Koch, van Eldik et al.  
Mechanism of tetrachloroplatinate(II) oxidation by hydrogen peroxide in hydrochloric acid solution
Mechanism of tetrachloroplatinate(II) oxidation by hydrogen peroxide in hydrochloric acid solution†

Pieter Murray,a,b Klaus R. Koch*a and Rudi van Eldik*a

Oxidation of tetrachloroplatinate(II) by hydrogen peroxide in hydrochloric acid was studied by UV-Vis spectrophotometry. Oxidation takes place via two parallel reactions with hypochlorous acid and hydrogen peroxide, respectively, according to the overall rate law \( \frac{d[\text{Pt(IV)}]}{dt} = k_1[\text{Pt(II)}][\text{H}_2\text{O}_2] \). For oxidation of \([\text{PtCl}_4]^{2-}\) at relatively low concentrations, \([\text{PtCl}_4]^{2-} \ll 0.5 \text{ mM}\), hypochlorous acid formation is fast relative to the oxidation of \([\text{PtCl}_4]^{2-}\) by hydrogen peroxide, as a result of the rate determining reaction \( \text{H}_2\text{O}_2 + \text{H}^+ + \text{Cl}^- \rightarrow \text{HOCl} + \text{H}_2\text{O}, \) resulting in a rate law \( \frac{d[\text{Pt(IV)}]}{dt} = k_2[\text{H}_2\text{O}_2] \) with a value \( k_2 = (8 \pm 2) \times 10^{-7} \text{ s}^{-1} \) at 35 °C. For concentrations of \([\text{PtCl}_4]^{2-} > 0.5 \text{ mM}\), oxidation by hydrogen peroxide becomes dominant, resulting in the pseudo-first order rate law \( \frac{d[\text{Pt(IV)}]}{dt} = k_3[\text{Pt(II)}][\text{H}_2\text{O}_2] \) with the value \( k_3 = (1.5 \pm 0.1) \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1} \) at 35 °C. The final oxidation product is a mixture of \([\text{PtCl}_5(\text{H}_2\text{O})]^{-}\) and \([\text{PtCl}_6]^{2-}\), with \([\text{PtCl}_4]^{2-}\) formed as a result of \([\text{PtCl}_4]^{2-}\) assisted chloride anation reactions.

Introduction

Oxidation of Pt(II) square-planar complexes by hydrogen peroxide has been exploited in many areas of research, particularly as a strategy towards the design of new complexes.1 Many of these studies rely on the formation of hydroxido complexes by the oxidation with hydrogen peroxide, which provides more stability and control. The square-planar configuration of the original Pt(II) complex is retained furnishing a Pt(IV) product with new ligands coordinated trans to each other. For instance, oxidation of \([\text{PtCl}_4]^{2-}\) by hydrogen peroxide in water yields trans-[\text{PtCl}_4(\text{OH})_2]^{2-}\) quantitatively according to eqn (1).2

\[
[\text{PtCl}_4]^{2-} + \text{H}_2\text{O} \rightarrow \text{trans-}[\text{PtCl}_4(\text{OH})_2]^{2-} \quad (1)
\]

195Pt NMR indicates that the trans coordinated hydroxido ligands originate from hydrogen peroxide and solvent water respectively.3 Inert hydroxido ligands can be protonated after oxidation to render the aqua ligands that are labile, promoting substitution reactions.4

By comparison, oxidation of \([\text{PtCl}_4]^{2-}\) by hydrogen peroxide in acidic medium yields trans-[\text{PtCl}_4(\text{H}_2\text{O})_2], while relatively fast Pt(II) assisted ligand scrambling reactions cause a redistribution of the oxidation product(s) to form a mixture of \([\text{PtCl}_{n-1}(\text{H}_2\text{O})_n]^{2-n}\) \((n = 0−4)\) complexes.5 The large-scale separation of platinum from other platinum group metals (PGMs) depends, amongst other factors, on the efficient oxidation of Pt(II) to Pt(IV) in solution. The oxidation states of the various PGMs dissolved in the hydrochloric acid process solutions are manipulated to allow for their separation by inter alia solvent extraction (SX), oxidative distillation and/or classical ion-exchange methods.6 Although hydrogen peroxide is not used in the refining industry, as part of ongoing work in this context, we examined in detail the oxidation of \([\text{PtCl}_4]^{2-}\) by hydrogen peroxide in hydrochloric acid as a benchmark system. In the oxidation of Pt(II) to Pt(IV) in solution, Pearson and Basolo proposed a reaction mechanism involving Pt(II) assisted ligand exchange more than 50 years ago.6 This mechanism was later revised to account for direct formation of \([\text{PtCl}_6]^{2-}\) from \([\text{PtCl}_4(\text{H}_2\text{O})_2]\) in a chloride rich solution.4

