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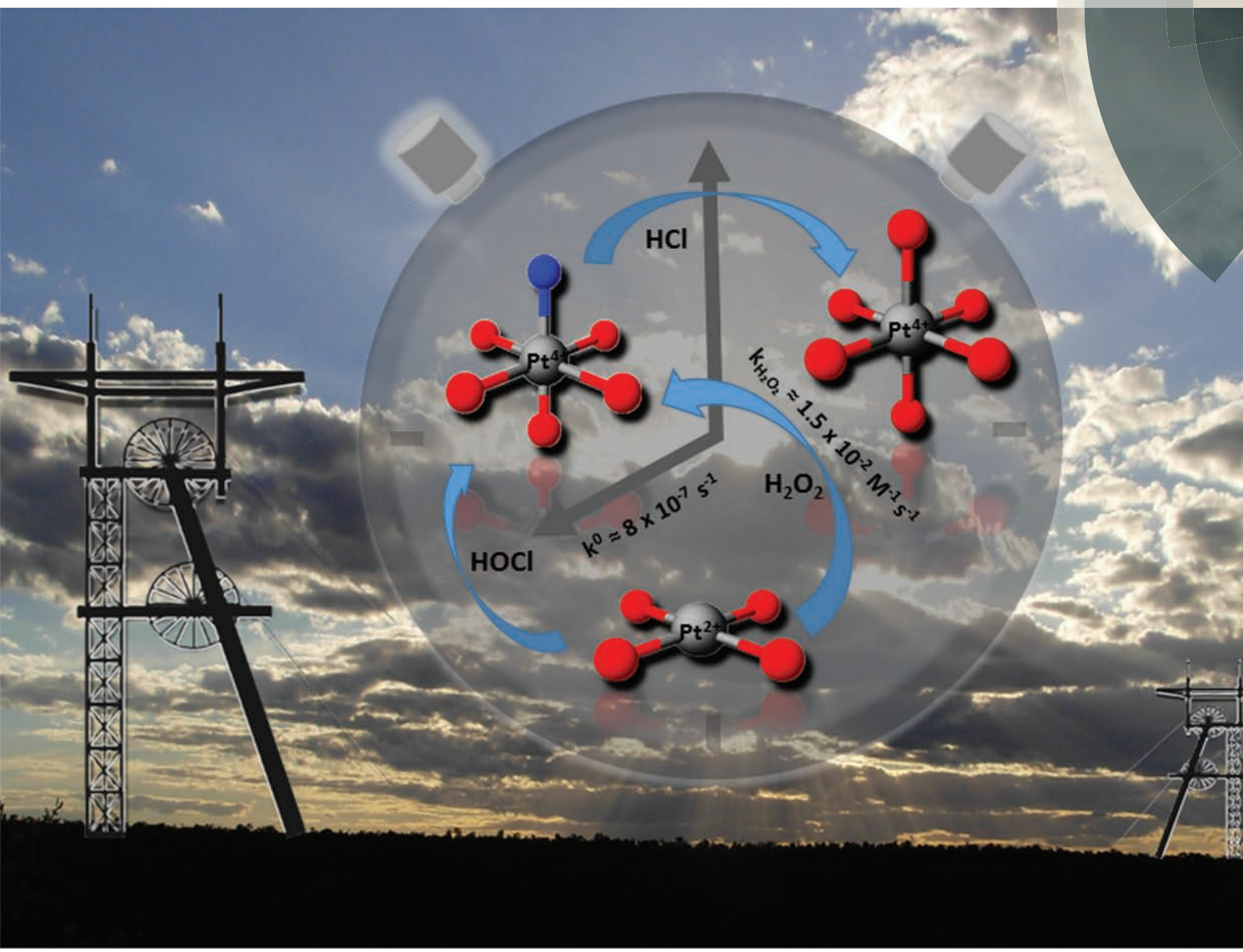

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Mechanism of tetrachloroplatinate(II) oxidation by hydrogen peroxide in hydrochloric acid solution†

