Inorganica Chimica Acta, 19 (1976) 165–171

A Reaction Mechanism for Oxidative Addition of Halogen to Platinum(II), Reductive Elimination of Halide from Platinum(IV) and Halide Assisted Anations of Platinum(IV) Complexes

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Received February 9, 1976

The oxidative addition of iodine to $Pt(CN)_4^{2-}$ *is first-order with respect to iodide, iodine and complex. The reverse reductive elimination of iodide from trans-*$Pt(CN)_4I_2^{2-}$ *is first-order with respect to iodide and* $Pt(CN)_4I_2^{2-}$*. The kinetics for the reaction between bromide and trans-*$Pt(CN)_4ClH_2O^-$ *involves a rate-determining reductive elimination of chloride, followed by a rapid oxidative addition of bromine to the formed* $Pt(CN)_4^{2-}$*. The reactions between trans-*$Pt(CN)_4BrH_2O^-$ *and bromide or chloride can be described as halide assisted anations. The rate constant for the bromide anation is* $k_{exp} = k'[Br^-]^2$ *and for the chloride anation (in the presence of bromide)* $k_{exp} = k'[Br^-][Cl^-] + k''[Cl^-]^2$*. All reactions were followed using a stopped-flow technique at 25° C in 0.50M perchloric acid medium. The equilibrium constant for the redox equilibrium between* $Pt(CN)_4^{2-}$*, iodine and* $Pt(CN)_4I_2^{2-}$ *was determined separately to be* $(1.29 \pm 0.03) \times 10^4 M^{-1}$*.*

Exploratory stopped-flow experiments indicate that the oxidative addition of chlorine to $PtCl_4^{2-}$ *is first-order with respect to both chlorine and tetrachloroplatinate.*

The experimental rate laws can be described by a reaction mechanism which resembles that introduced previously for Pt(II)-catalyzed anations and substitutions, in that both mechanisms can be considered as oxidative additions/reductive eliminations.

Introduction

Platinum(II)-catalyzed ligand substitutions in platinum(IV) complexes can be considered as oxidative additions to the platinum(II) complex or as reductive eliminations from the platinum(IV) complex.[1] Figure 1a shows a mechanism which we have recently proposed for some reactions of this type.[2]

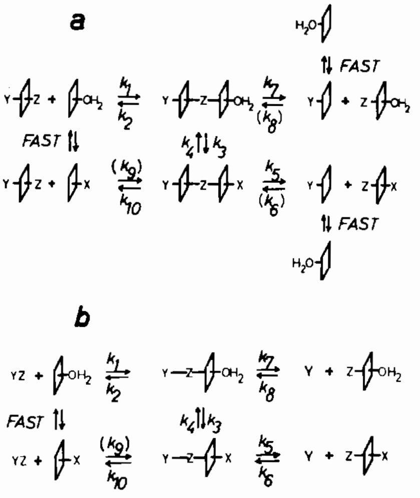

Figure 1. Suggested reaction models (*a*) for substitution reactions in platinum(IV) complexes in the presence of a platinum(II) complex according to Ref. 2, and (*b*) for oxidative additions of halogen to platinum(II) complexes, reductive eliminations of halide from platinum(IV) complexes and halide substitutions in platinum(IV) complexes. X, Y and Z denote halide.

The kinetics for many ligand substitutions in platinum(IV) complexes in the absence of added platinum (II) can also be described by redox processes.[3] Poë and coworkers[4,5] have shown that reactions between iodide and halogeno-platinate(IV) complexes proceed *via* a reductive attack of iodide on coordinated halide. Sometimes, this reductive elimination is followed by a rapid reoxidation of the formed platinum(II) complex (the so-called r.e.o.a. mechanism[5]). The over-all reaction will be a formal ligand substitution in the original platinum(IV) complex. Oxidative additions of halogen to platinum(II) complexes are generally fast reactions and have been little studied. Jones and Morgan[6] recently gave the first proposal for a reaction mechanism for oxidative addition of chlorine to tetrachloroplatinate(II) *(vide infra)*.

