pH = 5, at pH = 9, and in neutral solution but not in 10^{-2} M acid or base. Consequently, in the conductivity measurements no special corrections were necessary. Typical oscillograph traces obtained in conductivity measurements are shown in Figure 2. As may be seen, the electron pulse

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increased conductivity in the acidic solution and decreased it in the alkaline solution. Kinetics of the processes was observed and recorded simultanously for absorbance and conductivity. The following first-order rate constants have been calculated: decay of the 410-nm absorption, $(1.70 \pm 0.20) \times 10^5\ s^{-1}$; production of the 410-nm absorption, $(1.65 \pm 0.20) \times 10^5\ s^{-1}$; increase of conductivity in the acidic solution, $(1.70 \pm 0.20) \times 10^5\ s^{-1}$; decrease of conductivity in alkaline solution, $(1.50 \pm 0.20) \times 10^5\ s^{-1}$. On statistical grounds all these values may be considered to be equal. They are in good agreement with earlier results on the kinetics of 450–410-nm absorption transformation.[6,7] After termination of the fast transformation processes, a permanent increase or decrease in conductivity could be observed within at least 2 ms.

The yield of the change in conductivity was calculated under the assumption that the processes under investigation include production of a proton, responsible for the increase of conductivity in the acidic solution and for the decrease in the alkaline solution. The following mechanism has been applied:

$$PtCl_4^{2-} + OH \rightarrow PtCl_4OH^{2-} \qquad (3)$$

$$PtCl_4OH^{2-} + H_2O \rightarrow PtCl_4(OH)_2^{3-} + H^+ \qquad (4)$$

Assuming that the mobilities of $PtCl_4^{2-}$ and $PtCl_4(OH)_2^{3-}$ are equal, the yield was calculated as $G = 6.4 \pm 0.5$, in both acidic and alkaline solutions. Considering that this assumption is only partially true, this value is in satisfactory agreement with the expected value of 5.5. Reaction 3 is fast, $k_3 = 8.0 \times 10^9\ M^{-1}\ s^{-1}$ as determined by Ghosh-Mazumder and Hart.[7]

If, as proposed by Elding and Gustafson,[18] Pt(II) reacts as a hydrated, pentacoordinated $PtCl_4H_2O^{2-}$ complex, the product of (3) may be $PtCl_4(OH)H_2O^{2-}$ and that of (4) its dissociation to $PtCl_4(OH)_2^{3-}$; the essential mechanism will, however, remain unaltered. One may also argue that $PtCl_4OH^{2-}$ decays by disproportionation prior to (4); however, this does not seem to be the case. The 450-nm absorption decays according to first-order kinetics and disappears rapidly; disproportionation would be a second-order slow process and cannot explain the production of H^+.

Reduction of $PtCl_6^{2-}$. Solutions of $PtCl_6^{2-}$ were saturated with Ar and contained an excess of *tert*-butyl alcohol, to remove OH in the reaction

$$(CH_3)_3COH + OH \rightarrow CH_2(CH_3)_2COH + H_2O \qquad (5)$$

As the butoxy radical produced in (5) is unreactive toward Pt(IV), the expected yield of reduction was $G_{red} = G_{e_{aq}^-} + G_H = 2.6 + 0.6 = 3.2$. The H atom is able to reduce Pt(IV) in a manner similar to that of e_{aq}^-.[6] In this work we have checked the transient absorption of a pulse-irradiated ca. 1×10^{-4} M $PtCl_6^{2-}$ solution at pH ~ 5 or pH ~ 9 and found spectra as shown in Figure 3. Extinction coefficients have been calculated as $\epsilon^{440} = 2800 \pm 160\ M^{-1}\ cm^{-1}$ and $\epsilon^{410} = = 3550 \pm 160\ M^{-1}\ cm^{-1}$. The former coefficient, determined for the end-of-pulse absorption, is due to the precursor of the latter, observed 70 μs thereafter.

Similarly as in $PtCl_4^{2-}$ solutions, no pH effect on absorption of $PtCl_6^{2-}$ or transient absorptions at 410 and 440 nm were found within $5 < pH < 9$.