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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 $d[Pt(IV)]/dt = (k^0 + k_{H_2O_2}[Pt(II)])[H_2O_2]$. For oxidation of $[PtCl_4]^{2-}$ at relatively low concentrations, $[PtCl_4]^{2-} \ll 0.5$ mM, hypochlorous acid formation is fast relative to the oxidation of $[PtCl_4]^{2-}$ by hydrogen peroxide, as a result of the rate determining reaction $H_2O_2 + H^+ + Cl^- \rightarrow HOCl + H_2O$, resulting in a rate law $d[Pt(IV)]/dt = k^0[H_2O_2]$ with a value $k^0 = (8 \pm 2) \times 10^{-7}$ s^{-1} at 35 °C. For concentrations of $[PtCl_4]^{2-} > 0.5$ mM, oxidation by hydrogen peroxide becomes dominant, resulting in the pseudo-first order rate law $d[Pt(IV)]/dt = k_{H_2O_2}[Pt(II)][H_2O_2]$ with the value $k_{H_2O_2} = (1.5 \pm 0.1) \times 10^{-2}$ M^{-1} s^{-1} at 35 °C. The final oxidation product is a mixture of $[PtCl_5(H_2O)]^-$ and $[PtCl_6]^{2-}$, with $[PtCl_6]^{2-}$ formed as a result of $[PtCl_4]^{2-}$ 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 $[PtCl_4]^{2-}$ by hydrogen peroxide in water yields *trans*-$[PtCl_4(OH)_2]^{2-}$ quantitatively according to eqn (1).[2]

$$[PtCl_4]^{2-} + H_2O_2 \rightarrow \textit{trans}\text{-}[PtCl_4(OH)_2]^{2-} \quad (1)$$

^{195}Pt 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 $[PtCl_4]^{2-}$ by hydrogen peroxide in acidic medium yields *trans*-$[PtCl_4(H_2O)_2]$, while relatively fast Pt(II) assisted ligand scrambling reactions cause a redistribution of the oxidation product(s) to form a mixture of $[PtCl_{6-n}(H_2O)_n]^{2-n}$ (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.[5] 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 $[PtCl_4]^{2-}$ 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 $[PtCl_6]^{2-}$ from *trans*-$[PtCl_4(H_2O)_2]$ 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 $[PtCl_4]^{2-}$ by hydrogen peroxide in perchloric acid has been reported.[8]

In the present study, oxidation of $[PtCl_4]^{2-}$ by hydrogen peroxide is revisited, with the added complexity of free chloride ions in solution, presenting a more complex mechanism. Formation of $[PtCl_5(H_2O)]^-$ and possibly *trans*-$[PtCl_4(H_2O)_2]$ coincides with $[PtCl_4]^{2-}$ assisted ligand exchange. Apart from

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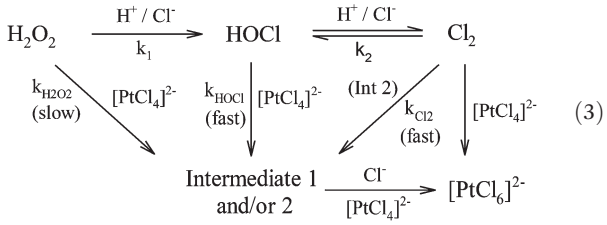
the complications associated with such reactions, hydrochloric acid catalyses the decomposition of hydrogen peroxide to form hypochlorous acid according to eqn (2).

$$H_2O_2 + H^+ + Cl^- \xrightarrow{k_1} HOCl + H_2O \quad (2)$$

Oxidation by hydrogen peroxide and hypochlorous acid may therefore coincide to yield two parallel reactions $k_{H_2O_2}$ and k_{HOCl} as depicted in the scheme in (3), where the intermediates are **1** = *trans*-$[PtCl_4(H_2O)_2]$ and **2** = $[PtCl_5(H_2O)]^-$.



(3)

