

## Mechanisms for Acceleration of Halide Anation Reactions of Platinum(IV) Complexes. REOA versus Ligand Assistance and Platinum(II) Catalysis Without Central Ion Exchange†

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### Abstract

Chloride anation of *trans*-Pt(CN)<sub>4</sub>ClOH<sub>2</sub><sup>-</sup> has been studied with and without Pt(CN)<sub>4</sub><sup>2-</sup> present at 25.0 °C by use of stopped-flow and conventional spectrophotometry and a 1.00 M perchlorate medium. The rate law in the absence of Pt(CN)<sub>4</sub><sup>2-</sup> is

$$\text{Rate} = (p_1 + p_2[\text{H}^+])[\text{Cl}^-]^2[\text{complex}]/(1 + q[\text{Cl}^-])$$

with  $p_1 = (3.0 \pm 0.1) \times 10^{-5} \text{ M}^{-2} \text{ s}^{-1}$ ,  $p_2 = (3.6 \pm 0.1) \times 10^{-5} \text{ M}^{-3} \text{ s}^{-1}$  and  $q = (0.62 \pm 0.02) \text{ M}^{-1}$ . It is compatible with a chloride assistance via an intermediate of the type Cl–Cl–Pt(CN)<sub>4</sub>···OH<sub>2</sub><sup>2-</sup>, in which the reactivity of the aqua ligand is enhanced due to a partial reduction of the platinum. This mechanism of halide assistance is in principle the same as the modified reductive elimination oxidative addition (REOA) mechanism proposed by Poë, in which the intermediate is not split into free halogen, platinum(II) and water, and in which electron transfer not necessarily involves complete reduction to platinum(II). To avoid confusion with complete reductive eliminations, reactions without split of the intermediates are here termed halide-assisted reactions. The pH-dependence indicates acid catalysis via a protonated intermediate Cl–Cl–Pt(CN)<sub>4</sub>···OH<sub>3</sub><sup>-</sup>.

The Pt(CN)<sub>4</sub><sup>2-</sup>-accelerated path has the rate law

$$\text{Rate} = \frac{k[\text{H}^+]}{K_a + [\text{H}^+]} [\text{Cl}^-] [\text{Pt(CN)}_4^{2-}] [\text{complex}]$$

where  $k = (39.9 \pm 0.5) \text{ M}^{-2} \text{ s}^{-1}$  and  $K_a = (4.0 \pm 0.2)10^{-2} \text{ M}$  is the protolysis constant of *trans*-Pt(CN)<sub>4</sub>ClOH<sub>2</sub><sup>-</sup>.

Reaction between PtCl<sub>5</sub>OH<sub>2</sub><sup>-</sup> and chloride is accelerated by Pt(CN)<sub>4</sub><sup>2-</sup> and gives PtCl<sub>6</sub><sup>2-</sup> as the reaction product. The rate law is

$$\text{Rate} = k[\text{Cl}^-] [\text{Pt(CN)}_4^{2-}] [\text{PtCl}_5\text{OH}_2^-]$$

with  $k = (5.6 \pm 0.2)10^{-3} \text{ M}^{-2} \text{ s}^{-1}$  at 35.0 °C and for a 1.50 M perchlorate acid medium. The reaction takes place without central ion exchange. Alternative mechanisms with two consecutive central ion exchanges can be excluded. The role of Pt(CN)<sub>4</sub><sup>2-</sup> in this reaction is very similar to that of the assisting halide in the halide assisted anations.

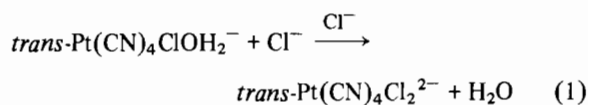
Reaction between *trans*-Pt(CN)<sub>4</sub>ClOH<sub>2</sub><sup>-</sup> and PtCl<sub>4</sub><sup>2-</sup> gives Pt(CN)<sub>4</sub><sup>2-</sup> and PtCl<sub>5</sub>OH<sub>2</sub><sup>-</sup> as products and has the rate law

$$\text{Rate} = k[\text{PtCl}_4^{2-}] [\text{trans-Pt(CN)}_4\text{ClOH}_2^-]$$

with  $k = (3.32 \pm 0.02) \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C for a 1.00 M perchloric acid medium. The formation of an aqua complex as the primary reaction product and the rate independent of [Cl<sup>-</sup>] shows that formation of a bridged intermediate of the type Pt(II)Cl<sub>4</sub>–Cl–Pt(IV)(CN)<sub>4</sub>–OH<sub>2</sub><sup>3-</sup> is formed in the initial reaction step, not five-coordinated PtCl<sub>5</sub><sup>3-</sup>.

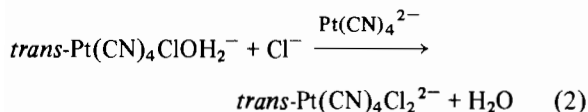
### Introduction

Oxidation of Pt(CN)<sub>4</sub><sup>2-</sup> by chlorine in aqueous solution has been the subject of a previous study [1]. Depending on pH and chloride concentration, reaction takes place with either molecular chlorine, hypochlorous acid or hypochlorite as oxidants, and those parallel pathways give different oxidation products. In acidic solution, oxidation with Cl<sub>2</sub> is predominant and *trans*-Pt(CN)<sub>4</sub>ClOH<sub>2</sub><sup>-</sup> is the reaction product [1]. The present report describes a study of the subsequent and much slower reaction between *trans*-Pt(CN)<sub>4</sub>ClOH<sub>2</sub><sup>-</sup> and chloride to form *trans*-Pt(CN)<sub>4</sub>Cl<sub>2</sub><sup>2-</sup>. This process is accelerated both by free chloride and by Pt(CN)<sub>4</sub><sup>2-</sup> according to eqns. (1) and (2).



