Inorganica Chimica Acta, 24 (1977) 239–246
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Rates and Mechanisms for Halide Anation Reactions of Platinum(IV) Complexes

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Received February 2, 1977

The bromide anation of tr-$PtCl_4BrH_2O^-$ *has been studied at 25 °C and the chloride anations of* tr-$PtCl_4BrH_2O^-$ *and* $PtBr_5H_2O^-$ *at 50 °C. These reactions proceed* via *halide assisted mechanisms, compatible with the experimental rate laws:*

$$-d[\text{tr-}PtCl_4BrH_2O^-]/dt = 0.43[Br^-]^2[\text{tr-}PtCl_4BrH_2O^-]s^{-1}M^{-2}$$

$$-d[\text{tr-}PtCl_4BrH_2O^-]/dt = (2.7[Br^-][Cl^-] + 2.95 \times 10^{-3}[Cl^-]^2)[\text{tr-}PtCl_4BrH_2O^-]s^{-1}M^{-2}$$

$$-d[PtBr_5H_2O^-]/dt = (0.47[Br^-][Cl^-] + 7.6 \times 10^{-4}[Cl^-]^2)[PtBr_5H_2O^-]s^{-1}M^{-2}$$

The bromide anation of tr-$PtBr_4ClH_2O^-$ *studied at 50 °C gives* $PtBr_5Cl^{2-}$ via *a bromide assisted path and* $PtBr_6^{2-}$ via *an REOA-path. The observed rate law is*

$$-d[\text{tr-}PtBr_4ClH_2O^-]/dt = (4.2 \times 10^{-4}s^{-1}M^{-2} \times [Br^-]^2 + 5.8 \times 10^{-4}s^{-1}M^{-1} \times [Br^-])[\text{tr-}PtBr_4ClH_2O^-]$$

$PtBr_5Cl^{2-}$ *reacts subsequently with bromide to form* $PtBr_6^{2-}$ via *a rate-determining (bromide assisted or REOA) formation of an intermediate aqua complex according to the mechanism*

$$PtBr_5Cl^{2-} + H_2O \xrightarrow{+Br^-} PtBr_5H_2O^- \xrightarrow[fast]{+Br^-} PtBr_6^{2-}$$

The observed rate law at 50 °C is

$$-d[PtBr_5Cl^{2-}]/dt = 4 \times 10^{-5}[Br^-][PtBr_5Cl^{2-}]s^{-1}M^{-1}$$

All reactions have been studied in a 0.50 M *perchloric acid medium.*

A general survey of reactivity correlations and mechanisms for platinum(IV) anation reactions is given. Effects of reductants, bridging and entering ligands, and of the four non-labile ligands in the plane around the platinum atom are quantitatively compared.

Introduction

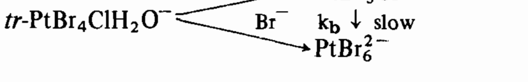
The mechanisms and rates for ligand substitution reactions of octahedral platinum(IV) complexes depend on the nature of the reducing agents present, for instance platinum(II) complexes or free halide ions, on the geometrical arrangement and the nature of the six ligands in the substrate complex and on the nature of the entering ligand. Mason [1] has previously reviewed a number of platinum(II)-dependent substitution reactions with respect to these factors, and Peloso [2] has surveyed some redox processes in platinum systems. Poë and co-workers [3] have given several examples of halide ions acting as reductants in so-called REOA substitutions. It has been shown [4–8] that halide anation reactions of platinum(IV) aqua complexes in some cases also might be assisted by free halide ions in a way which might be visualized as a partial reduction of the platinum(IV) complex. It has been suggested [7] that there is a mechanistic analogy between the platinum(II)-dependent reactions and the REOA and halide assisted reactions, as demonstrated by the schemes in Figure 1. Recent experiments [8–10] show that the entering halide ligand X in the platinum(II)-dependent reactions probably enters the complex after the formation of the bridged intermediate (*cf.* Figure 1 c) and not as previously believed [11, 1], in a primary rapid complex formation step with the square-planar platinum(II) complex.