Conductivity measurements gave results qualitatively similar to those obtained for $PtCl_4^{2-}$ and are shown in Figure 2; i.e., in acidic solutions conductivity increased and in alkaline solutions it decreased to a permanent value. The following first-order rate constants have been calculated: decay of the 440-nm absorption, $(1.1 \pm 0.2) \times 10^5\ s^{-1}$; production of the 410-nm absorption, $(1.2 \pm 0.2) \times 10^5\ s^{-1}$; increase of the conductivity in acidic solution, $(1.1 \pm 0.2) \times 10^5\ s^{-1}$; decrease of conductivity in alkaline solution, $(1.1 \pm 0.2) \times 10^5\ s^{-1}$. These rates are very close to each other, though smaller than the $1.8 \times 10^5\ s^{-1}$ observed for the production of the 410-nm absorption in the neutral solution of $PtCl_6^{2-}$.[6] The absorption at 410 nm and conductivity of the solution after the first 20 μs are stable over a few milliseconds. Similarly as in $PtCl_4^{2-}$ solutions, it was assumed that reactions responsible for the increase of conductivity in acidic solution and decrease in the alkaline one include production of a proton. The following mechanism was tested:

$$PtCl_6^{2-} + e_{aq}^- \rightarrow PtCl_6^{3-} \qquad (6)$$

$$PtCl_6^{3-} + 2H_2O \rightarrow PtCl_4(OH)_2^{3-} + 2H^+ + 2Cl^- \qquad (7)$$

The H atom reactions resemble (6) and (7). The calculated yields were $G = 3.1 \pm 0.2$ in the acidic solution and 3.0 ± 0.3 in the alkaline solution, each value obtained by assuming that mobility of $PtCl_6^{2-}$ is equal to that of $PtCl_4(OH)_2^{3-}$. Both yields are practically identical with the expected value of 3.2. In the calculations we have also considered that in fact not two H^+ ions produced in (7) but three H^+ ions contribute to the change in conductivity. The third H^+ ion is that produced in (1) and not neutralized by e_{aq}^-, due to its removal in (6). Reaction 6 is diffusion-controlled, and $k_6 = 1.4 \times 10^{10}\ M^{-1}\ s^{-1}$ has been determined by Anbar and Hart.[19]

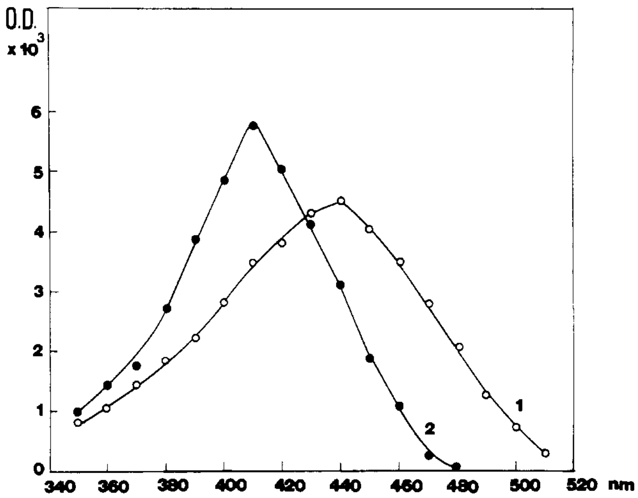

Figure 3. Absorption spectra of products arising from pulse irradiation of ca. 1×10^{-4} M $PtCl_6^{2-}$, 0.01 M *tert*-butyl alcohol, Ar-saturated solutions at pH = 4.74 or 9.57 (dose per pulse $3.04 \times 10^{16}\ eV \cdot g^{-1}$; OD per 1-cm analytical light beam pass): (1) end of pulse absorption; (2) absorption 70 μs after pulse.