The experimental rate laws for the bromide anations of *trans*-$Pt(CN)_4BrH_2O^-$,[7,8,9] *trans*-$Pt(NH_3)_4BrH_2O^{3+}$[8] and $PtBr_5H_2O^-$[10] contain terms which are proportional to the *squared* concentration of the entering bromide. These terms correspond to reaction paths which can be described as reversible partial redox processes.

In the present paper we report rate laws for the following reactions, which have been studied by the stopped-flow method:

$$Pt(CN)_4^{2-} + I_2 \overset{I^-}{\rightleftarrows} trans\text{-}Pt(CN)_4I_2^{2-} \qquad (1)$$

$$trans\text{-}Pt(CN)_4ClH_2O^- + 2Br^- \rightarrow trans\text{-}Pt(CN)_4Br_2^{2-} + Cl^- + H_2O \qquad (2)$$

$$trans\text{-}Pt(CN)_4BrH_2O^- + Br^- \rightarrow trans\text{-}Pt(CN)_4Br_2^{2-} + H_2O \qquad (3)$$

$$trans\text{-}Pt(CN)_4BrH_2O^- + Cl^- \rightarrow trans\text{-}Pt(CN)_4BrCl^{2-} + H_2O \qquad (4)$$

For the process (1), rate laws have been obtained both for the oxidative addition and for the reverse reductive elimination. Its equilibrium constant, defined by eqn. (8), has been determined separately.

Reaction (2) gives an example of the r.e.o.a.-mechanism with bromide as the reducing agent, and reaction (4) is the first example of a chloride assisted anation which has been reported. The bromide assisted anation (3) has been studied previously.[7, 8, 9]

The kinetics for these reactions – and for related reactions previously reported in the literature – can be described by the mechanism in Figure 1b. This model is analogous to that previously suggested for some platinum(II)-"catalyzed" reactions, given in Figure 1a.[2]

Experimental

Chemicals

Potassium tetracyanoplatinate(II) (Johnson and Matthey) and sodium iodide (Merck's *p.a.*) were used without further purification. All other chemicals were reagent grade.

The potassium salt of $trans$-$Pt(CN)_4Br_2^{2-}$ was prepared by oxidation of potassium tetracyanoplatinate(II) with excess bromine in $0.5M$ hydrobromic acid solution.

Solutions of $trans$-$Pt(CN)_4I_2^{2-}$ were prepared by oxidation of tetracyanoplatinate(II) ($5 \times 10^{-6}M$) with excess iodine in $0.50M$ perchloric acid solution. The concentration of iodide released in this oxidation was large enough to produce the di-iodo complex as the dominating platinum(IV) species.[11]

Solutions of $trans$-$Pt(CN)_4ClH_2O^-$ were prepared by oxidation of tetracyanoplatinate(II) ($4.6 \times 10^{-3}M$) with chlorine in $0.50M$ perchloric acid solution as described previously.[2]

Equilibrium Measurements

The equilibrium (1) was studied at (25.0 ± 0.1)° C by mixing solutions of $trans$-$Pt(CN)_4Br_2^{2-}$, $Pt(CN)_4^{2-}$ and sodium iodide. The replacement of the bromide ligands in the platinum(IV) complex is fast[12] and the small concentrations of bromide released from the complex did not disturb the equilibrium studied. Addition of perchloric acid gave a hydrogen ion concentration of $0.25M$. The ionic strength was $0.50M$ with sodium perchlorate as the supporting electrolyte.

The absorbances were measured both immediately after mixing and after about ten minutes. The readings were constant during this time. A Zeiss Quartz Spectrophotometer PMQII was used. The wavelength was 353 nm, where the absorptivities of $Pt(CN)_4^{2-}$ and I_2 are negligible compared to that of $trans$-$Pt(CN)_4I_2^{2-}$ and I_3^-.