We will here report kinetic results for the halide anation processes

$$tr\text{-}PtCl_4BrH_2O^- + Br^- \longrightarrow tr\text{-}PtCl_4Br_2^{2-} + H_2O \quad (1)$$

$$tr\text{-}PtCl_4BrH_2O^- + Cl^- \xrightarrow{Br^-} tr\text{-}PtCl_5Br^{2-} + H_2O \quad (2)$$

$$PtBr_5H_2O^- + Cl^- \xrightarrow{Br^-} PtBr_5Cl^{2-} + H_2O \quad (3)$$



$$tr\text{-}PtBr_4ClH_2O^- \begin{cases} \longrightarrow PtBr_5Cl^{2-} \\ \quad\; k_b \downarrow \text{slow} \\ \xrightarrow{Br^-} PtBr_6^{2-} \end{cases} \quad (4)$$

The rate laws for reactions (1), (2) and (3) and the formation of $PtBr_5Cl^{2-}$ in reaction (4) indicate halide assisted mechanisms for these reactions. The direct

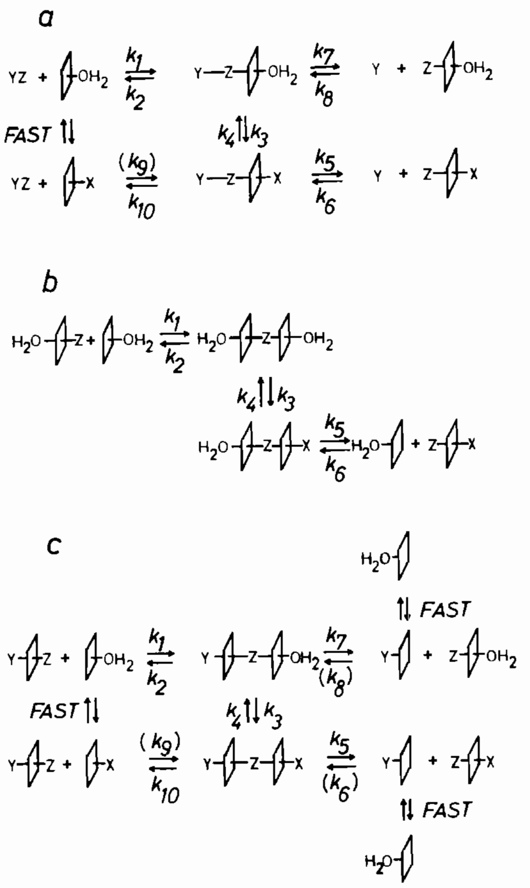


Figure 1. Proposed reaction mechanisms.

formation of $PtBr_6^{2-}$ in reaction (4) can be described by an REOA-mechanism.

The amount of experimental information on halide anation reactions of platinum(IV) aqua complexes is now sufficiently large to permit a summary of factors that determine their rates and mechanisms. A review and some quantitative comparisons are given in the final part of this paper.

Experimental

Chemicals

Potassium tetrachloroplatinate(II), K_2PtCl_4, (Johnson and Matthey) was used without further purification. Potassium tetrabromoplatinate(II), K_2PtBr_4, was prepared from potassium hexabromoplatinate(IV) (Heraeus) by reduction with hydrazine sulfate (Merck's *p.a.*) under carbon dioxide [12]. The hydrobromic acid (Merck's *p.a.*) was freshly distilled to remove free bromine. Other chemicals were reagent grade.