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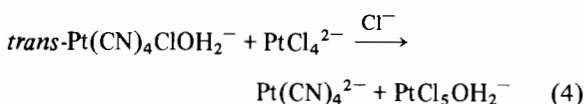
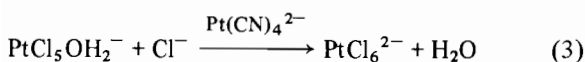
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The platinum(II)-accelerated reaction (2) has been studied previously by Elding and Gustafson [2] who interpreted their experiments in terms of a modification of the mechanism of Basolo, Pearson *et al.* for platinum(II)-accelerated substitutions on platinum(IV) [3–5], *cf.* also ref. 6.

The analogous bromide anation of *trans*-Pt(CN)<sub>4</sub>-BrOH<sub>2</sub><sup>-</sup> has been studied earlier by several groups of workers. This reaction is also accelerated by free bromide [7–10] and by Pt(CN)<sub>4</sub><sup>2-</sup> [9]. The previous work on the bromide assisted reaction was more recently extended to much higher bromide concentrations by Vuik and Poë [11], who summarized their own and all other experimental results in terms of a modified REOA-mechanism, which appears to be very similar to the ligand-assistance-mechanism suggested by others [6–10, 12–14]. The present results for reaction (1) can be used to further elucidate those mechanisms.

For some platinum(II)-accelerated reactions, for instance reaction (2), it has been previously suggested [14] that the mechanistic role of the platinum(II) complex might be similar to that of the assistant halides in the halide assisted reactions. In those cases no central ion exchange is expected to be associated with the platinum(II)-accelerated ligand substitution. The kinetics of reactions (3) and (4) have been studied to check this suggestion.



Reaction (3) appears to be an example of a reaction which is accelerated by platinum(II) without any central ion exchange.

## Experimental

### Chemicals and Solutions

Potassium tetracyanoplatinate(II) trihydrate, potassium chloroplatinate(II) and potassium chloroplatinate(IV) (all from Johnson and Matthey), sodium chloride (Merck Suprapur), perchloric acid (Baker's p.a.) and hydrochloric acid (Merck p.a.) were used without further purification. Sodium perchlorate was recrystallized once. Water was doubly distilled from quartz.

Aqueous stock solutions of chlorine (*ca.* 70 mM) were prepared from potassium permanganate (Merck p.a.) and hydrochloric acid as described previously [1]. Solutions of *trans*-Pt(CN)<sub>4</sub>ClOH<sub>2</sub><sup>-</sup> were prepared by oxidation of 2.0 mM Pt(CN)<sub>4</sub><sup>2-</sup> with chlorine in an aqueous solution containing HCl, HClO<sub>4</sub>, NaCl and NaClO<sub>4</sub> with the ionic strength 1.00 M, whereafter residual chlorine was removed by flushing with nitrogen. Those solutions were freshly prepared before use. In 1.00 M chloride medium, the concentration of *trans*-Pt(CN)<sub>4</sub>ClOH<sub>2</sub><sup>-</sup> slowly decreases due to reaction (1), whereas if oxidation is performed in perchloric acid without added chloride, a fairly rapid chloride anation takes place, accelerated by catalytic concentrations of Pt(II), giving complete conversion to *trans*-Pt(CN)<sub>4</sub>Cl<sub>2</sub><sup>2-</sup> within a few hours [15].

Solutions of PtCl<sub>5</sub>OH<sub>2</sub><sup>-</sup> were prepared by oxidation of a freshly prepared solution of 2.0 mM PtCl<sub>4</sub><sup>2-</sup> in aqueous perchloric acid (1.50 M) with excess chlorine. After flushing with nitrogen a small amount of aqueous chlorine was added to prevent formation of catalytic concentrations of Pt(III) (0.02 mM chlorine to 0.10 mM Pt). Those solutions were protected from light.

All solutions had the ionic strength 1.00 M, where not otherwise stated.

### Spectra and Stoichiometry

Spectra were recorded by use of a Beckman 25 recording instrument and Hellma Quartz Suprasil cells. Figure 1 shows spectra of the relevant complexes.

Figure 2a shows the spectrum of the product mixture of reaction (3) at equilibrium, obtained by equilibrating a solution of 2.0 mM Pt(CN)<sub>4</sub><sup>2-</sup> and 2.0 mM PtCl<sub>5</sub>OH<sub>2</sub><sup>-</sup> in 1.00 M HCl in the dark at 25.0 °C, for three weeks. The spectrum is identical to the sum of the spectra of 2.0 mM Pt(CN)<sub>4</sub><sup>2-</sup> and 2.0 mM PtCl<sub>6</sub><sup>2-</sup> (*cf.* Fig. 1), in accordance with the stoichiometry of reaction (3).