Oxidation of $[PtCl_4]^{2-}$ by hydrogen peroxide is slow, whereas oxidation by hypochlorous acid is rapid in comparison, but yields the same product.[8,9] 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 $[PtCl_4]^{2-}$ 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(II) (99.9+%, K_2PtCl_4), sodium chloride (99+%, NaCl) and sodium perchlorate (99+%, $NaClO_4$) were obtained from Sigma-Aldrich. Hydrogen peroxide (30% w/w, H_2O_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 $[PtCl_4]^{2-}$ were prepared in 1 M or 2 M HCl from which further dilutions were made. Solutions containing Pt(II) were kept in the dark to eliminate photo-induced aquation reactions.[10,11] Concentrations of $[PtCl_4]^{2-}$ were evaluated by UV-Vis spectrophotometry at 331 nm (ε_{331} = 59 M^{-1} cm^{-1}) or 390 nm (ε_{390} = 56 M^{-1} cm^{-1}).[12] Chloride concentrations >0.1 M are sufficient to suppress aquation of $[PtCl_4]^{2-} \rightarrow [PtCl_3(H_2O)]^-$, and in 1 M HCl, all Pt(II) essentially exists as $[PtCl_4]^{2-}$.[13] 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.[14] Activation volume measurements for relatively fast reactions were performed on a laboratory-made high-pressure stopped-flow instrument.[15] 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 $[PtCl_5(H_2O)]^-$ and $[PtCl_6]^{2-}$ were identified in the final spectra after oxidation of $[PtCl_4]^{2-}$ by hydrogen peroxide. The $[PtCl_5(H_2O)^-]/[PtCl_6^{2-}]$ ratio is proportional to the oxidation rate which in turn is influenced by the concentration of $[PtCl_4]^{2-}$, H_2O_2, acid and chloride. Slow reactions led to almost complete conversion of $[PtCl_4]^{2-} \rightarrow [PtCl_6]^{2-}$ (>90% of Pt(IV) identified as $[PtCl_6]^{2-}$), while for fast oxidation reactions $[PtCl_5(H_2O)]^-$ is the major product. Since chloride anation of $[PtCl_5(H_2O)]^-$ is slow in the absence of $[PtCl_4]^{2-}$, conversion of $[PtCl_5(H_2O)]^- \rightarrow [PtCl_6]^{2-}$ is effectively quenched after oxidation when $[PtCl_4]^{2-}$ is depleted.[4] For the oxidation of $[PtCl_4]^{2-}$ 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 $[PtCl_5(H_2O)^-]/[PtCl_6^{2-}]$ ratio for Pt(II) ≤ 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.[2,16] For $[PtCl_5(H_2O)]^-$, ε_{230} = 12 500 M^{-1} cm^{-1} and ε_{262} = 11 600 M^{-1} cm^{-1}, whereas for $[PtCl_6]^{2-}$, ε_{230} = 3300 M^{-1} cm^{-1} and ε_{262} = 24 500 M^{-1} cm^{-1}. Since the visible spectra of $[PtCl_5(H_2O)]^-$ and $[PtCl_6]^{2-}$ are very similar (ε_{353} = 490 M^{-1} cm^{-1} for both complexes), it was not possible to determine accurate values for the $[PtCl_5(H_2O)^-]/[PtCl_6]^{2-}$ concentration ratio from the visible spectra for concentrations of Pt(II) ≥ 0.2 mM. Dilution of such solutions, however, indicated that $[PtCl_6]^{2-}$ is the dominant species. Typical spectral changes observed for the oxidation of $[PtCl_4]^{2-}$ at relatively high concentration are illustrated in Fig. 2.

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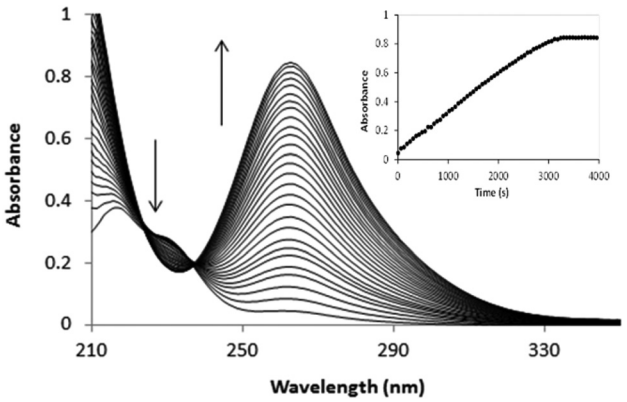

Fig. 1 Spectral changes recorded for the oxidation of 0.04 mM $[PtCl_4]^{2-}$ by 4 mM H_2O_2 in 1 M HCl.

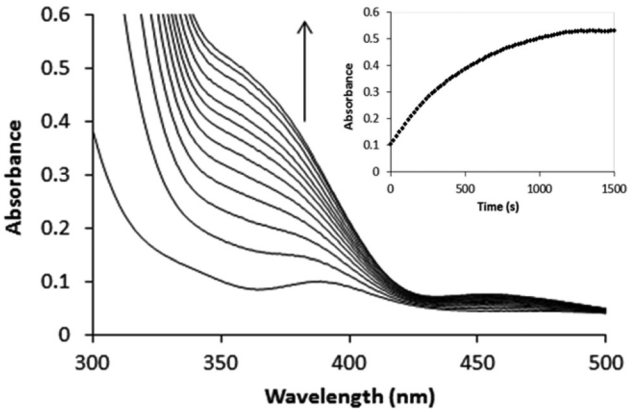

Fig. 2 Spectral changes recorded for the oxidation of 1 mM $[PtCl_4]^{2-}$ by 100 mM H_2O_2 in 1 M HCl.