The origin of the difference in behaviour between trans-Pt(IV) aqua and hydroxido analogues is attributed to the labile trans aqua ligands which are susceptible to bond breakage.7 Kinetic studies dealing with oxidation of Pt(II) complexes by hydrogen peroxide have been neglected, particularly in the presence of free chloride. A kinetic study dealing with the oxidation of \([\text{PtCl}_4]^{2-}\) by hydrogen peroxide in perchloric acid has been reported.8

In the present study, oxidation of \([\text{PtCl}_4]^{2-}\) by hydrogen peroxide is revisited, with the added complexity of free chloride ions in solution, presenting a more complex mechanism. Formation of \([\text{PtCl}_5(\text{H}_2\text{O})]^{-}\) and possibly trans-[\text{PtCl}_4(\text{H}_2\text{O})_2] coincides with \([\text{PtCl}_4]^{2-}\) assisted ligand exchange.

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the complications associated with such reactions, hydrochloric acid catalyses the decomposition of hydrogen peroxide to form hypochlorous acid according to eqn (2).

$$\text{H}_2\text{O}_2 + \text{H}^+ + \text{Cl}^- \xrightarrow{k_{\text{HOCli}}} \text{HOCI} + \text{H}_2\text{O} \quad (2)$$

Oxidation by hydrogen peroxide and hypochlorous acid may therefore coincide to yield two parallel reactions $k_{\text{H OCI}}$ and $k_{\text{HOCli}}$ as depicted in the scheme in (3), where the intermediates are $1 = \text{trans-PtCl}_4(\text{H}_2\text{O}_2)_2$ and $2 = \text{PtCl}_6(\text{H}_2\text{O})^2$.

$$\begin{align*}
\text{H}_2\text{O}_2 & \quad \text{HOCI} & \quad \text{H}_2\text{O} \\
1 \quad & \quad 2 \quad & \quad \text{Cl}_2
\end{align*} \quad (3)$$

Oxidation of $[\text{PtCl}_4]^{2−}$ by hydrogen peroxide is slow, whereas oxidation by hypochlorous acid is rapid in comparison, but yields the same product. Furthermore, depending on the reaction conditions, hypochlorous acid may form chlorine which can also act as an oxidant, further complicating this process. These aspects are explored and discussed in the present study to elucidate the overall oxidation mechanism of $[\text{PtCl}_4]^{2−}$ by hydrogen peroxide in the presence of an excess of hydrogen cations and chloride anions.

Experimental section

Chemicals and solutions

All chemicals were of reagent grade quality and used without further purification. Potassium tetrachloroplatinate(n) (99.9+%, K$_2$PtCl$_4$), sodium chloride (99+%, NaCl) and sodium perchlorate (99+% NaClO$_4$) were obtained from Sigma-Aldrich. Hydrogen peroxide (30% w/w, $\text{H}_2\text{O}_2$, Sigma-Aldrich) was of reagent grade quality and used as received. Solutions of hydrogen peroxide were prepared immediately before use. Analytically pure concentrated perchloric acid (70% w/w, HClO$_4$, 1 L = 1.68 kg, Merck) and hydrochloric acid (HCl, Sigma-Aldrich) were used to prepare solutions. Stock solutions of 1 mM or 10 mM $[\text{PtCl}_4]^{2−}$ were prepared in 1 M or 2 M HCl from which further dilutions were made. Solutions containing Pt(n) were kept in the dark to eliminate photo-induced aquation reactions. Concentrations of $[\text{PtCl}_4]^{2−}$ were evaluated by UV-Vis spectrophotometry at 331 nm ($\varepsilon_{331} = 59$ M$^{-1}$ cm$^{-1}$) or 390 nm ($\varepsilon_{390} = 56$ M$^{-1}$ cm$^{-1}$). Chloride concentrations $>0.1$ M are sufficient to suppress aquation of $[\text{PtCl}_4]^{2−}$ → $[\text{PtCl}_6(\text{H}_2\text{O})]^2$. In 1 M HCl, all Pt(n) essentially exists as $[\text{PtCl}_4]^{2−}$. All aqueous solutions were made with ultra-pure de-ionised water.