The molar absorptivity of $trans$-$Pt(CN)_4I_2^{2-}$ was determined separately as 430 $cm^{-1}M^{-1}$ using solutions containing $trans$-$Pt(CN)_4I_2^{2-}$ ($4.8 \times 10^{-4}M$), a small excess of iodide ($5 \times 10^{-5}M$) and $Pt(CN)_4^{2-}$ ($4.67 \times 10^{-3}M$) in order to prevent reduction of the platinum(IV) complex. The molar absorptivity of I_3^- at this wavelength is 2.64×10^4 $cm^{-1}M^{-1}$.[13]

Kinetic Measurements

A modified Durrum–Gibson stopped-flow instrument[14] was used. For reaction (2) and for the reverse of reaction (1) one of the solutions mixed in the flow system contained the platinum(IV) complex and the other halide. For the other reactions, one of the solutions contained $Pt(CN)_4^{2-}$ and the other halogen and halide. All reactions were studied under pseudo-first-order conditions. The hydrogen ion concentration and the ionic strength were $0.50M$ with perchloric acid as the supporting electrolyte. The temperature was (25.0 ± 0.1)° C. The first-order rate constants were calculated by a least-squares program from the transmittance *vs.* time curves. Their reproducibility was generally better than ± 3%.

Results

Equilibrium Measurements

Table I reviews the results. At the chosen wavelength, the absorptivity was

$$e = \varepsilon_{trans\text{-}Pt(CN)_4I_2^{2-}}[trans\text{-}Pt(CN)_4I_2^{2-}]_{eq} + \varepsilon_{I_3^-}[I_3^-]_{eq} \qquad (5)$$

The molar absorptivities were separately determined. Since no extra iodine was added, the total concentration of iodine at equilibrium was

$$[I_2]_{eq} + [I_3^-]_{eq} = [Pt(CN)_4I_2^{2-}]_o - [Pt(CN)_4I_2^{2-}]_{eq} = [Pt(CN)_4^{2-}]_{eq} - [Pt(CN)_4^{2-}]_o \qquad (6)$$

The equilibrium constant

$$K' = [I_2]_{eq}[I^-]_{eq}/[I_3^-]_{eq} \qquad (7)$$

has been determined previously to be $1.40 \times 10^{-3}M$ using the same medium.[15]

TABLE I. Equilibrium Measurements on Reaction (1). The initial concentration of *trans*-$Pt(CN)_4I_2^{2-}$ was 9.32×10^{-5} M.

$[Pt(CN)_4^{2-}] \times 10^4/M$	$[I^-] \times 10^3/M$	e/cm$^{-1}M^{-1}$	$K \times 10^{-4}/M^{-1}$
9.82	100.0	0.898	1.31
4.91	100.0	1.300	1.31
9.82	50.0	0.559	1.32
4.91	50.0	0.881	1.34
9.82	25.0	0.335	1.29
4.91	25.0	0.552	1.33
9.82	20.0	0.286	1.27
4.91	20.0	0.470	1.32
9.85	15.0	0.233	1.23
4.91	15.0	0.378	1.31
9.85	10.0	0.172	1.24
4.91	10.0	0.278	1.26
			Mean: 1.29 ± 0.03

Equations (5), (6) and (7) give the concentrations of the various species at equilibrium and the equilibrium constant

$$K = \frac{[trans\text{-}Pt(CN)_4I_2^{2-}]_{eq}}{[Pt(CN)_4^{2-}]_{eq}[I_2]_{eq}} = (1.29 \pm 0.03) \times 10^4 M^{-1} \quad (8)$$

A previous determination by Poë[12] gave $K = 3 \times 10^4$ M^{-1} for an unspecified medium.

Reaction (1)

The kinetics for this reversible reaction were followed in both directions. The equilibrium was displaced to the right by oxidizing $Pt(CN)_4^{2-}$ with iodine in the presence of iodide and to the left by adding iodide to solutions previously oxidized with iodine in the absence of extra iodide.[11] The experimental rate constants, given in Table II, follow a two-term expression as expected for a relaxation:

$$k_{exp} = (k' + k''[R])[I^-] \quad (9)$$

where R denotes the reactant in excess, $Pt(CN)_4^{2-}$ or I_2 (for excess I_2, *vide* Fig. 2).