Kinetic Measurements

The platinum(IV) halo–aqua complexes used for the kinetic runs were prepared by oxidizing solutions of K_2PtCl_4 or K_2PtBr_4 with excess bromine or chlorine. Since the oxidation is fast compared to the subsequent anation [8] the following procedures were used. For reactions (1) and (2) solutions of K_2PtCl_4 (for reaction (1) 1×10^{-4} *M* in 0.050 *M* hydrochloric acid and for reaction (2) 6.7×10^{-4} *M* in 0.500 *M* hydrochloric acid) were mixed with solutions containing bromine and the appropriate halide or halides. For reactions (3) and (4) the oxidations were performed immediately before the start of the kinetic runs. Solutions of $PtBr_5H_2O^-$ (1.6×10^{-3} *M*) and *trans*-$PtBr_4ClH_2O^-$ (3.2×10^{-3} *M*) were prepared by oxidation of solutions of K_2PtBr_4 in 0.50 *M* perchloric acid with bromine and chlorine, respectively. The kinetic runs were started by mixing such oxidized solutions with solutions containing hydrobromic and/or hydrochloric acid.

The reactions were studied under pseudo first-order conditions. The concentration of halide was always large enough to suppress the reverse reactions. The hydrogen ion concentration and ionic strength were 0.50 *M* supported by perchloric acid. The concentration of bromine in the reacting solutions was 5×10^{-5} *M* to 10^{-4} *M* (*cf.* Ref. 8, p. 206).

A Zeiss PMQII spectrophotometer equipped with a thermostated cellholder was used. For reaction (1) the solutions were mixed directly in the cell using thermostated syringes. The temperature was (25.0 ± 0.1) °C. The reacting solutions for reactions (2) to (4) were stored in bottles in closed water thermostats at (50.0 ± 0.1) °C. The anation reactions (1) to (3) are followed by slower substitutions. They were studied at 295 (1), 270 (2) and 300 nm (3), where the initial fast reactions give large changes of absorbance, and the changes for the subsequent reactions are small. The absorptivity e_∞ at the end of the first reaction was obtained by linear extrapolation of the absorptivity *vs.* time curves for the slow reaction. With this value of e_∞ good linear pseudo first-order plots were obtained for two to three half-lives. The reproducibility of the rate constants was generally better than ±3%.

Reaction (4) was followed at the absorption maximum of $PtBr_6^{2-}$ at 315 nm. The plots of $\ln(e_\infty - e)$ *vs.* time indicated two reactions, and the rate constants were calculated from

$$e_\infty - e = \alpha c^{-k_a t} + \beta e^{-k_b t} \qquad (5)$$

The last step in this reaction is very slow with half-lives of 10 to 50 h. Its rate constant k_b could only be determined approximately since it was not possible to keep the concentration of bromine constant during the long reaction time. This also somewhat decreased the accuracy of the rate constant for the fast step, k_a, which was obtained from plots of $\ln(e_\infty - e - \beta e^{-k_b t})$ *vs.* time.

TABLE I. Bromide Anation of *trans*-$PtCl_4BrH_2O^-$. Rate Constants with Their Standard Deviations at 25 °C. The concentration of platinum(IV) complex was about 5×10^{-5}*M*.

$[Br^-] \times 10^3/M$	$k_{exp} \times 10^3/s^{-1}$	$\frac{k_{exp}}{[Br^-]^2}/s^{-1}M^{-2}$
50	0.92 ± 0.01	0.37
100	4.4 ± 0.1	0.44
150	9.0 ± 0.3	0.40
200	16.6 ± 0.4	0.42
250	25.9 ± 0.7	0.41
	Weighted mean:	0.43 ± 0.001.

TABLE II. Rate Constants for the Chloride Anation of *trans*-$PtCl_4BrH_2O^-$ at 50 °C. The concentration of platinum(IV) complex was 6.9×10^{-5}M or 3.5×10^{-5}*M*. The standard deviation in k_{exp} was about 3%.

$[Cl^-] \times 10^3/M$	$[Br^-] \times 10^5/M$	$k_{exp} \times 10^4/s^{-1}$
100	6.9	0.51
200	6.9	1.60
300	6.9	3.3
400	3.5	5.3
400	6.9	5.7
500	3.5	7.4
500	6.8	8.0
500	16.8	9.6
500	36.8	12.0
500	56.8	14.4

TABLE III. Chloride Anation of $PtBr_5H_2O^-$. Rate Constants with Standard Deviations at 50 °C. The concentration of platinum(IV) complex was 1.6×10^{-4}*M*.