Figure 2b shows the spectrum of the product mixture of reaction (4) at equilibrium, obtained by reacting 2.0 mM Pt(CN)<sub>4</sub>ClOH<sub>2</sub><sup>-</sup> and 2.0 mM PtCl<sub>4</sub><sup>2-</sup>

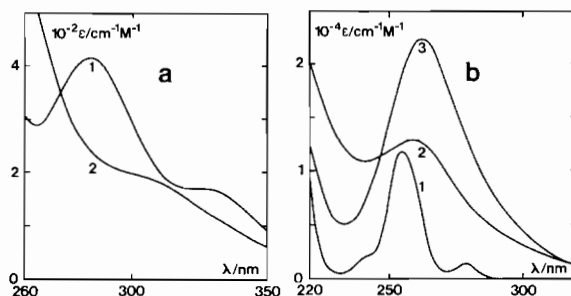


Fig. 1. Spectra of (a) curve 1, *trans*-Pt(CN)<sub>4</sub>Cl<sub>2</sub><sup>2-</sup>, curve 2, *trans*-Pt(CN)<sub>4</sub>ClOH<sub>2</sub><sup>-</sup>; (b) curve 1, Pt(CN)<sub>4</sub><sup>2-</sup>, curve 2, PtCl<sub>5</sub>OH<sub>2</sub><sup>-</sup> and curve 3, PtCl<sub>6</sub><sup>2-</sup>. Medium 1.00 M HCl.

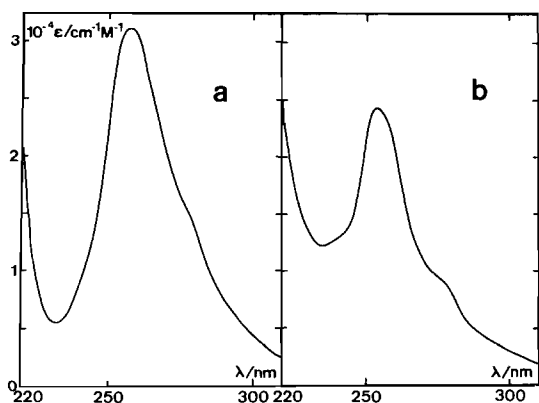


Fig. 2. (a) Spectrum of the product of reaction (3) three weeks after mixing, identical to a calculated spectrum of  $\text{PtCl}_6^{2-} + \text{Pt}(\text{CN})_4^{2-}$ . (b) Spectrum of the product of reaction (4) 1 h after mixing, identical to a calculated spectrum of  $\text{PtCl}_5\text{OH}_2^- + \text{Pt}(\text{CN})_4^{2-}$ . Conditions: 2.0 mM reactants kept in the dark at 25 °C, 1.00 M HCl medium.

in 1.00 M hydrochloric acid for 1 h in the dark at 25.0 °C. This spectrum is identical to one calculated for a mixture of 2.0 mM  $\text{Pt}(\text{CN})_4^{2-}$  and 2.0 mM  $\text{PtCl}_5\text{OH}_2^-$  (cf. Fig. 1), in accordance with the stoichiometry of reaction (4).

### Kinetics

Rapid reactions were followed by use of a modified Durrum-Gibson stopped-flow instrument, and slower ones by a Zeiss Quartz Spectrophotometer PMQ II, with a thermostated cell compartment and recorder. Pseudo-first-order rate constants were evaluated from logarithmic plots or directly from transmittance vs. time curves by use of least-squares programs. Rate constants listed in the Tables represent the mean of several experiments.

Reaction (1) was monitored by use of the Zeiss instrument at 290 nm, where there is an increase of

TABLE I. Observed Rate Constants for Reaction (1)<sup>a</sup>

[Cl <sup>-</sup> ] (M)	10 <sup>5</sup> k <sub>exp</sub> (s <sup>-1</sup> )		
	[H <sup>+</sup> ] = 0.20 M	[H <sup>+</sup> ] = 0.50 M	[H <sup>+</sup> ] = 1.00 M
0.20	—	—	0.228
0.30	0.282	0.37	0.49
0.40	0.47	0.61	0.84
0.50	0.71	0.91	1.27
0.60	—	1.25	1.72
0.70	1.27	1.66	2.25
0.80	1.60	2.05	2.78
0.90	—	—	3.4
1.00	2.27	2.92	4.0

<sup>a</sup>C<sub>Pt(IV)</sub> = 1.0 × 10<sup>-3</sup> M, 25.0 °C, 1.00 M ionic strength, 290 nm.

absorbance, cf. Fig. 1a. Reaction was started by mixing equal volumes of aqueous solutions of 2.0 × 10<sup>-3</sup> M  $\text{Pt}(\text{CN})_4^{2-}$  and ca. 6 × 10<sup>-3</sup> M chlorine which had [H<sup>+</sup>] = 0.20, 0.50 or 1.00 M, 0.20 M ≤ [Cl<sup>-</sup>] ≤ 1.00 M and ionic strength 1.00 M (mixed from HCl, HClO<sub>4</sub>, NaCl and NaClO<sub>4</sub>). After flushing with nitrogen to remove residual chlorine a small amount of aqueous chlorine was added (to ca. 0.1 mM) to the solution to suppress catalysis by small concentrations of  $\text{Pt}(\text{CN})_4^{2-}$ . This is important, since the  $\text{Pt}(\text{CN})_4^{2-}$ -accelerated reaction (2) is several orders of magnitude faster than reaction (1). The reacting solutions were protected from light in flasks in a closed thermostat, and samples were withdrawn at intervals of time. Table I summarizes those experiments\*.