The parameters k' and k'' were determined as

$$k' = (1.2 \pm 0.1) \times 10^5 \text{ s}^{-1}M^{-1}$$
$$k'' = (1.56 \pm 0.08) \times 10^9 \text{ s}^{-1}M^{-2}$$

The agreement between the quotient $k''/k' = (1.3 \pm 0.2) \times 10^4 M^{-1}$ and the separately determined equilibrium constant $K = (1.29 \pm 0.03) \times 10^4 M^{-1}$, indicates that k'' is the rate constant for the forward and k' that for the reverse reaction. Therefore, the oxidative addition of iodine to $Pt(CN)_4^{2-}$ in the presence of excess iodide can be described by the rate law

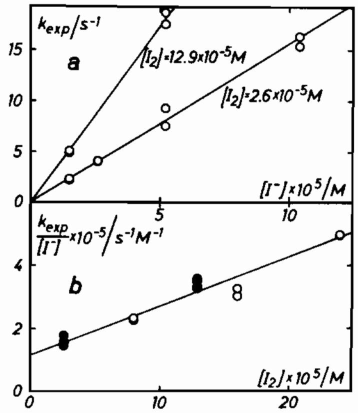

Figure 2. (*a*) The experimental rate constant for reaction (1) as a function of iodide concentration and (*b*) $k_{exp}/[I^-]$ *vs.* the concentration of iodine. Reaction followed in forward direction (○) and in reverse direction (●). Because of the low concentration of iodide, the amount of I_3^- present is negligible and $[I_2]$ is set equal to the total concentration of iodine.

TABLE II. Observed Rate Constants for Reaction (1). The start solutions contained *a*, $Pt(CN)_4^{2-}$ and I_2 and *b*, *trans*-$Pt(CN)_4I_2^{2-}$.

	$C_{Pt} \times 10^5/M$	$[I_2] \times 10^5/M$	$[I^-] \times 10^5/M$	λ/nm	k_{exp}/s^{-1}
a	1.90	8	7.5	405	17.2
a	1.90	16	7.5	405	23.6
a	1.90	24	7.5	405	37.2
a	2.60	0.26	2.49	270	4.14
a	13.0	0.26	2.49	270	8.7
b	0.243	2.6	1.50	270	2.26
b	0.243	2.6	2.59	270	4.06
b	0.243	2.6	5.20	270	8.5
b	0.243	2.6	10.4	270	15.9
b	0.243	12.9	1.50	270	5.1
b	0.243	12.9	5.20	270	18.1

$$\vec{v} = k''[\mathrm{I^-}][\mathrm{I_2}][\mathrm{Pt(CN)_4^{2-}}] \qquad (10)$$

and the reductive elimination of the *trans*-di-iodo complex by the eqn.

$$\overleftarrow{v} = k'[\mathrm{I^-}][\mathrm{Pt(CN)_4I_2^{2-}}] \qquad (11)$$

with the values of k' and k'' given above.

Reaction (2)

According to the spectrum at infinite time, *trans*-$\mathrm{Pt(CN)_4Br_2^{2-}}$ is the product in this reaction. Table III reviews the results. The experimental rate constant is described by (*cf.* Figure 3):

$$k_{\mathrm{exp}} = k'[\mathrm{Br^-}] \qquad (12)$$

with $k' = (5.37 \pm 0.04)\ \mathrm{s^{-1}}M^{-1}$.

The rate increases when $\mathrm{Pt(CN)_4^{2-}}$ is added. But the concentration of platinum(II) complex must be large in order to accelerate the reaction noticeably, so the rate obtained in the absence of added $\mathrm{Pt(CN)_4^{2-}}$ is not due to impurities of this complex in the platinum(IV) solutions. Addition of chloride did not affect the rate.

The replacement of chloride by bromide in *trans*-$\mathrm{Pt(CN)_4BrCl^{2-}}$ has been studied by Mason.[16] The rate constant for the platinum(II) independent reaction path was 0.25 $\mathrm{s^{-1}}M^{-1}$. Since this rate constant is much smaller than the rate constant k' for the overall reaction from *trans*-$\mathrm{Pt(CN)_4ClH_2O^-}$ to *trans*-$\mathrm{Pt(CN)_4Br_2^{2-}}$, it can be concluded that *trans*-$\mathrm{Pt(CN)_4BrCl^{2-}}$ is not formed as an intermediate in this reaction (*vide infra*).