Small differences in absorbance *versus* time plots collected at a specific wavelength were noticed when compared to spectra collected in the wavelength range 200–500 nm on a rapid-scan UV-Vis spectrophotometer. It has long been known that Pt(II/IV) complexes are sensitive to light resulting in photo-induced reactions.[10,11] The rates of $[PtCl_4]^{2-}$ and/or $[PtCl_6]^{2-}$ aquation as well as $[PtCl_5(H_2O)]^-$ chloride anion reactions are enhanced when spectra are recorded in the 200–500 nm wavelength range, which accounts for the small differences observed in the kinetic traces. To suppress such effects, changes in absorbance were monitored at 262 or 353 nm, close to the absorbance maxima of $[PtCl_6]^{2-}$.

Oxidation of $[Pt(CN)_4]^{2-}$ by chlorine yields *trans*-$[Pt(CN)_4Cl(H_2O)]^-$ as the primary product even when the free chloride ion concentration in solution is as high as 1 M.[9] A preference for solvent water to coordinate the negatively charged Pt(II) precursor complex, *trans* to the oxidant, was considered here. The spectrum of *trans*-$[PtCl_4(H_2O)_2]$ is known and has been reported before.[2] No evidence could be found for the presence of significant concentrations of *trans*-$[PtCl_4(H_2O)_2]$ under the reaction conditions and in the time scale studied here. Associations between $[PtCl_4]^{2-}$ and *trans*-$[PtCl_4(H_2O)_2]$, rapidly resulting in the formation of $[PtCl_5(H_2O)]^-$ and/or $[PtCl_6]^{2-}$ within the time scale investigated here, is possible as suggested by the rate constants estimated in this study (*vide infra*).

Results

Oxidation of $[PtCl_4]^{2-} \leq 0.07$ mM

Oxidation of $[PtCl_4]^{2-}$ by excess hydrogen peroxide quantitatively converts all Pt(II) → Pt(IV) so that $-d[Pt^{II}]/dt = d[Pt(IV)]/dt$. Oxidation reactions of $[PtCl_4]^{2-} \leq 0.07$ mM with $[H_2O_2]$ (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(II) and the observed rate is defined by rate law eqn (4).

$$d[Pt(IV)]/dt = k^0[H_2O_2] = k^0_{obs}\ (M\ s^{-1}) \quad (4)$$

The observed rate constants (k^0_{obs}) were obtained directly from the slope of concentration *versus* time plots. Plots of k^0_{obs} *versus* $[H_2O_2]$ are linear with zero intercept for the $[PtCl_4]^{2-}$ concentration range 0.02–0.04 mM (ESI Fig. S1A†). A small intercept ~1.0×10^{-8} M s^{-1} (ESI Fig. S1B†) was observed for $[PtCl_4]^{2-}$ concentrations between 0.05 and 0.07 mM. Pseudo-zero order rate constants k^0 (s^{-1}) calculated from eqn (5) are

Table 1 Experimental conditions and kinetic data for the oxidation of 0.02–0.07 mM $[PtCl_4]^{2-}$ yielding pseudo-zero order kinetics at 35 °C

$[PtCl_4]^{2-}$ (mM)	H_2O_2 (mM)	k^0_{obs} (M s^{-1})	$k_0 = k^0_{obs}/[H_2O_2]$ (s^{-1})
0.02	100	6.49×10^{-8}	6.49×10^{-7}
0.02	70	4.64×10^{-8}	6.63×10^{-7}
0.02	50	3.19×10^{-8}	6.38×10^{-7}
0.02	30	1.97×10^{-8}	6.56×10^{-7}
0.02	10	6.83×10^{-8}	6.83×10^{-7}
0.02	5	3.67×10^{-8}	7.34×10^{-7}
0.03	100	5.49×10^{-8}	5.49×10^{-7}
0.03	70	3.84×10^{-8}	5.49×10^{-7}
0.03	50	2.89×10^{-8}	5.78×10^{-7}
0.03	30	1.68×10^{-8}	5.60×10^{-7}
0.03	10	0.67×10^{-8}	6.74×10^{-7}
0.03	5	0.39×10^{-8}	7.74×10^{-7}
0.04	100	6.68×10^{-8}	6.68×10^{-7}
0.04	70	4.86×10^{-8}	6.94×10^{-7}
0.04	50	3.34×10^{-8}	6.68×10^{-7}
0.04	30	2.06×10^{-8}	6.87×10^{-7}
0.04	10	0.85×10^{-8}	8.52×10^{-7}
0.04	5	0.46×10^{-8}	9.12×10^{-7}
0.05	100	7.96×10^{-8}	7.96×10^{-7}
0.05	70	6.54×10^{-8}	9.34×10^{-7}
0.05	60	5.51×10^{-8}	9.18×10^{-7}
0.05	50	4.52×10^{-8}	9.04×10^{-7}
0.05	40	3.82×10^{-8}	9.55×10^{-7}
0.06	100	8.69×10^{-8}	8.69×10^{-7}
0.06	70	6.58×10^{-8}	9.4×10^{-7}
0.06	60	5.83×10^{-8}	9.72×10^{-7}
0.06	50	4.96×10^{-8}	9.92×10^{-7}
0.06	40	4.27×10^{-8}	10.68×10^{-7}
0.07	100	8.75×10^{-8}	8.75×10^{-7}
0.07	70	6.47×10^{-8}	9.24×10^{-7}
0.07	60	6.14×10^{-8}	10.23×10^{-7}
0.07	50	4.85×10^{-8}	9.70×10^{-7}
0.07	40	4.45×10^{-8}	11.13×10^{-7}
		Mean value = $(8 \pm 2) \times 10^{-7}$ s^{-1}	