For reaction (2), 2.0 × 10<sup>-3</sup> M  $\text{Pt}(\text{CN})_4^{2-}$  was oxidized by an excess of chlorine in a perchlorate solution which also contained acid (0.01, 0.02 or 1.00 M) and all chloride required for the experiment for [Cl<sup>-</sup>] ≤ 0.500 M. After flushing with nitrogen, the kinetics were started by mixing this solution of  $\text{Pt}(\text{CN})_4\text{ClOH}_2^-$  directly in the stopped-flow apparatus (or with syringes in a spectrophotometer cell) with an equal volume of  $\text{Pt}(\text{CN})_4^{2-}$  (2.0 to 12.0 mM) in a perchlorate medium with the same pH and, for experiments with [Cl<sup>-</sup>] > 0.500 M, containing 0.60 to 1.00 M chloride also. Chloride concentrations after mixing were 0.20 to 1.00 M. The reaction was monitored at 288 nm, cf. Fig. 1a. The experiments are summarized in Table II.

Reaction (3) is slow and was followed at 35.0 °C by use of an ionic strength of 1.50 M. The kinetics were started by addition of 50 ml 0.40 mM  $\text{PtCl}_5\text{OH}_2^-$  in 1.50 M perchloric acid to thermostated flasks containing 150 ml  $\text{Pt}(\text{CN})_4^{2-}$  (0.67 to 2.67 mM), chloride (0.80 to 1.53 mM) and 1.50 M acid. Solutions were protected from illumination to prevent formation of Pt(III) which might catalyze the reaction. To further prohibit such catalysis, chlorine was added to the  $\text{PtCl}_5\text{OH}_2^-$ -solution (ca. 0.02 mM Cl<sub>2</sub> in the reacting solution). A corresponding concentration of *trans*- $\text{Pt}(\text{CN})_4\text{Cl}_2^{2-}$  is then rapidly formed from the  $\text{Pt}(\text{CN})_4^{2-}$  present. This complex is an oxidant which prevents Pt(III) formation from  $\text{PtCl}_5\text{OH}_2^-$ . Samples were withdrawn at intervals of time and the reaction was observed as an absorbance

\*In the previous study [2] reaction (1) was not observed and it was concluded that this was due to the slowness of the reaction even at 50 °C. In the light of the present results a more probable explanation is that the solutions of *trans*- $\text{Pt}(\text{CN})_4\text{ClOH}_2^-$  used in ref. 2 were not freshly prepared and that most of the platinum had been transformed into *trans*- $\text{Pt}(\text{CN})_4\text{Cl}_2^{2-}$  before observations started. Oxidation of  $\text{Pt}(\text{CN})_4^{2-}$  in chloride-deficient solutions as in ref. 2 gives *trans*- $\text{Pt}(\text{CN})_4\text{Cl}_2^{2-}$  within 1 h at 25 °C due to a rapid reaction accelerated by catalytic amounts of  $\text{Pt}(\text{CN})_4^{2-}$  after flushing with nitrogen [15].

TABLE II. Observed Rate Constants for Reaction (2)<sup>a</sup>

10 <sup>3</sup> [Pt(CN) <sub>4</sub> <sup>2-</sup> ] (M)	[Cl <sup>-</sup> ] (M)	10 <sup>2</sup> k <sub>exp</sub> (s <sup>-1</sup> )		
		[H <sup>+</sup> ] = 0.01 M	[H <sup>+</sup> ] = 0.02 M	[H <sup>+</sup> ] = 1.00 M
1.0	0.20			0.76
1.0	0.30			1.23
1.0	0.50			1.91
1.0	0.80			3.1
1.0	1.00			3.8
2.0	0.20			1.74
2.0	0.30			2.27
2.0	0.40			3.1
2.0	0.50	0.82		3.9
2.0	1.00	1.46	2.70	7.9
4.0	0.50	1.63	2.77	7.9
4.0	0.80	2.40	4.6	
4.0	1.00	3.0	5.6	
6.0	0.20	1.03	1.90	
6.0	0.40	1.91	3.6	
6.0	0.50	2.35	4.2	

<sup>a</sup>C<sub>Pt(IV)</sub> = 1.0 × 10<sup>-3</sup> M, 25.0 °C, 1.00 M ionic strength, 288 nm.

TABLE III. Observed Rate Constants for Reaction (3)<sup>a</sup>

10 <sup>3</sup> [Pt(CN) <sub>4</sub> <sup>2-</sup> ] (M)	[Cl <sup>-</sup> ] (M)	10 <sup>6</sup> k <sub>exp</sub> (s <sup>-1</sup> )	10 <sup>3</sup> k <sub>exp</sub> /([Pt(CN) <sub>4</sub> <sup>2-</sup> ][Cl <sup>-</sup> ]) (M <sup>-2</sup> s <sup>-1</sup> )
0.48	1.15	2.98	5.4
0.98	0.80	4.4	5.6
0.98	1.00	5.6	5.7
1.98	0.60	6.6	5.6
1.98	0.85	9.3	5.5

<sup>a</sup>C<sub>Pt(IV)</sub> = 1.0 × 10<sup>-4</sup> M, 35 °C, 1.50 M ionic strength, [H<sup>+</sup>] = 1.50 M, 295 nm. Reacting solutions protected from light.

increase at 295 nm, where Pt(CN)<sub>4</sub><sup>2-</sup> is transparent (*cf.* Fig. 1b). Table III reviews those measurements\*.