Reaction (3)

The results are given in Table IV and Figure 4. The experimental rate constant is given by

$$k_{\mathrm{exp}} = k'[\mathrm{Br^-}]^2 \qquad (13)$$

with $k' = (1.59 \pm 0.02) \times 10^5\ \mathrm{s^{-1}}M^{-2}$. The rate is independent of the concentration of bromine. k' agrees satisfactorily with previously obtained values.[7,8,9]

TABLE III. Kinetics for Reaction (2). The concentration of platinum(IV) complex was 1.15 × 10^{-4} M. The kinetics were followed at 342 nm, which is an absorption maximum for *trans*-$\mathrm{Pt(CN)_4Br_2^{2-}}$.

$[\mathrm{Br^-}] \times 10^3/M$	$k_{\mathrm{exp}}/\mathrm{s^{-1}}$	Added Substance
25	0.129	
25	0.143	$[\mathrm{Pt(CN)_4^{2-}}] = 5.2 \times 10^{-3} M$
25	0.199	$[\mathrm{Pt(CN)_4^{2-}}] = 15.1 \times 10^{-3} M$
50	0.262	
100	0.533	
150	0.79	
150	0.77	$[\mathrm{Cl^-}] = 25 \times 10^{-3} M$
150	1.19	$[\mathrm{Pt(CN)_4^{2-}}] = 15.1 \times 10^{-3} M$
250	1.34	
250	2.09	$[\mathrm{Pt(CN)_4^{2-}}] = 15.2 \times 10^{-3} M$

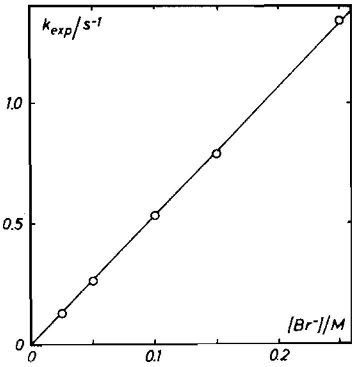

Figure 3. The observed rate constant for reaction (2) as a function of the bromide concentration.

TABLE IV. Kinetics for Reaction (3). The concentration of platinum complex was 2.32 × 10^{-4} M. The concentration of bromine given is the concentration before oxidation. λ = 395 nm.

$[\mathrm{Br^-}] \times 10^3/M$	$[\mathrm{Br_2}] \times 10^4/M$	$k_{\mathrm{exp}}/\mathrm{s^{-1}}$
5.0	2.5	4.59
5.0	5.0	4.56
5.0	10.0	4.49
5.0	15.0	4.61
10.0	2.5	16.6
15.0	2.5	38.9
20.0	2.5	65
25.0	2.5	98

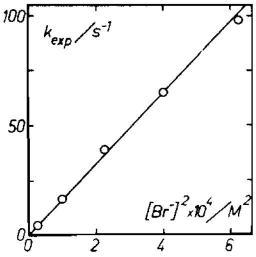

Figure 4. The observed rate constant for reaction (3) as a function of the squared concentration of bromide.

Reaction (4)

Table V reviews the results. In Figure 5a the experimental rate constant k_{exp} has been plotted as a function of the concentration of chloride. An analysis of the plot shows that the rate expression contains a term which is second order in chloride.

When $\mathrm{Pt(CN)_4^{2-}}$ is oxidized with bromine to *trans*-$\mathrm{Pt(CN)_4BrH_2O^-}$, the concentration of bromide in the solutions will be equal to that of platinum(IV) com-

TABLE V. Kinetics for Reaction (4). The concentration of platinum was $2.0 \times 10^{-4} M$. The wavelength was 375 mn.

$[Cl^-] \times 10^3/M$	$[Br^-] \times 10^4/M$	k_{exp}/s^{-1}
12.5	2.0	0.289
50	2.0	1.05
100	2.0	1.96
150	2.0	3.22
200	2.0	3.14
250	2.0	5.03
250	3.0	6.81
250	4.0	8.89
250	5.0	10.7
250	6.0	12.5
250	7.0	14.9
300	2.0	6.8
300	3.0	8.4
300	5.0	12.9
300	7.0	16.8
400	2.0	9.6
500	2.0	11.8