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Table 2 Kinetic data for the oxidation of $[PtCl_4]^{2-}$ by H_2O_2 as a function of temperature with calculated activation parameters

$[PtCl_4]^{2-}$ (mM)	$[H_2O_2]$ (mM)	Temp. (°C)	k^0 (s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
0.04	100	15	0.76×10^{-7}	78 ± 5	−109 ± 7
0.04	100	20	1.53×10^{-7}		
0.04	100	25	2.75×10^{-7}		
0.04	100	30	4.57×10^{-7}		
0.04	100	35	6.68×10^{-7}		
			$k_{H_2O_2}$ (M^{-1} s^{-1})		
1	300	15	3.18×10^{-3}	52 ± 1	−111 ± 4
1	300	20	4.43×10^{-3}		
1	300	25	6.81×10^{-3}		
1	300	30	9.57×10^{-3}		
1	300	35	13.83×10^{-3}		

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.

$$k^0 = k^0_{obs}\,[H_2O_2]^{-1} \quad (5)$$

The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were estimated from the variation of k^0_{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 $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ 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.

$$\text{Slope} = -\Delta H^{\ddagger}/R \quad (6)$$

$$\text{Intercept} = \ln(k_B/h) + \Delta S^{\ddagger}/R \quad (7)$$

The activation volume of the oxidation reaction ($\Delta V^{\ddagger}$) 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 $\Delta V^{\ddagger}$ was obtained from the slope of the plot according to eqn (8). The calculated activation parameters are included in Table 3.

Table 3 Kinetic data for the oxidation of $[PtCl_4]^{2-}$ by H_2O_2 as a function of pressure with calculated activation volumes at 35 °C

$[PtCl_4]^{2-}$ (mM)	$[H_2O_2]$ (mM)	Pressure (MPa)	k^0 (s^{-1})	$\Delta V^{\ddagger}$ (cm^3 mol^{-1})
0.04	100	10	1.38×10^{-6}	−8 ± 2
0.04	100	51	1.59×10^{-6}	
0.04	100	91	1.79×10^{-6}	
0.04	100	132	2.02×10^{-6}	
			$k_{H_2O_2}$ (M^{-1} s^{-1})	
1	15	5	1.67×10^{-2}	−7.8 ± 0.4
1	15	51	1.86×10^{-2}	
1	15	101	2.23×10^{-2}	
1	15	152	2.58×10^{-2}	

$$[d(\ln k^0)/dP]_T = -\Delta V^{\ddagger}/RT \quad (8)$$

Oxidation of $[PtCl_4]^{2-} \geq 0.2$ mM

Oxidation of $[PtCl_4]^{2-}$ at concentration levels ≥0.2 mM by $[H_2O_2]$ 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 $[PtCl_4]^{2-}$. The observed rate constants (k_{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_{obs} values, as obtained from least-squares fits.

$$d[Pt(IV)]/dt = k_{H_2O_2}[Pt(II)][H_2O_2] \quad (9)$$

Plots of k_{obs} *versus* $[H_2O_2]$ demonstrate a linear dependence (ESI Fig. S5†), suggesting that the reaction is first order with respect to hydrogen peroxide. The second order rate constants $k_{H_2O_2}$ were calculated from eqn (10) to give the average value $(1.5 \pm 0.1) \times 10^{-2}$ M^{-1} s^{-1}.

$$k_{H_2O_2} = k_{obs}[H_2O_2]^{-1} \quad (10)$$

Oxidation of 1 mM $[PtCl_4]^{2-}$ with 300 mM H_2O_2 generated traces illustrating pseudo-first order character. Activation parameters were estimated under these reaction conditions from the variation of $k_{H_2O_2}$ in the temperature range 15–35 °C and eqn (6) and (7) (Table 2). Values of $\Delta V^{\ddagger}$ were estimated by varying the pressure between 5 and 152 MPa for the oxidation of 1 mM $[PtCl_4]^{2-}$ with 15 mM H_2O_2. A plot of ln $k_{H_2O_2}$ *versus* pressure is linear (Fig. S6, ESI†) and allowed the estimation of $\Delta V^{\ddagger}$ 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)