Spectrophotometry

Photo-induced reactions necessitate kinetic measurements in UV-Vis absorption spectra at a specific wavelength. UV-Vis spectra in the range 200–600 nm were recorded after the oxidation was complete. Measurements were performed on a Shimadzu UV-2010PC spectrophotometer. The instrument was equipped with a thermoelectrically controlled cell holder using 1 cm tandem quartz cuvettes. Activation volume measurements for slow reactions were performed on a Shimadzu UV-2010PC spectrophotometer equipped with a high pressure cell fitted with a 1.5 cm pill-box quartz-cuvette. Activation volume measurements for relatively fast reactions were performed on a laboratory-made high-pressure stopped-flow instrument. The temperature was controlled and maintained in these instruments at 35.0 ± 0.1 °C using a circulating water bath (Julabo MP-5).

Kinetics

Observed rate constants for pseudo-zero order reactions were obtained directly from the slope of concentration versus time plots. Observed rate constants for reactions showing pseudo-first order character were calculated directly from absorbance versus time plots using a least-squares program. The ionic strength was kept constant at 1 M in all experiments by using the correct ratios of hydrogen chloride, sodium chloride, sodium perchlorate and perchloric acid. Hydrogen peroxide was always present in large excess (>15 times) with regard to the substrate ensuring pseudo-order reaction conditions.

Spectra

Both $[\text{PtCl}_4(\text{H}_2\text{O})]^{−}$ and $[\text{PtCl}_4]^{2−}$ were identified in the final spectra after oxidation of $[\text{PtCl}_4]^{2−}$ by hydrogen peroxide. The $[\text{PtCl}_4(\text{H}_2\text{O})]^{−}/[\text{PtCl}_6]^{2−}$ ratio is proportional to the oxidation rate which in turn is influenced by the concentration of $[\text{PtCl}_4]^{2−}$, $\text{H}_2\text{O}_2$, acid and chloride. Slow reactions led to almost complete conversion of $[\text{PtCl}_4]^{2−}$ → $[\text{PtCl}_6]^{2−}$ (>90% of Pt(n) identified as $[\text{PtCl}_6]^{2−}$), while for fast oxidation reactions $[\text{PtCl}_4(\text{H}_2\text{O})]^{−}$ is the major product. Since chloride anation of $[\text{PtCl}_6(\text{H}_2\text{O})]^2$ is slow in the absence of $[\text{PtCl}_4]^{2−}$, conversion of $[\text{PtCl}_6(\text{H}_2\text{O})]^{−}$ → $[\text{PtCl}_6]^{2−}$ is effectively quenched after oxidation when $[\text{PtCl}_6]^{2−}$ is depleted. For the oxidation of $[\text{PtCl}_4]^{2−}$ an absorbance increase is observed between 200 and 500 nm except for the region between 222 and 236 nm in which isosbestic points occur and an absorbance decrease is observed, as shown in Fig. 1.

The $[\text{PtCl}_4(\text{H}_2\text{O})]^{−}/[\text{PtCl}_6]^{2−}$ ratio for Pt(n) ≤ 0.07 mM was determined at 230 and 262 nm where these complexes show absorbance maxima and minima, respectively. The UV spectra of these complexes are known and have been reported elsewhere. Concentrations of $[\text{PtCl}_4]^{2−}$ were evaluated by UV-Vis spectrophotometry at 331 nm ($\varepsilon_{331} = 59$ M$^{-1}$ cm$^{-1}$) or 390 nm ($\varepsilon_{390} = 56$ M$^{-1}$ cm$^{-1}$). Chloride concentrations $>0.1$ M are sufficient to suppress aquation of $[\text{PtCl}_4]^{2−}$ → $[\text{PtCl}_6(\text{H}_2\text{O})]^2$. In 1 M HCl, all Pt(n) essentially exists as $[\text{PtCl}_4]^{2−}$. All aqueous solutions were made with ultra-pure de-ionised water.
observed in the kinetic traces. To suppress such changes in absorbance were monitored at 262 or 353 nm, close to solvent water to coordinate the negatively charged Pt(II) precursor complex, trans to the oxidant, was considered here. The spectrum of trans-[PtCl(H2O)2] is known and has been reported before.2 No evidence could be found for the presence of significant concentrations of trans-[PtCl(H2O)2] under the reaction conditions and in the time scale studied here. Associations between [PtCl4]2− and trans-[PtCl(H2O)2], rapidly resulting in the formation of [PtCl3(H2O)]− and/or [PtCl5]2− within the time scale investigated here, is possible as suggested by the rate constants estimated in this study (vide infra).