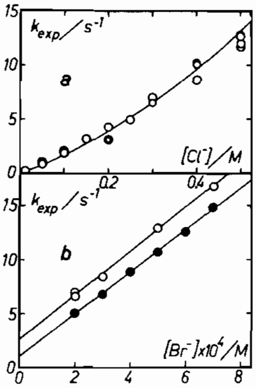

Figure 5. The experimental rate constant for reaction (4) (*a*) as a function of the concentration of chloride for a constant concentration of bromide, $2 \times 10^{-4} M$, and (*b*) as a function of the concentration of bromide for $[Cl^-] = 0.300M$ (○) and $[Cl^-] = 0.250M$ (●).

plex. In order to check the influence of such small concentrations of bromide on the rate, some experiments were performed in which the concentration of bromide was varied while keeping the chloride concentration constant (*cf.* Table V). Figure 5b shows that the observed rate constant depends on the bromide concentration. The experimental rate constant is described by the expression

$$k_{exp} = k'[Br^-][Cl^-] + k''[Cl^-]^2 \tag{14}$$

with $k' = (7.4 \pm 0.1) \times 10^4\ s^{-1}M^{-2}$
$k'' = (22 \pm 3)\ s^{-1}M^{-2}$

The full-drawn curve in Figure 5a has been calculated from eqn. (14) using these values of the parameters k' and k''.

Discussion

The experimental results are consistent with the redox mechanism in Figure 1b. The reactions are thought to proceed *via* intermediates, present in steady-state concentrations, analogous to the bridged intermediates postulated for the platinum(II)-"catalyzed" reactions in Figure 1a.

Oxidative Addition of Halogen

The magnitude of $k_3[X]$ and k_5 compared to k_7 determines whether the fully coordinated complex Z–Pt(IV)–X, the monoaqua complex Z–Pt(IV)–OH_2, or a mixture of these two species are formed as primary products in the oxidation.

(i). When both $k_3[X] \gg k_7$ and $k_5 \gg k_7$ (*vide* Figure 1b), the fully coordinated complex is formed directly. This condition applies to reaction (1). If the halides X and Y and one of the reactants R (*i.e.* platinum(II) complex or halogen) are present in large excess compared to the other reactant, the model gives the following rate constant:

$$k_{exp} = \frac{k_1k_3k_5[R][X] + k_2k_6(k_4 + k_{10})[Y] + k_3k_6k_{10}[X][Y]}{k_2(k_4 + k_5 + k_{10}) + k_3(k_5 + k_{10})[X]} \tag{15}$$

For $k_3[X] \ll k_2$ and X = Y = Z = I this eqn. transforms to

$$k_{exp} = \frac{k_1k_3k_5[R][I^-] + k_2k_6(k_4 + k_{10})[I^-]}{k_2(k_4 + k_5 + k_{10})} \tag{16}$$

which agrees with the experimental eqn. (9) for the relaxation (1).

(ii). For $k_7 \gg k_3[X]$ the *trans*-haloaqua complex is formed primarily. The rate constant for its formation is given by

$$k_{exp} = \frac{k_1k_7[R] + k_2k_8[Y]}{k_2 + k_7} \tag{17}$$

where R denotes the reactant present in excess, *i.e.* platinum(II) complex or halogen. This eqn. should be valid for oxidation of platinum(II) complexes with chlorine or bromine, which gives *trans*-haloaqua complexes as primary products.[6, 9]

We have performed a preliminary study on the oxidative addition

$$PtCl_4^{2-} + Cl_2 \rightarrow PtCl_5H_2O^- + Cl^- \tag{18}$$

and found a rate law

$$\vec{v} = k[PtCl_4^{2-}][Cl_2] \tag{19}$$

for 25.0° C, 0.50M sodium perchlorate medium and 0.4–10 mM hydrogen ion concentration. Experiments

TABLE VI. Rate Data for Oxidative Addition of Chlorine to $PtCl_4^{2-}$, Reaction (18). 25.0° C, $\mu = 0.50M$ ($NaClO_4$), λ = 300 nm. The last experiment was performed under second-order conditions.