$[Cl^-] \times 10^3/M$	$[Br^-] \times 10^3/M$	$k_{exp} \times 10^4/s^{-1}$
103	0.160	0.188 ± 0.003
206	0.160	0.51 ± 0.01
309	0.160	1.01 ± 0.03
412	0.160	1.55 ± 0.03
412	0.360	1.90 ± 0.06
412	0.560	2.22 ± 0.06
412	0.760	2.66 ± 0.07
412	1.160	3.5 ± 0.1
464	0.160	1.92 ± 0.02

Results

The results are given in Tables I to IV. The rate constant for reaction (1) at 25 °C is given by

$$k_{exp} = k'[Br^-]^2 \tag{6}$$

$k' = (0.43 \pm 0.01)\ s^{-1}M^{-2}$ was obtained from a least-squares analysis of the straight line $k_{exp}/[Br^-]$ *vs.* $[Br^-]$.

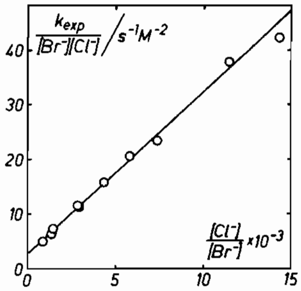


Figure 2. Chloride anation of *trans*-$PtCl_4BrH_2O^-$, reaction (2). Plot according to eqn. (7).

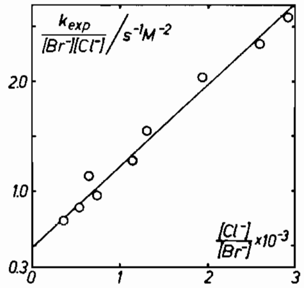


Figure 3. Chloride anation of $PtBr_5H_2O^-$, reaction (3). Plot according to eqn. (7).

For reactions (2) and (3), plots of $k_{exp}/[Br^-][Cl^-]$ *vs.* $[Cl^-]/[Br^-]$ give straight lines with non-zero intercepts (*cf.* Figures 2 and 3). Thus, the experimental rate constants for these two reactions at 50 °C can be expressed as

$$k_{exp} = k'[Br^-][Cl^-] + k''[Cl^-]^2 \tag{7}$$

A least-squares calculation gave $k' = (2.7 \pm 0.2)\ s^{-1}M^{-2}$, $k'' = (2.95 \pm 0.07) \times 10^{-3}\ s^{-1}M^{-2}$ for reaction (2) and $k' = (0.47 \pm 0.05)\ s^{-1}M^{-2}$, $k'' = (7.6 \pm 0.5) \times 10^{-4}\ s^{-1}M^{-2}$ for reaction (3).

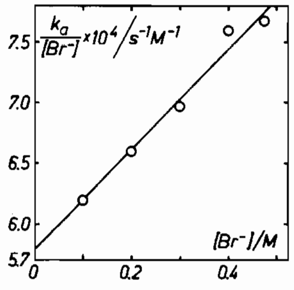


Figure 4. Bromide anation of *trans*-$PtBr_4ClH_2O^-$. Fast reaction step. Plot according to eqn. (8).

According to Figure 4 the rate constant for the fast step of reaction (4) is consistent with the expression

$$k_a = k'[Br^-]^2 + k''[Br^-] \tag{8}$$

TABLE IV. Rate Constants with Standard Deviations for the Bromide Anation of *trans*-$PtBr_4ClH_2O^-$ at 50 °C. The concentration of platinum(IV) complex was $1.6 \times 10^{-4}M$.