Reaction (4) was observed as an absorbance increase at 285 nm, where *trans*-Pt(CN)<sub>4</sub>ClOH<sub>2</sub><sup>-</sup>, PtCl<sub>4</sub><sup>2-</sup> (the excess reactant), and Pt(CN)<sub>4</sub><sup>2-</sup> absorb little (*ca.* 200, 50 and 500 cm<sup>-1</sup> M<sup>-1</sup>, respectively), whereas the product PtCl<sub>5</sub>OH<sub>2</sub><sup>-</sup> has a molar absorptivity of *ca.* 5500 cm<sup>-1</sup> M<sup>-1</sup> (*cf.* Fig. 1). Reaction was started by mixing equal volumes of freshly prepared, thermostated solutions of *trans*-Pt(CN)<sub>4</sub>ClOH<sub>2</sub><sup>-</sup>

\*Those solutions of PtCl<sub>5</sub>OH<sub>2</sub><sup>-</sup> also contain some PtCl<sub>4</sub>(OH<sub>2</sub>)<sub>2</sub>, and during the first 1 h period of reaction (3), the Pt(CN)<sub>4</sub><sup>2-</sup>-accelerated chloride anation of PtCl<sub>4</sub>(OH<sub>2</sub>)<sub>2</sub> was observed as a small, additional increase of absorbance. Separate experiments with larger concentrations of PtCl<sub>4</sub>(OH<sub>2</sub>)<sub>2</sub> indicated that this reaction has a rate constant of 2.5 × 10<sup>-2</sup> M<sup>-1</sup> s<sup>-1</sup> for [Cl<sup>-</sup>] = 1.00 M, [H<sup>+</sup>] = 1.50 M and ionic strength 1.50 M, *ie.* about five times greater than that of reaction (3). About the same ratio between rate constants was previously found for the corresponding reactions with PtCl<sub>4</sub><sup>2-</sup> as a catalyst [6].

TABLE IV. Observed Rate Constants for Reaction (4)<sup>a</sup>

10 <sup>4</sup> [PtCl <sub>4</sub> <sup>2-</sup> ] (M)	[Cl <sup>-</sup> ] (M)	10 <sup>3</sup> k <sub>exp</sub> (s <sup>-1</sup> )
5.22	0.25	1.60
5.37	0.50	1.64
5.37	1.00	1.69
10.7	1.00	3.4
19.9	1.00	6.6

<sup>a</sup>C<sub>Pt(IV)</sub> = 2.62 × 10<sup>-5</sup> M, 25.0 °C, 1.00 M ionic strength, [H<sup>+</sup>] = 1.00 M, 285 nm.

(5.2 × 10<sup>-5</sup> M) and PtCl<sub>4</sub><sup>2-</sup> (1.0 to 4.0 mM) directly in a 1 cm thermostated cell in the Zeiss instrument with recorder, by use of thermostated syringes. Both solutions had the same concentration of chloride (0.25 to 1.00 M) and acid (1.00 M). Table IV reviews those experiments.

## Results

The plots of Fig. 3 indicate a first-order rate constant for reaction (1) according to eqn. (5).

$$k_{\text{exp}} = \frac{p'[\text{Cl}^-]^2}{1 + q[\text{Cl}^-]}; \quad \text{pH} = \text{const.} \quad (5)$$

The parameter  $q = (0.62 \pm 0.01) \text{ M}^{-1}$  is independent of pH, whereas  $p' = (3.7 \pm 0.3) \times 10^{-5}$ ,  $(4.7 \pm 0.3) \times 10^{-5}$  and  $(6.6 \pm 0.3) \times 10^{-5} \text{ M}^{-2} \text{ s}^{-1}$  for [H<sup>+</sup>] = 0.200, 0.50 and 1.00 M, respectively. The pH-dependence is best described by eqn. (6)

$$p' = p_1 + p_2[\text{H}^+] \quad (6)$$

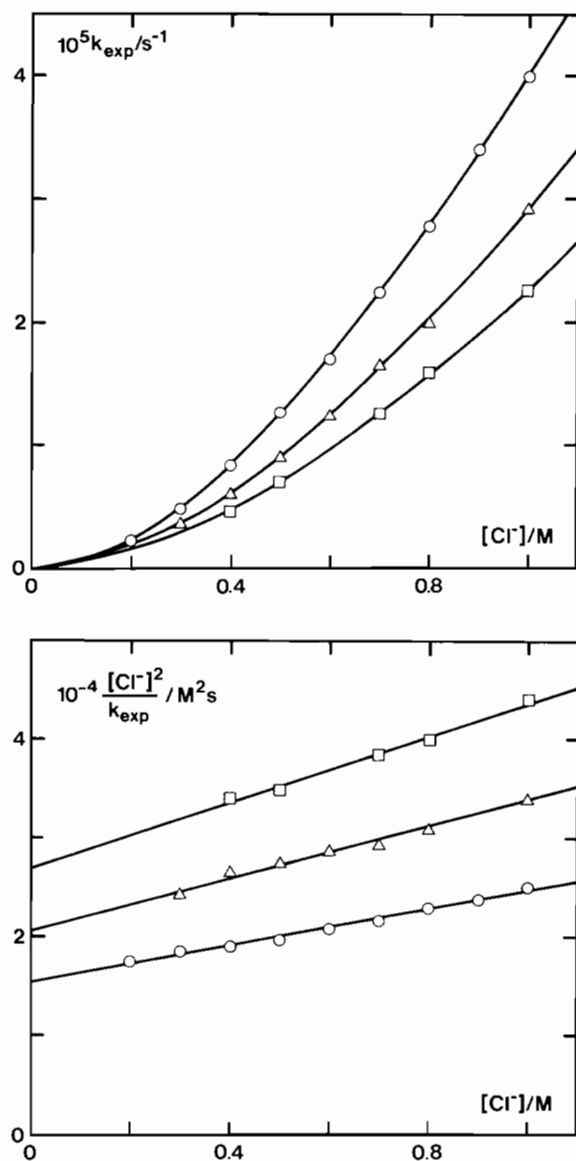


Fig. 3. Plots of  $k_{\text{exp}}$  and  $[\text{Cl}^-]^2/k_{\text{exp}}$  vs.  $[\text{Cl}^-]$  for reaction (1) at 25.0 °C and 1.00 M ionic strength.  $[\text{H}^+]$  was 0.05 M ( $\circ$ ), 0.20 M ( $\Delta$ ) and 1.00 M ( $\square$ ).