Table 4 Experimental conditions and kinetic data for the oxidation of 0.2–1.0 mM $[PtCl_4]^{2-}$ yielding pseudo-first order kinetics at 35 °C

$[PtCl_4]^{2-}$ (mM)	$[H_2O_2]$ (mM)	k_{obs} (s^{-1})	$k_{H_2O_2} = k_{obs}/[H_2O_2]$ (M^{-1} s^{-1})
1.0	300	3.94×10^{-3}	1.31×10^{-2}
1.0	100	1.52×10^{-3}	1.52×10^{-2}
1.0	50	0.81×10^{-3}	1.62×10^{-2}
1.0	15	0.30×10^{-3}	2.00×10^{-2}
0.6	300	4.49×10^{-3}	1.50×10^{-2}
0.6	100	1.57×10^{-3}	1.57×10^{-2}
0.6	50	0.78×10^{-3}	1.56×10^{-2}
0.6	15	0.23×10^{-3}	1.53×10^{-2}
0.2	300	3.84×10^{-3}	1.28×10^{-2}
0.2	100	1.27×10^{-3}	1.27×10^{-2}
0.2	50	0.74×10^{-3}	1.48×10^{-2}
0.2	15	0.23×10^{-3}	1.53×10^{-2}
		Mean value = $(1.5 \pm 0.1) \times 10^{-2}$ M^{-1} s^{-1}	

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Table 5 Oxidation of $[PtCl_4]^{2-}$ performed to determine the effect of chloride and acid concentrations on the observed reaction order at 35 °C

HCl (M)	$HClO_4$ (M)	$NaClO_4$ (M)	k^0_{obs} (M s^{-1})	$k^0 = k^0_{obs}/[H_2O_2]$ (s^{-1})
0.5	0.5	—	7.71×10^{-7}	9.64×10^{-6}
0.5	0.3	0.2	5.92×10^{-7}	7.40×10^{-6}
0.5	0.1	0.4	4.27×10^{-7}	5.34×10^{-6}
1	0	—	1.02×10^{-7}	1.28×10^{-6}
0.6	0.4	—	7.07×10^{-8}	8.84×10^{-7}
0.2	0.8	—	3.65×10^{-8}	4.56×10^{-7}
0.02	0.98	—	2.17×10^{-8}	2.71×10^{-7}

and hydrogen peroxide were kept constant at 0.04 mM and 80 mM, respectively. For the high end concentration range, zero-order kinetics predominated (ESI Fig. S7, ESI,† for the variation of $[Cl^-]$), while a gradual change to first-order kinetics was observed for sufficiently low concentrations of $[H^+]$ and/or $[Cl^-]$. Rate constants (k^0_{obs}) were estimated from the slope of concentration *versus* time plots. Traces that display a degree of first-order character were evaluated for the first 500 s (Fig. S7,† plots 3 and 4). The values for k^0_{obs}, obtained in this manner, are listed in Table 5. Plots of k^0_{obs} *versus* $[H^+]$ and k^0_{obs} *versus* $[Cl^-]$ are linear ($R^2 > 0.99$) with a small intercept in both cases (Fig. S8, ESI,† -3.4×10^{-7} M s^{-1} and 20.3×10^{-7} M s^{-1}, respectively), suggesting that k^0_{obs} varies with $[H^+]$ and $[Cl^-]$ according to eqn (11):

$$k^0_{obs} = a + b[Q] \quad (11)$$

where Q represents $[H^+]$ or $[Cl^-]$, $a = 3.4 \times 10^{-7}$ M s^{-1}/20.3×10^{-7} M s^{-1} and $b = 8.6 \times 10^{-7}$ s^{-1}/82.3×10^{-7} s^{-1}, respectively. These values were obtained directly from the intercept and gradient of the plots in Fig. S8.†

Discussion

Rate law for hypochlorous acid formation

An oxidation mechanism for $[PtCl_4]^{2-}$ 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]

$$H_2O_2 + Cl^- \rightarrow H_2O + ClO^- \quad (12)$$

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

$$-d[H_2O_2]/dt = k_1[H_2O_2][Cl^-][H^+] + k^0_1[H_2O_2][Cl^-] \quad (13)$$

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).