$[Br^-] \times 10^3/M$	$k_a \times 10^4/s^{-1}$	$k_b \times 10^6/s^{-1}$	$\frac{k_b}{[Br^-]} \times 10^5/s^{-1}M^{-1}$
100	0.62 ± 0.02	4.0 ± 0.4	4.0
200	1.32 ± 0.08	8.0 ± 0.8	4.0
300	2.09 ± 0.03	14 ± 1	4.7
400	3.04 ± 0.02	16 ± 1	4.0
475	3.7 ± 0.3	19 ± 2	4.0

with $k' = (4.2 \pm 0.8) \times 10^{-4}\ s^{-1}M^{-2}$ and $k'' = (5.8 \pm 0.2) \times 10^{-4}\ s^{-1}M^{-1}$. The slow step is first-order in bromide (*cf.* Table IV)

$$k_b = k'[Br^-] \qquad (9)$$

with a rate constant k' of about $4 \times 10^{-5}\ s^{-1}M^{-1}$.

Discussion

All known platinum(II)-independent reactions, in which one halide ligand is exchanged for another halide, are first-order with respect to entering ligand. Eqns. (6) and (7) show that the rate expressions for the initial fast steps of the reactions between *trans*-$PtCl_4BrH_2O^-$ and bromide and between $PtBr_5H_2O^-$ and chloride are second-order in halide. Therefore, it is reasonable to assume that they correspond to the halide anations, described by reactions (1) and (3).

Provided that the concentration of platinum(II) is negligibly small, an REOA-process will give no net change for reactions (1) to (3) (*vide infra*), so these reactions can be described by the path $k_8, k_7; k_3, k_4$ and k_5, k_6 in Figure 1 a. For excess entering halide and with steady-state conditions for the intermediates, the following rate constant for the anation is obtained:

$$k = \frac{k_3k_5k_8[Y][X]}{k_7(k_4 + k_5) + k_3k_5[X]} \qquad (10)$$

If $k_3[X] \ll k_7$ (*cf.* Ref. 8) this expression agrees with the experimental eqn. (6) for reaction (1), having X = Y = Br. The experimental eqn. (7) for reactions (2) and (3) contains a sum of two terms of the same form as eqn. (10). This implies two parallel paths, one assisted by chloride and the other by bromide. The latter term appears, since the reactions were followed in the presence of small concentrations of bromide in addition to the added chloride (*cf.* Tables II and III). A similar case has previously been described in detail for the chloride anation of *trans*-$Pt(CN)_4BrH_2O^-$ [7].

trans-$PtBr_4ClH_2O^-$ disappears *via* two parallel paths in the initial fast step of reaction (4). $PtBr_6^{2-}$ can be formed by the REOA-process (11), (12) followed by the fast bromide assisted anation (13) [8]:

$$tr\text{-}PtBr_4ClH_2O^- + Br^- \longrightarrow BrCl + PtBr_4^{2-} + H_2O \qquad (11)$$

$$BrCl + PtBr_4^{2-} + H_2O \xrightarrow{\text{fast}} PtBr_5H_2O^- + Cl^- \qquad (12)$$

$$PtBr_5H_2O^- + Br^- \xrightarrow{\text{fast}} PtBr_6^{2-} + H_2O \qquad (13)$$

The rate determining step (11) corresponds to the formation of $PtBr_4^{2-}$ *via* the paths $k_8, k_2; k_8, k_3, k_{10}$ in Figure 1a (*cf.* eqn. (15)).

Simultaneously, $PtBr_5Cl^{2-}$ is formed by a parallel bromide assisted anation which is followed by a much slower formation of $PtBr_6^{2-}$:

$$tr\text{-}PtBr_4ClH_2O^- \xrightarrow[\text{fast}]{+Br^-} PtBr_5Cl^{2-} \xrightarrow[k_b]{+Br^-} PtBr_6^{2-} \qquad (14)$$

An REOA-process cannot give $PtBr_5Cl^{2-}$, since chlorine is more electronegative than bromine (*vide infra*). The model in Figure 1a gives the following rate constant for the formation of the products, assuming $k_3[X] \ll k_7$ (*cf.* Ref. 8), steady-state for the intermediates and excess bromide:

$$k = \frac{k_2k_8[Y]}{k_2 + k_7} + \frac{k_3k_8k_{10}[X][Y]}{(k_2 + k_7)(k_4 + k_5 + k_{10})} + \frac{k_3k_5k_8[X][Y]}{(k_2 + k_7)(k_4 + k_5 + k_{10})} \qquad (15)$$