Discussion

In 1967 Adams, Broszkiewicz, and Michael[6] observed that oxidizing $PtCl_4^{2-}$ with OH radical produced a transient species absorbing at 450 nm, the species being subsequently transformed into another, relatively stable, species, absorbing at 410 nm. Rate constants of decay of the 450-nm absorption and of 410-nm production being equal and only one isosbestic point being found, the explanation has been proposed that the responsible process was that of intramolecular transformation. The $PtCl_6^{2-}$ ion, reduced by e_{aq}^-, produced a transient also absorbing at 410 nm. Consequently, the 450-nm absorption was ascribed to the square pyramid of pentacoordinated Pt(III) produced by addition of OH to the plane of $PtCl_4^{2-}$. The 410-nm absorption was attributed to the trigonal bipyramid of pentacoordinated Pt(III), a structure more stable at the coordination number 5 than at that of the square pyramid.

The same and similar systems have been later investigated by other authors, who either did not comment on this mechanism[7] or found it still questionable.[8]

An alternative mechanism has been proposed by Wright and Laurence,[20] who investigated flash photolysis of $PtCl_6^{2-}$ solutions and concluded that the species absorbing at 410 nm is planar $PtCl_4^-$, produced by elimination of two Cl^- ions out of the reduced $PtCl_6^{3-}$. This was reexamined by Broszkiewicz and Grodkowski,[9] who pulse irradiated $PtCl_4^{2-}$ in solutions containing an excess of Cl^- or Br^- and found that production of Pt(III) is due to addition

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of the oxidizing Cl_2^- or Br_2^- to the plane of Pt(II).

The present results, obtained with help of another experimental method, add further evidence and promote a more uniform mechanism. Elimination of Cl^- alone, as claimed by Wright and Laurence,[20] cannot explain the increase of conductivity in acidic solution and decrease in the alkaline solution, which can be done in terms of H^+ production. Identity of rate constants determined by optical absorption and conductivity methods in respective solutions of $PtCl_4^{2-}$ or $PtCl_6^{2-}$ indicates that both methods describe the same phenomenon in terms of its different properties. Finally, the 410-nm absorption of the long-lived transient both in oxidation of $PtCl_4^{2-}$ and reduction of $PtCl_6^{2-}$ can now be ascribed to the same species, $PtCl_4(OH)_2^{3-}$, and not to two different species, as considered previously.[6]

These conclusions allow us to assume that, as believed earlier,[6] reaction 3 produces the OH adduct of $PtCl_4^{2-}$, absorbing at 450 nm and, probably, of square-pyramidal structure. Furthermore, reaction 4 is not a first-order internal rearrangement of ligands but a pseudo-first-order hydroxylation to the octahedral $PtCl_4(OH)_2^{3-}$, absorbing at 410 nm. Under this assumption, $k_4 = (2.9 \pm 0.3) \times 10^3\ M^{-1}\ s^{-1}$ may be calculated.

In $PtCl_6^{2-}$ solutions, after the rapid reaction 6, which produces octahedral $PtCl_6^{3-}$ absorbing at 440 nm, the latter transient experiences a pseudo-first-order substitution (eq 7) of two Cl^- ions by two OH^- ions with a rate constant $k_7 = (2.0 \pm 0.2) \times 10^3\ M^{-1}\ s^{-1}$. The product of (7), $PtCl_4(OH)_2^{3-}$, is identical with that of (4), both absorbing at 410 nm and most probably featuring distorted octahedral rather than trigonal-bipyramidal symmetry.

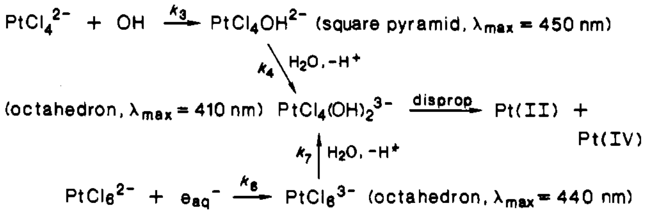
$PtCl_4(OH)_2^{3-}$ is fairly stable, though under the applied experimental conditions its fast decay is rather unlikely. It does not seem to enter into a redox reaction with water, or if it does, such a process is a very slow one. H_2O_2 produced in reaction 1 is present in the irradiated solution at a concentration lower than 10^{-6} M, and lacking any other redox reagent, $PtCl_4(OH)_2^{3-}$ probably disproportionates to Pt(II) and Pt(IV), though at $[Pt(III)] \sim 10^{-6}$ M this reaction may be expected to be very slow. All these factors stabilize Pt(III) over several milliseconds. Similar stability of octahedral ions at atypical valency has been already observed in, e.g., Rh(IV)[21] and Os(V).[22]