Results
Oxidation of [PtCl4]2− ≤ 0.07 mM
Oxidation of [PtCl4]2− by excess hydrogen peroxide quantitatively converts all Pt(n) → Pt(iv) so that -d[Pt(iii)]/dt = d[Pt(iv)]/dt. Oxidation reactions of [PtCl4]2− ≤ 0.07 mM with [H2O2] (5–100 mM) generate predominantly linear absorbance vs. time plots at 262 nm (Fig. 1; data summarized in Table 1), indicating that the reaction is pseudo-zero order with respect to Pt(n) and the observed rate is defined by rate law eqn (4).

\[
d[Pt(iv)]/dt = k_0[H_2O_2] = k_{obs} (M \text{ s}^{-1}) \tag{4}
\]

The observed rate constants (\(k_{obs}\)) were obtained directly from the slope of concentration versus time plots. Plots of \(k_{obs}\) vs \([H_2O_2]\) are linear with zero intercept for the [PtCl4]2− concentration range 0.02–0.04 mM (ESI Fig. S1A†). A small intercept \(\approx 1.0 \times 10^{-8} \text{ M s}^{-1}\) (ESI Fig. S1B†) was observed for [PtCl4]2− concentrations between 0.05 and 0.07 mM. Pseudo-zero order rate constants \(k_0\) (s−1) calculated from eqn (5) are

<table>
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<th>[PtCl4]2− (mM)</th>
<th>H2O2 (mM)</th>
<th>(k_{obs}) (M s−1)</th>
<th>(k_0 = k_{obs}[H_2O_2]) (s−1)</th>
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<td>1.13 × 10−7</td>
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Mean value = (8 ± 2) × 10−7 s−1
The zero-order process was estimated by varying the pressure from the variation of $[\text{PtCl}_4^{2-}]$.

Kinetic data for the oxidation of $[\text{PtCl}_4^{2-}]$ are listed in Table 1, from which it follows that $k^0 = (8 \pm 2) \times 10^{-7}$ s$^{-1}$ over the entire concentration range investigated.

$$k^0 = k_{\text{obs}}[\text{H}_2\text{O}_2]^{-3}$$

The activation parameters $\Delta H^1$ and $\Delta S^1$ were estimated from the variation of $k_{\text{obs}}$ in the temperature range 15–35 °C (Table 2), and plots of $\ln (k^0/T)$ versus $1/T$ according to the Eyring equation gave linear correlations (ESI Fig. S2†). Values for $\Delta H^1$ and $\Delta S^1$ were subsequently calculated from the slope and intercept of such plots according to eqn (6) and (7), where $k_B$ is Boltzmann’s constant and $h$ is Planck’s constant. The calculated parameters are listed in Table 2.

$$\text{Slope} = -\Delta H^1/R$$

$$\text{Intercept} = \ln(k_B/h) + \Delta S^1/R$$

The activation volume of the oxidation reaction ($\Delta V^1$) for the zero-order process was estimated by varying the pressure in the range 10–132 MPa. A plot of $\ln k^0$ versus pressure is linear (Fig. S3, ESI†) and $\Delta V^1$ was obtained from the slope of the plot according to eqn (8). The calculated activation parameters are included in Table 3.