where  $p_1 = (3.0 \pm 0.1) \times 10^{-5} \text{ M}^{-2} \text{ s}^{-1}$  and  $p_2 = (3.6 \pm 0.1) \times 10^{-5} \text{ M}^{-3} \text{ s}^{-1}$ . The rate law is given by eqn. (7), where complex denotes the disappearing platinum-(IV) complex

$$\text{Rate} = (p_1 + p_2[\text{H}^+]) \frac{[\text{Cl}^-]^2}{1 + q[\text{Cl}^-]} [\text{complex}] \quad (7)$$

Figure 4 shows plots for reaction (2) which give the first-order rate constant of eqn. (8).

$$k_{\text{exp}} = r[\text{Cl}^-][\text{Pt}(\text{CN})_4^{2-}]; \quad \text{pH} = \text{constant} \quad (8)$$

with  $r = (7.9 \pm 0.3)$ ,  $(13.8 \pm 0.5)$  and  $(38.4 \pm 0.6) \text{ M}^{-2} \text{ s}^{-1}$  for  $[\text{H}^+] = 0.0100$ , 0.0200 and 1.00 M,

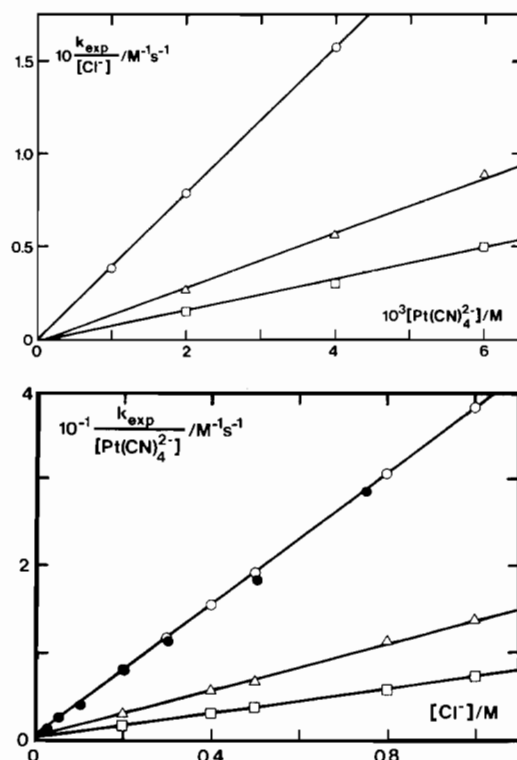


Fig. 4. Plots of  $k_{\text{exp}}/[\text{Cl}^-]$  vs.  $[\text{Pt}(\text{CN})_4^{2-}]$  and  $k_{\text{exp}}/[\text{Pt}(\text{CN})_4^{2-}]$  vs.  $[\text{Cl}^-]$  for reaction (2) at 25.0 °C and 1.00 M ionic strength.  $[\text{H}^+]$  was 0.010 M ( $\circ$ ), 0.020 M ( $\Delta$ ) and 1.00 M ( $\square$ ). Data from ref. 2 for  $[\text{H}^+] = 1.00 \text{ M}$  have also been included ( $\bullet$ ).

respectively. Equation (9) describes the pH-dependence

$$r = \frac{k[\text{H}^+]}{K_a + [\text{H}^+]} \quad (9)$$

where  $k = (39.9 \pm 0.5) \text{ M}^{-2} \text{ s}^{-1}$  is the extrapolated rate constant when all platinum is in the form of the aqua complex and  $K_a = (4.0 \pm 0.2) \times 10^{-2} \text{ M}$  can be identified as the protolysis constant of *trans*-Pt(CN)<sub>4</sub>-ClOH<sub>2</sub><sup>-</sup>. Equation (10) gives the rate law.

$$\text{Rate} = \frac{k[\text{H}^+]}{K_a + [\text{H}^+]} [\text{Cl}^-][\text{Pt}(\text{CN})_4^{2-}][\text{complex}] \quad (10)$$

A preliminary study of reaction (2) has been published [2]. The small intercepts in the plots of  $k_{\text{exp}}$  vs.  $[\text{Pt}(\text{CN})_4^{2-}]$  reported in that study were probably due to a side reaction that was negligible in the present experiments. The plots of Fig. 4 are strictly linear corresponding to the simple rate law of eqn. (10). The uncorrected rate constants from ref. 2 agree perfectly with the present results, *cf.* Fig. 4.