$[PtCl_4^{2-}] \times 10^5/M$	$[Cl_2] \times 10^5/M$	$([Cl^-] = [H^+]) \times 10^3/M$	k_{exp}/s^{-1}	$k \times 10^{-5}/s^{-1}M^{-1}$
2.0	15	1	78	5.2
2.0	25	1	106	4.2
0.8	10	0.4	41	4.1
0.8	12	0.4	56	4.7
0.4	4	0.4	18	4.5
20.0	2.4	10	88	4.4
7.0	4.5	10	–	4.7

made under pseudo-first-order conditions with either platinum complex or chlorine in excess gave a rate constant $k = 4.5 \times 10^5\ s^{-1}M^{-1}$ (*cf.* Table VI).

The rate law (19) agrees with eqn. (17), since the reverse reaction described by the term $k_2k_8[Cl^-]$ can be neglected in this case.

Our results are not compatible with the rate law reported previously for reaction (18) by Jones and Morgan.[6] They concluded that the rate was independent of one or both of the reactants. We have repeated one of their experiments, included in Table VI ($C_{Pt} = 7 \times 10^{-5}M$, $C_{Cl_2} = 4.5 \times 10^{-5}M$, *cf.* also ref. 6, Table 2) under identical conditions and found second-order kinetics. The second-order rate constant was calculated to be $4.7 \times 10^5\ s^{-1}M^{-1}$ in good agreement with that obtained under pseudo-first-order conditions. We therefore conclude that Jones and Morgan have calculated first-order rate constants from experiments actually performed under second-order conditions. Probably they used so short running times, that the deviations from first-order behaviour were not observed. Such deviations are obvious, however, if the reaction is followed for several half-lives as in our experiment.

Reactions between Platinum(IV)–Haloaqua complexes and Halide.

The relative magnitude of the parameters k_2 and k_3 [X] determines whether reduction to a platinum(II) complex or substitution in the intermediate aqua complex Y–Z–Pt–OH_2 takes place.

(i). For $k_2 \gg k_3[X]$ reduction to platinum(II) occurs. The model in Figure 1b gives the following rate constant for this reductive elimination

$$k_{exp} = \frac{k_2k_8[Y]}{k_2 + k_7} \qquad (19)$$

Reoxidation of the formed platinum(II) complex may sometimes occur according to the r.e.o.a. mechanism described by Poë.[5]

The experimental results obtained for reaction (2) can be interpreted in this way. The experimental rate expression (12) agrees with eqn. (19). The rate determining step is the reduction:

$$trans\text{-}Pt(CN)_4ClH_2O^- + Br^- \rightarrow Pt(CN)_4^{2-} + ClBr + H_2O \qquad (20)$$

For excess bromide, bromine is formed

$$ClBr + Br^- \rightarrow Cl^- + Br_2 \qquad (21)$$

Free bromine rapidly (*cf.* ref. 9) oxidizes $Pt(CN)_4^{2-}$:

$$Pt(CN)_4^{2-} + Br_2 + H_2O \rightarrow trans\text{-}Pt(CN)_4BrH_2O^- + Br^- \qquad (22)$$

The subsequent anation

$$trans\text{-}Pt(CN)_4BrH_2O^- + Br^- \rightarrow trans\text{-}Pt(CN)_4Br_2^{2-} + H_2O \qquad (23)$$

is also a very fast reaction (*cf.* Table IV). The fact that *trans*-$Pt(CN)_4ClBr^{2-}$ is not formed as an intermediate (*cf.* Kinetic Measurements, Reaction (2) above) supports our interpretation.

(ii). For $k_3[X] \gg k_2$ substitution occurs. If furthermore k_{10} is small compared to k_5 the dihalocomplex is formed *via* the reaction paths described by the rate constants k_8, k_7, k_3, k_4 and k_5, k_6. The model in Figure 1b gives the following rate constant

$$k_{exp} = \frac{k_3k_5k_8[X][Y] + k_6k_7k_4[Y]}{k_3k_5[X] + k_7(k_4 + k_5)} \qquad (24)$$

When $Pt(CN)_4^{2-}$ is oxidized with bromine, *trans*-Pt $(CN)_4BrH_2O^-$ is formed primarily, even in the presence of excess bromide. This means, that $k_7 \gg k_3[X]$ for X = Y = Z = Br. Eqn. (24) is then reduced to

$$k_{exp} = \frac{k_3k_5k_8[Br^-]^2 + k_4k_6k_7[Br^-]}{k_7(k_4 + k_5)} \qquad (25)$$