Oxidation of $[\text{PtCl}_4^{2-}] \geq 0.2$ mM

Oxidation of $[\text{PtCl}_4^{2-}]$ at concentration levels $\geq 0.2$ mM by $[\text{H}_2\text{O}_2]$ in the concentration range 15–300 mM resulted in absorbance vs. time traces at 353 nm which exhibited first-order character. These kinetic traces show inflection points once equilibrium is reached (ESI Fig. S4†), reminiscent of zero-order kinetics prevailing at relative low concentrations of $[\text{PtCl}_4^{2-}]$. The observed rate constants ($k_{\text{obs}}$) were estimated from the second-order rate law eqn (9) and are listed in Table 4. Only absorbance data points prior to the inflection point were used for the estimation of $k_{\text{obs}}$ values, as obtained from least-squares fits.

$$d[\text{Pt(H)}]/dt = k_{\text{H}_2\text{O}_2}[\text{Pt(H)}][\text{H}_2\text{O}_2]$$

Plots of $k_{\text{obs}}$ versus $[\text{H}_2\text{O}_2]$ demonstrate a linear dependence (ESI Fig. S5†), suggesting that the reaction is first order with respect to hydrogen peroxide. The second order rate constants $k_{\text{H}_2\text{O}_2}$ were calculated from eqn (10) to give the average value $(1.5 \pm 0.1) \times 10^{-2}$ M$^{-1}$ s$^{-1}$.

$$k_{\text{H}_2\text{O}_2} = k_{\text{obs}}[\text{H}_2\text{O}_2]^{-1}$$

Oxidation of 1 mM $[\text{PtCl}_4^{2-}]$ with 300 mM $\text{H}_2\text{O}_2$ generated traces illustrating pseudo-first-order character. Activation parameters were estimated under these reaction conditions from the variation of $k_{\text{H}_2\text{O}_2}$ in the temperature range 15–35 °C and eqn (6) and (7) (Table 2). Values of $\Delta V^1$ were estimated by varying the pressure between 5 and 152 MPa for the oxidation of 1 mM $[\text{PtCl}_4^{2-}]$ with 15 mM $\text{H}_2\text{O}_2$. A plot of $\ln k_{\text{H}_2\text{O}_2}$ versus pressure is linear (Fig. S6, ESI†) and allowed the estimation of $\Delta V^1$ from eqn (8) listed in Table 3.

**Effect of acid and chloride concentrations on the oxidation rate and reaction order**

The effect of variation of acid and/or chloride concentration on the reaction rate and order was evaluated in the ranges 0.6–1 M and 0.02–1 M, respectively. Concentrations of Pt(II) 0.2–1.0 mM $[\text{PtCl}_4^{2-}]$ yielding pseudo-first-order kinetics at 35 °C.
Table 5: Oxidation of [PtCl₄]²⁻ performed to determine the effect of chloride and acid concentrations on the observed reaction order at 35 °C

<table>
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<th>HCl (M)</th>
<th>HClO₃ (M)</th>
<th>NaClO₃ (M)</th>
<th>(k^0_{\text{obs}}) (M⁻¹ s⁻¹)</th>
<th>(k^0 = k^0_{\text{obs}}[\text{H}_2\text{O}_2]) (s⁻¹)</th>
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<td>—</td>
<td>2.17 × 10⁻⁸</td>
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Discussion

Rate law for hypochlorous acid formation

An oxidation mechanism for [PtCl₄]²⁻ displaying zero-order kinetics can be envisaged as a result of the rapid formation of hypochlorous acid according to eqn (2). Catalytic decomposition of hydrogen peroxide in hydrochloric acid has been studied in detail. It was concluded that hydrogen peroxide decomposes via the acid-dependent reaction eqn (2), in addition to an acid-independent pathway eqn (12).¹⁷⁻¹⁹

\[
\text{H}_2\text{O}_2 + \text{Cl}^- \rightarrow \text{H}_2\text{O} + \text{ClO}^-
\]  

The general rate law eqn (13) was established to define the overall rate of decomposition via the parallel reactions eqn (2) and (12).

\[
-d[\text{H}_2\text{O}_2]/dt = k_1[\text{H}_2\text{O}_2][\text{Cl}^-][\text{H}^+]+k_2^0[\text{H}_2\text{O}_2][\text{Cl}^-]
\]  

Reaction (12) is slow relative to the acid-dependent decomposition of hydrogen peroxide, reaction (2), especially in an acidic matrix which will enhance the acid-dependent reaction. The second term in eqn (13) becomes negligible in 1 M H⁺, as used in this study, so that the rate law for decomposition of hydrogen peroxide reduces to eqn (14).