$$-d[H_2O_2]/dt = k_1[H_2O_2][Cl^-][H^+] \quad (14)$$

Zero-order reaction mechanism

If a $[PtCl_4]^{2-}$ solution is mixed with excess hydrogen peroxide and hydrochloric acid, hydrogen peroxide is consumed *via* reactions denoted by $k_{H_2O_2}$ and k_{HOCl} in the scheme outlined in eqn (3). Since oxidation of $[PtCl_4]^{2-}$ with hypochlorous acid is rapid, the k_1 reaction is expected to be the major oxidation reaction under the condition of eqn (15).[9,19]

$$k_{H_2O_2}[PtCl_4{}^{2-}] \ll k_1[Cl^-][H^+] \quad (15)$$

The condition is fulfilled where $[PtCl_4]^{2-} \ll 0.5$ mM for $[Cl^-] = [H^+] = 1$ M.‡ Under such conditions hydrogen peroxide will disappear *via* the consecutive reactions $k_1 \rightarrow k_{HOCl}$ depicted in the scheme in (3), where k_1 is the rate-determining reaction for the conditions of eqn (16).

$$k_{HOCl}[PtCl_4{}^{2-}] \gg k_1[Cl^-][H^+] \quad (16)$$

Eqn (16) is fulfilled if $[PtCl_4]^{2-} \gg 4.6 \times 10^{-9}$ mM.§ Hence, oxidation proceeds mainly *via* hypochlorous acid formation in the concentration range 4.6×10^{-9} mM $\ll [PtCl_4]^{2-} \ll 0.5$ mM, with $[Cl^-] = [H^+] = 1$ M. Oxidation *via* hydrogen peroxide under these conditions becomes negligibly slow, and the conversion of $H_2O_2 \rightarrow HOCl$ is the rate-determining step. Under such conditions the reaction appears to be pseudo-zero-order with respect to $[PtCl_4]^{2-}$. 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 s^{-1} according to eqn (14). These values are in the same range as values of k^0 determined for the oxidation of $[PtCl_4]^{2-}$ reported in Table 1.

First-order reaction mechanism

If the concentration range of $[PtCl_4]^{2-} > 0.5$ mM, with $[Cl^-] = [H^+] = 1$ M, oxidation of $[PtCl_4]^{2-}$ 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 $k_1 \rightarrow k_{HOCl}$ competes for the oxidation of $[PtCl_4]^{2-}$ with reaction $k_{H_2O_2}$ depicted in the scheme given in eqn (3). In the absence of free chloride ions, oxidation of $[PtCl_4]^{2-}$ by hydrogen peroxide is first-order with respect to both $[PtCl_4]^{2-}$ and H_2O_2 according to the rate law in eqn (9).[8] The "curvature" observed in kinetic traces for oxidation of $[PtCl_4]^{2-} \geq 0.2$ mM (Fig. 2) thus illustrates this parallel pseudo-first-order oxidation mechanism by hydrogen peroxide. The calculated k_{obs} values according to eqn (9) for the hydrogen peroxide concentration range 15–300 mM vary between 6.38×10^{-5} and 1.28×10^{-3} M s^{-1}. The experimentally determined k_{obs} values for oxidation of $[PtCl_4{}^{2-}] \geq 0.2$ mM in

‡ Calculated from eqn (15) with $k_{H_2O_2} = 4.25 \times 10^{-3}$ M^{-1} s^{-1} and $k_1 = 2.07 \times 10^{-6}$ M^{-2} s^{-1}.[8,18]

§ Calculated from eqn (16) with $k_{HOCl} = (4.5 \pm 0.5) \times 10^5$ M^{-1} s^{-1}.[9]

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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 $[PtCl_4]^{2-}$ is directly proportional to both chloride and acid concentrations as illustrated by the k_{obs} values shown in Table 5. Under conditions where $[Cl^-][H^+] \gg 0.082\ M^2$ for concentrations of $[PtCl_4]^{2-}$ = 0.04 mM and $[H_2O_2]$ = 80 mM, the condition of eqn (15) will be valid.‡ On the other hand, if $[Cl^-][H^+] \ll 0.082\ M^2$, the first-order mechanism becomes dominant resulting in more prominent "curvature" in the kinetic trace 4 as indicated in Fig. S7, ESI.†

Under these conditions, oxidation is first-order with respect to both $[Cl^-]$ and $[H^+]$ as suggested by the linear dependence of k^0_{obs} on $[Cl^-]$ and $[H^+]$ (Fig. S8, ESI†). In order to keep the rate law consistent for the range of reaction conditions investigated, values of k^0_{obs} were obtained directly from concentration *versus* time plots. This approach does not account for the parallel first-order oxidation reaction, a possible consequence of the small intercept in these graphs. The overall rate law accounting for both reaction pathways is expressed by eqn (17), and is the sum of eqn (4) and (9).