For reaction (3), a plot of  $k_{\text{exp}}/[\text{Pt}(\text{CN})_4^{2-}]$  vs.  $[\text{Cl}^-]$  (Table III) is linear through the origin indicating the rate law of eqn. (11),

$$\text{Rate} = k [\text{Cl}^-] [\text{Pt}(\text{CN})_4^{2-}] [\text{PtCl}_5\text{OH}_2^-] \quad (11)$$

with  $k = (5.6 \pm 0.2) \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$  for 35 °C, 1.50 M ionic strength and  $[\text{H}^+] = 1.50 \text{ M}$ . The hydrogen ion concentration is sufficiently large to completely suppress protolysis of  $\text{PtCl}_5\text{OH}_2^-$  which is expected to have a protolysis constant of the same order of magnitude as  $\text{PtBr}_5\text{OH}_2^-$  [16], *ca.*  $2 \times 10^{-6} \text{ M}$ .

Similarly, the values of Table IV for reaction (4) give the rate law

$$\text{Rate} = k [\text{PtCl}_4^{2-}] [\text{trans-Pt}(\text{CN})_4\text{ClOH}_2^-] \quad (12)$$

with  $k = (3.32 \pm 0.02) \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C for 1.00 M perchloric acid medium. The rate is independent of chloride concentration up to  $[\text{Cl}^-] = 1.00 \text{ M}$ .

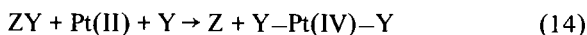
## Discussion

### REOA and Ligand Assisted Substitutions

The intimate mechanism for the platinum(II)-independent ligand substitutions of platinum(IV) halide complexes has been a matter of some controversy as to the extent of charge separation and reduction of platinum(IV) during the process, and the nature of the intermediates. The original reductive elimination oxidative addition (REOA) mechanism proposed first by Grinberg and Shagisultanova [17] and elaborated by Poë and coworkers [18–22] involves a complete reduction of the platinum(IV) halide complex to platinum(II) by attack of an incoming halide Y on one of the halide ligands Z of the complex, according to eqn. (13), ionic charges omitted.

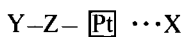


This is equivalent to a transfer of  $\text{Z}^+$  to the incoming halide Y and concomitant two-electron transfer to the platinum(IV). In a subsequent rapid reoxidation step, the platinum(II) complex is oxidized by YZ and another Y is incorporated in the complex, for instance according to eqn. (14).



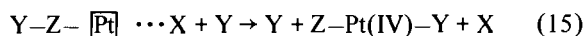
A large extent of charge separation is supported by correlations between kinetic parameters for substitution and thermodynamic parameters for reduction [21].

Skinner and Jones [7], Elding and Gustafson [10, 13, 14, 23, 24] and Mason [8] have instead favoured a mechanism, which involves formation of an intermediate of the type

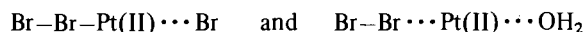


Here association of the assisting ligand Y to the *trans*-ligand Z of the platinum(IV) complex is assumed to cause a partial displacement of negative charge to the

central atom, equivalent to a partial reduction of the platinum(IV). This should increase the reactivity of the remote halide or aqua ligand X and facilitate its substitution for another Y, according to eqn. (15).

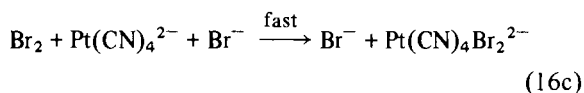
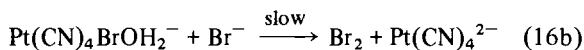
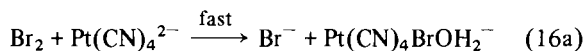


Rate laws with terms second-order in entering halide  $[\text{Y}]^2$  can be easily explained by this mechanism. Association in *trans*-position is supported by the fact that second-order rate laws are obtained only for complexes having an efficient bridging ligand Z in *trans*-position to the ligand X to be replaced [24]. More recently, Vuik and Poë [11] have modified the original REOA-mechanism in the direction of this ligand-assistance mechanism as formulated in ref. 10 with intermediates of the types



in which there is a large extent of reduction of the platinum(IV) but where – most important – the halogen and the remote halide or aqua ligand to be substituted remain attached to the platinum. The only difference between the two mechanisms as formulated presently seems to be the actual charge of the central metal ion: either a platinum completely reduced to Pt(II) according to [11] or a partially reduced platinum, for instance according to [7–10, 13]. The charge displacement within the intermediate cannot be judged from the kinetics. The term ‘ligand assistance’ seems preferable for this type of mechanism, since REOA is usually associated with complete separation into halogen molecule, platinum(II) complex and free halide as depicted by eqn. (13).

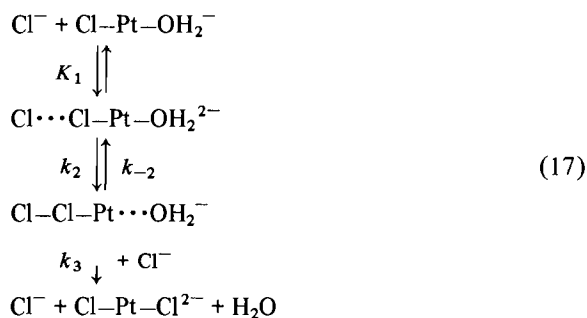
Moreover, for some reactions, it is questionable if the REOA-mechanism in its original form is compatible with thermodynamics. For instance the rapid oxidation of  $\text{Pt}(\text{CN})_4^{2-}$  with bromine followed by slow formation of  $\text{Pt}(\text{CN})_4\text{Br}_2^{2-}$  has been described by the following series of elementary steps [22]



in which reaction (16b) is assumed to be spontaneous in the opposite direction compared to the other two processes. Reaction (16a) is known to occur spontaneously.