Our earlier hypothesis concerning the decay of Pt(III) by disproportionation[6] found support in results by Karaban and Shagisultanova,[23] who investigated γ-ray radiolysis of $PtCl_6^{2-}$ solutions as well as reduction of this ion by H atoms produced in high-frequency electrodeless discharge. They observed a decrease in pH and production of $PtCl_4^{2-}$. The concentration of the produced $PtCl_4^{2-}$ corresponded with a decrease in $[PtCl_6^{2-}]$. The decrease in pH, recalculated on the basis of their data, corresponds with ca. two H^+ produced per each $PtCl_6^{2-}$ reduced and ca. three H^+ per H atom supplied to the solution. These results indicate that indeed Pt(II) was produced by disproportionation rather than by any other reaction, though the final products were probably not chloro but aquo–chloro complexes of Pt(II) or Pt(IV).

Our results cannot be explained in terms of bielectron oxidation of Pt(II) to Pt(IV) nor by reduction of Pt(IV) directly to Pt(II). The absorption spectra determined in this and earlier works do not correspond with those obtained in solutions of chloro and aquo–chloro complexes of Pt(II) and Pt(IV). Elding and Olsson[24] found that complexes of the formula $PtCl_{4-n}(H_2O)_n^{n-2}$ have absorption maxima within 400–500 nm with extinction coefficients smaller than 50 $M^{-1}\ cm^{-1}$. Cox and Peters[25] made the same observation on $PtCl_4(OH)_2^{2-}$ and $PtCl_4(H_2O)_2$. Bardin and Ketrush[26] published the absorption spectrum of $Pt(OH)_6^{2-}$, indicating only an insignificant absorption at $\lambda > 300$ nm. To explain our results, we had to apply the ϵ's of transients being about 100 times higher than those presented above. This is particularly relevant to the case of $PtCl_4(OH)_2^{2-}$,[25] a Pt(IV) complex with the same ligands as $PtCl_4(OH)_2^{3-}$ proposed by us. It may be therefore concluded that the analysis of extinction coefficients excludes the possibility of production of Pt(II) and Pt(IV) directly within the duration of the electron pulse and shortly afterward.

Conclusions

The data discussed in this work allow us to propose the following scheme of the REOA reactions of Pt(II) and Pt(IV) at their early stage:



The one-electron oxidizing agent used in radiation chemistry experiments (e.g. OH, Cl_2^-, Br_2^-) adds itself to the Pt(II) plane in a manner similar to that of two-electron agents (e.g. Cl_2, Br_2, I_2) in thermal reactions.[27–30] This is probably the reason why Pt(III) produced in short-time pulse-radiolysis experiments is relatively stable. Pt(III) is also an initial product of Pt(IV) reduction. Pt(III), able to oxidize Fe(II)[8,18] and Cu(II),[8] apparently does not react with water and undergoes disproportionation. The symmetry of the most stable Pt(III) complexes with Cl^- and OH^- is probably that of a distorted octahedron, similar to that observed for Pt(III) complexes with various ammine ligands.[8,10,11] The hexacoordinated structures, $PtCl_4(OH)(H_2O)^{2-}$ or $PtCl_4(OH)_2^{3-}$, of Pt(III) have been indicated by Goursot et al.[31] as the only models whose calculated CT spectra are in agreement with the experimental ones.

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Registry No. $PtCl_4^{2-}$, 13965-91-8; OH, 3352-57-6; $PtCl_6^{2-}$, 16871-54-8.

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