\[
-d[\text{H}_2\text{O}_2]/dt = k_1[\text{H}_2\text{O}_2][\text{Cl}^-][\text{H}^+]
\]  

Zero-order reaction mechanism

If a [PtCl₄]²⁻ solution is mixed with excess hydrogen peroxide and hydrochloric acid, hydrogen peroxide is consumed via reactions denoted by \(k_{\text{H}_2\text{O}_2}\) and \(k_{\text{HOCl}}\) in the scheme outlined in eqn (3). Since oxidation of [PtCl₄]²⁻ with hypochlorous acid is rapid, the \(k_1\) reaction is expected to be the major oxidation reaction under the condition of eqn (15).³⁵⁻¹⁹

\[
k_{\text{H}_2\text{O}_2}[\text{PtCl}_4^{2-}] \ll k_1[\text{Cl}^-][\text{H}^+]
\]  

The condition is fulfilled where [PtCl₄]²⁻ ≪ 0.5 mM for \([\text{Cl}^-] = [\text{H}^+] = 1\) M. Under such conditions hydrogen peroxide will disappear via the consecutive reactions \(k_1 \rightarrow k_{\text{HOCl}}\) depicted in the scheme in (3), where \(k_1\) is the rate-determining reaction for the conditions of eqn (16).

\[
k_{\text{HOCl}}[\text{PtCl}_4^{2-}] \gg k_1[\text{Cl}^-][\text{H}^+]
\]  

Eqn (16) is fulfilled if [PtCl₄]²⁻ ≥ 4.6 × 10⁻⁹ mM. Hence, oxidation proceeds mainly via hypochlorous acid formation in the concentration range 4.6 × 10⁻⁹ M ≪ [PtCl₄]²⁻ ≪ 0.5 mM, with \([\text{Cl}^-] = [\text{H}^+] = 1\) M. Oxidation via hydrogen peroxide under these conditions becomes negligibly slow, and the conversion of \(\text{H}_2\text{O}_2 \rightarrow \text{HOCl}\) is the rate-determining step. Under such conditions the reaction appears to be pseudo-zero-order with respect to [PtCl₄]²⁻. The rate of hypochlorous acid formation \(k_1\) in the hydrogen peroxide concentration range 5–100 mM varies from 1.04 × 10⁻⁸ to 2.07 × 10⁻⁷ M⁻¹ s⁻¹ according to eqn (14). These values are in the same range as values of \(k_0\) determined for the oxidation of [PtCl₄]²⁻ reported in Table 1.

First-order reaction mechanism

If the concentration range of [PtCl₄]²⁻ > 0.5 mM, with \([\text{Cl}^-] = [\text{H}^+] = 1\) M, oxidation of [PtCl₄]²⁻ by hydrogen peroxide becomes dominant and the rate of hypochlorous acid formation is small by comparison. Under such reaction conditions, oxidation via the consecutive reactions \(k_1 \rightarrow k_{\text{HOCl}}\) competes for the oxidation of [PtCl₄]²⁻ with reaction \(k_{\text{H}_2\text{O}_2}\) depicted in the scheme given in eqn (3). In the absence of free chloride ions, oxidation of [PtCl₄]²⁻ by hydrogen peroxide is first-order with respect to both [PtCl₄]²⁻ and \(\text{H}_2\text{O}_2\) according to the rate law in eqn (9).²⁸ The “curvature” observed in kinetic traces for oxidation of [PtCl₄]²⁻ ≥ 0.2 mM (Fig. 2) thus illustrates this parallel pseudo-first-order oxidation mechanism by hydrogen peroxide. The calculated \(k_{\text{obs}}\) values according to eqn (9) for the hydrogen peroxide concentration range 15–300 mM vary between 6.28 × 10⁻⁵ and 1.28 × 10⁻³ M⁻¹ s⁻¹. The experimentally determined \(k_{\text{obs}}\) values for oxidation of [PtCl₄]²⁻ ≥ 0.2 mM in
this work as listed in Table 4 are at the upper limit of this range. A deviation between expected and calculated values may be reasonable, since estimation of $k_{obs}$ values from rate law eqn (9) does not account for any oxidation by hypochlorous acid, the parallel reaction under these reaction conditions.