The first two terms correspond to the REOA-formation of $PtBr_6^{2-}$ and the third one to the bromide assisted formation of $PtBr_5Cl^{2-}$. Eqn. (15) agrees with eqn. (8) for X = Y = Br and shows that the experimental parameter k' in eqn. (8) probably is a composite quantity containing contributions from both parallel paths.

The subsequent slow process in reaction (4), (14) described by the rate constant k_b is most likely a formation of $PtBr_6^{2-}$ *via* a rate-determining formation of an intermediate aqua complex

$$PtBr_5Cl^{2-} + H_2O \xrightarrow[k_b]{Br^-} PtBr_5H_2O^- \xrightarrow[fast]{Br^-} PtBr_6^{2-} \tag{16}$$

The formation of the aqua complex might take place by the halide assisted path k_6, k_4, k_7 or by the REOA-path k_6, k_{10}, k_1, k_7 in Figure 1a. The mechanism (16) agrees with the observed first-order dependence on bromide – eqn. (9). The rate data for the $PtBr_5H_2O^-$–bromide reaction [8] show that this anation is fast compared to the first step in (16). Further support to this description of k_b as the rate constant for the acid hydrolysis of $PtBr_5Cl^{2-}$ is given by a comparison with the rate constant k for the corresponding acid hydrolysis (17) defined by *Rate* = $k[Br^-][PtBr_6^{2-}]$.

$$PtBr_6^{2-} + H_2O \xrightarrow{Br^-} PtBr_5H_2O^- + Br^- \tag{17}$$

The stepwise stability constant of $PtBr_6^{2-}$ [6] and the rate constant for the bromide assisted bromide anation of $PtBr_5H_2O^-$ [8] give approximately $k = 6.4 \times 10^{-2}\ s^{-1}M^{-2}/1.9 \times 10^{3}\ M^{-1} = 3 \times 10^{-5}\ s^{-1}\ M^{-1}$ at 25 °C and for 0.5 *M* perchloric acid medium. The agreement between this value and the value of $k_b = 4 \times 10^{-5}\ s^{-1}M^{-1}$ at 50 °C (*cf.* Table IV) is compatible with Mason's observation for other platinum(IV) substitutions that bromide and chloride have about the same efficiency as leaving ligands [1].

Rates and Mechanisms

The chloride and bromide anations of platinum(IV) halo aqua complexes reported so far, together with their experimental rate constants are summarized in Table V. The platinum(IV) substrates have been written Z–PtL_4–OH_2 or Z–PtL_4–Y. OH_2 or Y is the ligand in *trans*-position to Z which is attacked by the reducing agent. L_4 denotes the four non-labile in-plane ligands which are not necessarily identical. Figure 1 reviews the proposed mechanisms. Most of the reactions have been studied at 25 °C. Some rate parameters for reactions followed at 50 °C have been recalculated to 25 °C using the activation parameters for reaction (M) [8]. This estimation will be sufficiently accurate for the comparisons made below.

The rate constants for reactions (A), (D), (M), (Q), and (R) indicate that even in the presence of platinum(II), reaction paths independent of platinum(II) are of importance for the observed over-all kinetics. The rate laws for all the platinum(II)-independent reactions are consistent with either REOA or halide assisted processes. The REOA-substitutions are supposed to occur *via* a rate-determining reduction to platinum(II). A subsequent fast reoxidation gives a *trans*-halo–aqua complex as the primary product. Poë [3] has demonstrated that the least electronegative of the halides in the halogen YZ enters the complex in this reoxidation (*cf.* Tobe [14], p. 165). This means that anation reactions *via* the REOA-process are possible only when Y is less electronegative than Z. Examples are the k″-path for (C) and the k′-path for (E). When Z is less electronegative than Y or Z = Y, the REOA-process for a halo–aqua complex Z–PtL_4–OH_2 will give no net reaction. Second-order kinetics with respect to halide is obtained in these cases. Examples of such halide assisted reactions, in which the halide Y assists the water replacement (path k_8, k_3, k_5 in Fig. 1a) are (H), (K), (L), (N), (P), and the k′-path of (M), (Q), and (R).