$$d[Pt(IV)]/dt = (k^0 + k_{H_2O_2}[Pt(II)])[H_2O_2] \quad (17)$$

Chlorine as an oxidant

Several attempts to determine a rate constant for the oxidation of $[PtCl_4]^{2-}$ by chlorine have failed.[9,20,21] Nevertheless, the rapid oxidation of Pt(II) complexes by chlorine is well established. Oxidation of $[Pt(CN)_4]^{2-}$ by chlorine for instance exceeds the oxidation rate of $[Pt(CN)_4]^{2-}$ by hypochlorous acid by five orders of magnitude.[9] Hypochlorous acid and chlorine are in rapid equilibrium in aqueous solution according to eqn (18).

$$HOCl + H^+ + Cl^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Cl_2 + H_2O \quad (18)$$

Equilibrium (18) has been responsible for some of the confusion in the literature, where apparent oxidation by chlorine was in fact oxidation by hypochlorous acid.[9,20,21] If the formation of chlorine as a result of eqn (18) and subsequent oxidation of $[PtCl_4]^{2-}$ exceeds the rate of formation and oxidation by hypochlorous acid as defined by eqn (19), the overall oxidation reaction will proceed *via* consecutive reactions depicted by $k_1 \rightarrow k_2 \rightarrow k_{Cl2}$ in the scheme given in eqn (3) and chlorine must be considered as an oxidant in the mechanism discussed here.

$$k_{HOCl}[PtCl_4{}^{2-}] \ll k_2[H^+][Cl^-] \quad (19)$$

Chlorine is the dominant species present in hypochlorous acid/chlorine solutions at equilibrium (> 99.9%, Cl_2 = 1 mM). However, since $[PtCl_4]^{2-}$ is present in large excess relative to the catalytic concentrations of hypochlorous acid formed by eqn (2), chlorine hydrolysis *via* k_{-2} according to eqn (19) will be negligibly slow by comparison. The value of k_2 is given as $2.66 \times 10^4\ M^{-2}\ s^{-1}$ in the literature.[9] Substituting this value into eqn (19) gives the condition that $[Pt(II)] \ll 60$ mM when $[H^+]$ and $[Cl^-]$ are 1 M. This is the case in our solutions where $[Pt(II)]$ = 1–20 mM, and implies that Cl_2 must be considered as an oxidant here if we assume that $k_{Cl2} \geq k_{H_2O_2}$, which is not unreasonable. Oxidation of $[PtCl_4]^{2-}$ by chlorine will favour formation of $[PtCl_6]^{2-}$ as opposed to the formation of $[PtCl_5(H_2O)]^-$ when hypochlorous acid is the major oxidant. Since the $[PtCl_5(H_2O)]^-/[PtCl_6]^{2-}$ 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 $[PtCl_4]^{2-}$ by H_2O_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 $d[Pt(IV)]/dt = (k^0 + k_{H_2O_2}[Pt(II)])[H_2O_2]$ accounts for this process. For oxidation of $[PtCl_4]^{2-}$ at relatively low concentrations, $[PtCl_4]^{2-} \ll 0.5$ mM, hypochlorous acid formation is faster relative to oxidation of $[PtCl_4]^{2-}$ by hydrogen peroxide, as a result of the rate determining reaction $H_2O_2 + H^+ + Cl^- \rightarrow HOCl + H_2O$, such that the rate law $d[Pt(IV)]/dt = k^0[H_2O_2]$ gives the value $k_1 = (8 \pm 2) \times 10^{-7}\ s^{-1}$ at 35 °C. For oxidation of $[PtCl_4]^{2-} \gg 0.5$ mM, oxidation by hydrogen peroxide becomes dominant resulting in a pseudo-first order rate law $d[Pt(IV)]/dt = k_{H_2O_2}[Pt(II)][H_2O_2]$, which results in values $k_{H_2O_2} = (1.5 \pm 0.1) \times 10^{-2}\ M^{-1}\ s^{-1}$ at 35 °C.

The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values support bond formation prior to electron transfer for oxidation by both H_2O_2 and HOCl (Table 2). These values are comparable to values reported for the oxidation of $[PtCl_4]^{2-}$ by H_2O_2 in 1 M $HClO_4$ (*viz.* $\Delta H^{\ddagger}$ = 76 ± 3 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −35 ± 9 J K^{-1} mol^{-1}) pointing toward a similar mechanism.[8] 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.* H_2O_2–Pt and/or HOCl–Pt bond formation prior to electron transfer, indicating that oxidation takes place *via* a similar mechanism for both oxidants.[22] These observations are in line with an inner-sphere one-step two-electron transfer mechanism typical of Pt(II) square planar complexes. Since square-planar Pt(II) 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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