**Rate dependence on chloride and acid concentrations**

The oxidation rate and order of $[\text{PtCl}_4]^{2-}$ is directly proportional to both chloride and acid concentrations as illustrated by the $k_{obs}$ values shown in Table 5. Under conditions where $[\text{Cl}^-][\text{H}^+] \gg 0.082$ $\text{M}^2$ for concentrations of $[\text{PtCl}_4]^{2-} = 0.04$ $\text{mM}$ and $[\text{H}_2\text{O}_2] = 80$ $\text{mM}$, the condition of eqn (15) will be valid. The small intercept in these graphs. The overall rate of oxidation of Pt(II) complexes by chlorine is well established. Oxidation of $[\text{PtCl}_4]^{2-}$ by chlorine will favour formation of $[\text{PtCl}_6]^{2-}$ as opposed to the formation of $[\text{PtCl}_6(\text{H}_2\text{O})]^{2-}$ when hypochlorous acid is the major oxidant. Since the $[\text{PtCl}_6(\text{H}_2\text{O})]^{2-}/[\text{PtCl}_6]^{2-}$ ratio increases under conditions that favour the pseudo-zero order mechanism, it supports the idea that hypochlorous acid is the major oxidant and not chlorine.

**Conclusions and final comments**

The mechanism of oxidation of aqueous $[\text{PtCl}_4]^{2-}$ by $\text{H}_2\text{O}_2$ in the presence of excess hydrochloric acid is remarkably complex. Our results obtained show that oxidation takes place at least via two parallel reactions with hypochlorous acid and hydrogen peroxide. The overall rate law $d[\text{Pt(IV)}]/dt = (k_0 + k_{\text{HOCl}}[\text{Pt(II)}])[\text{H}_2\text{O}_2]$ accounts for this process. For oxidation of $[\text{PtCl}_4]^{2-}$ at relatively low concentrations, $[\text{PtCl}_4]^{2-} \approx 0.5$ $\text{mM}$, hypochlorous acid formation is faster relative to oxidation of $[\text{PtCl}_4]^{2-}$ by hydrogen peroxide, as a result of the rate determining reaction $\text{H}_2\text{O}_2 + \text{H}^+ + \text{Cl}^- \rightarrow \text{HOCl} + \text{H}_2\text{O}$, such that the rate law $d[\text{Pt(IV)}]/dt = k_0[\text{H}_2\text{O}_2]$ gives the value $k_0 = (8 \pm 2) \times 10^{-7}$ $\text{s}^{-1}$ at 35 °C. For oxidation of $[\text{PtCl}_4]^{2-} \approx 0.5$ $\text{mM}$, oxidation by hydrogen peroxide becomes dominant resulting in a pseudo-first order rate law $d[\text{Pt(IV)}]/dt = k_{\text{H}_2\text{O}_2}[\text{Pt(II)}][\text{H}_2\text{O}_2]$, which results in values $k_{\text{H}_2\text{O}_2} = (1.5 \pm 0.1) \times 10^{-2}$ $\text{M}^{-1} \text{s}^{-1}$ at 35 °C.

The $\Delta H^\circ$ and $\Delta S^\circ$ values support bond formation prior to electron transfer for oxidation by both $\text{H}_2\text{O}_2$ and HOCl (Table 2). These values are comparable to values reported for the oxidation of $[\text{PtCl}_4]^{2-}$ by $\text{H}_2\text{O}_2$ in 1 $\text{M}$ $\text{HClO}_4$ (viz. $\Delta H^\circ = 76 \pm 3$ $\text{kJ mol}^{-1}$ and $\Delta S^\circ = -35 \pm 9$ $\text{J K}^{-1} \text{mol}^{-1}$) pointing toward a similar mechanism. Activation volumes estimated here for the first-order and zero-order mechanisms are almost identical (Table 3). The negative $\Delta V^\ddagger$ values are characteristic of oxidative addition reactions, i.e. $\text{H}_2\text{O}_2$ and/or HOCl-Pt bond formation prior to electron transfer, indicating that oxidation takes place via a similar mechanism for both oxidants. These observations are in line with an inner-sphere one-step two-electron transfer mechanism typical of Pt(n) square planar complexes. Since square-planar Pt(n) complexes have a vacant coordination site in the axial plane, formation of an inner-sphere complex prior to electron transfer seems reasonable.

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