When the reverse reaction described by the term $k_4k_6k_7$ $[Br^-]$ can be neglected, this expression agrees with the experimental eqn. (13) and the rate laws for other bromide assisted reactions.[7–10]

The chloride anation of *trans*-$Pt(CN)_4BrH_2O^-$, reaction (4), has been studied previously by Mason.[8] The rate was found to be first-order in chloride and this was interpreted as a direct reaction between the substrate complex and chloride. However, this author neglected the fact that the rate constant increased substantially when the substrate concentration and then also the concentration of free bromide was increased (*vide* ref. 8, Table II). Our experiments on the same reaction show that small concentrations of bromide affect the rate considerably (*cf.* Figure 5b). The small amounts of bromide present due to the method of preparation of the substrate complex are large enough to produce the associated complex Br–Br–Pt–OH_2. The first term in eqn. (14) should therefore be interpreted as a bromide assisted reaction path with chloride as entering ligand, rather than as a direct reaction between chloride and *trans*-$Pt(CN)_4BrH_2O^-$.

The second term which is proportional to the squared concentration of chloride indicates a chloride assisted reaction path. A comparison of the rate parameters k' and k'' in eqn. (14) shows that bromide is about 10^3 times more effective than chloride as reductant, Y. Therefore, the chloride assisted anation path becomes of importance for the observed over-all rate only for large chloride concentrations. For instance, when $[Cl^-] = 0.2M$ and $[Br^-] = 0.2$ mM, it contributes with only about 15% to the over-all rate.

Conclusions

The reaction model in Figure 1b gives a simple, unified description of the experimental results for oxidative additions of halogen to platinum(II) complexes, for reductive eliminations of halide from platinum(IV) complexes, and for halide assisted and r.e.o.a. substitutions in platinum(IV) complexes.

The resemblance between the suggested mechanism and that recently[2] postulated for substitutions in the presence of platinum(II) complexes is obvious from a comparison of Figures 1a and b. In both cases, either a platinum(II) complex is oxidized by an oxidant, which is platinum(IV) (1a) or halogen (1b), or a platinum(IV) complex is reduced by platinum(II) (1a) or halide (1b). Both in 1a and 1b the reactions are thought to proceed *via* intermediates in which the reducing agent is associated to a halide atom of the oxidant. Within these intermediates, a displacement of charge might occur, depending on the nature of Y, Z, X and the four ligands in the plane around the platinum atom or atoms. This displacement of charge will affect the reactivity of the intermediates and then also the product distribution for a given reaction. Either a direct cleavage of the intermediate will occur, or the cleavage will be preceded by a substitution.

Acknowledgments

Our thanks are due to Professor Ido Leden for valuable discussions, to Fil. mag. Ingegerd Lind for excellent technical assistance, and to the *Swedish Natural Science Research Council* for financial support (K 161–21).

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11 The oxidation of $Pt(CN)_4^{2-}$ with excess iodine in the absence of iodide might give $Pt(CN)_4IH_2O^-$ and/or $Pt(CN)_4I_2^{2-}$ as the reaction product. The experiments indicate that the concentration of iodide released in the oxidation was large enough to produce the di-iodo complex as the dominating platinum(IV) species:
When iodide was added to these previously oxidized solutions in the stopped-flow instrument, the magnitude and rate of change of transmittance were consistent with a formation of $Pt(CN)_4^{2-}$, from $Pt(CN)_4I_2^{2-}$, *i.e.* with a displacement of equilibrium (1) to the left. This means that if considerable amounts of *trans*-$Pt(CN)_4IH_2O^-$ had been formed during the preceding oxidation, the reaction of this complex with iodide must be fast, giving *trans*-$Pt(CN)_4I_2^{2-}$ in a primary step. However, the mathematical form of the experimental rate constant, eqn. (9), indicates that the condition $k_3[X] \ll k_2$ must be fulfilled – *cf.* eqn. (16). In other words, the reduction of *trans*-$Pt(CN)_4IH_2O^-$ giving $Pt(CN)_4^{2-}$ is faster than the anation, giving $Pt(CN)_4I_2^{2-}$.

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