The present results for reaction (1) support the more recent conclusions by Vuik and Poë [11] for the similar *trans*- $\text{Pt}(\text{CN})_4\text{BrOH}_2^-$ -bromide reaction.

Using the same notation as previously [10, 11] the experimental rate law of eqn. (5) with a second-order dependence on  $[\text{Cl}^-]$  can be described by the mechanism (17), cyanide ligands being omitted



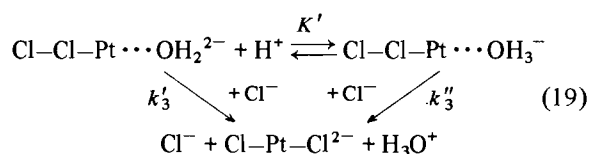
If the rapid formation of the ion-pair in the pre-equilibrium is displaced to the left, *ie.*  $K_1[\text{Cl}^-] \ll 1$ , and the intermediates are assumed to be present in steady-state concentrations only, we arrive at the rate law (18)

$$k = \frac{K_1 k_2 (k_3/k_{-2}) [\text{Cl}^-]^2}{1 + (k_3/k_{-2}) [\text{Cl}^-]} \quad (18)$$

which by comparison with eqn. (5) gives  $k_3/k_{-2} = (0.62 \pm 0.01) \text{ M}^{-1}$  independent of pH. For reaction (1) there is no indication of a third-order term in chloride as observed by Vuik and Poë for the much faster  $\text{Pt}(\text{CN})_4\text{BrOH}_2^-$ -bromide reaction at high  $[\text{Br}^-]$  (as expected, because of the much weaker Cl-Cl interactions).

In addition to the rate law, a further argument in favour of the mechanism of eqn. (17) is that the present experiments were performed in the presence of a small concentration of chlorine (*ca.* 0.1 mM), which should prohibit complete reduction to platinum(II).

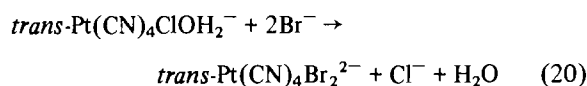
Reaction (1) was studied in a pH interval, where the equilibrium  $\text{trans-Pt}(\text{CN})_4\text{ClOH}_2^-/\text{trans-Pt}(\text{CN})_4\text{-ClOH}_2^{2-}$  is displaced towards the aqua complex;  $\text{p}K_a$  is 1.4, *cf.* reaction (2) above. The pH-dependence of eqn. (6) is most likely due to a parallel acid catalyzed reaction path. In acid medium, protonated forms of the intermediate complexes might be formed, which are more reactive than the unprotonated complex, for instance according to



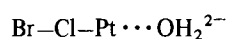
With  $K'[\text{H}^+] \ll 1$  we get  $k_3 = k'_3 + k''_3 K'[\text{H}^+]$  which gives a two-term expression of the same form as eqn. (7). Proton exchange in  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  and

$\text{Ni}(\text{H}_2\text{O})_6^{2+}$  are known to proceed by a similar mechanism of acid catalysis [25].

Sometimes the form of the rate law has been used as an argument for a REOA-process. For instance, reaction (20)



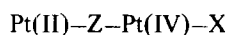
has a rate constant proportional to  $[\text{Br}^-]$ . An REOA-mechanism, involving a rate-determining reduction by bromide followed by rapid reoxidation by  $\text{Br}_2$ , has been proposed [10]. However, the simple rate law might eventually be a special case of the general rate law of eqns. (5) and (18) with  $q[\text{Br}^-] \gg 1$ . A bromide assisted reaction as in eqn. (17) with an intermediate of the type



cannot be excluded.

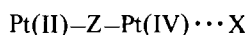
#### Platinum(II)-Accelerated Reactions

It has been pointed out earlier [14] that there is a mechanistic analogy between the halide assisted and platinum(II)-accelerated substitution reactions of platinum(IV) complexes. Acceleration by platinum(II) involves formation of halide bridged intermediates of the type



where Z is a halide and X is the leaving halide or aqua ligand to be replaced by an incoming halide Y. For those reactions, as for the halide assisted ones, there is an electron displacement towards the platinum(IV) centre of the intermediate. As a rule, this displacement has been considered to give complete redox and central ion exchange coupled with addition of the entering halide Y at the original Pt(II)-side of the intermediate [6, 14].

It has been suggested [14], however, that if there is a labilization of the terminal *trans*-ligand X at the platinum(IV)-side of the complex

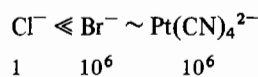


connected with the electron displacement, a direct substitution of X for Y cannot be excluded. In such cases, substitution should take place without central ion exchange, and the mechanistic role of the platinum(II) complex in this case should be similar to that of the assisting halide Y in the halide assisted reactions discussed above [14].

The stoichiometry for reaction (3) and its rate law, eqn. (11), is compatible with a mechanism of the postulated type without central ion exchange as described by eqn. (21).







for a given bridging ligand Z. Thus, bromide and  $\text{Pt}(\text{CN})_4^{2-}$  are about equally effective in assisting halide anation reactions of those complexes.

In accordance with previous results [14], a comparison of the  $p$  values of the two last entries of the table also shows that a bromide is *ca.*  $10^4$  times more efficient than chloride as a bridging ligand for electron transfer.

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