Platinum(II)-dependent reactions are generally supposed to involve a central-ion exchange, occurring with the same rate as the exchange of ligands. This has been demonstrated experimentally in a few cases [1]. Such reactions can be considered as oxidative additions to the platinum(II) complex or as reductive eliminations from the platinum(IV) complex. In this respect they are analogous to the REOA-substitutions, for which the rate-determining step is a reductive elimination of halide from platinum(IV). However, platinum(II)-dependent reaction paths taking place without exchange of central ion cannot be excluded (*vide infra*).

Comparisons of the rate parameters in Table V for the different types of reactions give the correlations summarized in Table VI. For the halide assisted anations, bromide is more efficient than chloride both as assistant, bridging, and entering ligand. The ratios k″/k′ for reactions (H), (L), and (P) give the relative rates Cl:Br = $1:10^3$ for assistant ligands. The k′-paths for (C) [17] and (M) show that bromide is also about 10^3 times more efficient than chloride as bridging ligand, as expected because of its greater polarizability and better electron-mediating properties (*cf.* Ref. 1). Comparison of the k′-values for (H) and (K), (L) and (M), and (P) and (Q) shows that the entering ligand effect is small:Cl:Br ≈ 1:2.

When the four non-labile ligands L in the platinum(IV) complex are compared, the rate increases in the order $Br^-:Cl^-:CN^- \approx 1:5:10^6$, *cf.* (H), (L), (P) and (K), (M), (Q). Replacement of halide by water increases the rates. For instance, *cis*-$PtBr_4(H_2O)_2$ (N) reacts ten times faster than $PtBr_5H_2O^-$ (k′-path of (M)). The higher rate for $PtBr_4(H_2O)_2$ might be due to its more favourable ionic charge. For reaction (R), K_a has been estimated [5] to be ⩾5 *M*, which means that the third-order rate constant for this reaction is $\geqslant 3 \times 10^{2}\ s^{-1}M^{-2}$. Thus, ammonia is more efficient than chloride and bromide as non-labile *cis*-ligand but probably less efficient than cyanide.

For the two REOA-processes in Table V, *viz.* the k″-path in (C) and the k′-path in (E), only the four non-labile *cis*-ligands differ. Also in this case, cyanide is much more efficient than bromide.

TABLE V. Observed Pseudo First-Order Rate Constants for Halide Anation Reactions. The rate parameters refer to 25 °C except where otherwise noted. The ionic strength was 1.00 *M* for reactions (A), (B), (D), and the k′ path of (R), and 0.50 *M* in all other cases. The supporting electrolyte was sodium perchlorate in (F), (G), (R), (S) and the k″-path of (Q) and perchloric acid in all other cases.

	Reaction	Entering ligand	Reductant	Observed rate constant	Parameters	Ref.
(A)	$Cl{-}PtCl_4{-}OH_2^- \rightleftharpoons Cl{-}PtCl_4{-}Cl^{2-}$	Cl^-	$PtCl_4^{2-}$	$k=k_0+\frac{k'+k''[Cl^-]}{1+k'''[Cl^-]}[PtCl_4^{2-}]$	k_0/s^{-1} 1×10^{-5} (50°) $k'/s^{-1}M^{-1}$ 6×10^{-3} (50°) $k''/s^{-1}M^{-2}$ 2.0×10^{-1} (50°) $\sim2\times10^{-2}$ (25°) k'''/M^{-1} 9×10^{-1} (50°)	10
(B)	$Cl{-}PtCl_2(H_2O)_2{-}Cl$ (trans) $\rightarrow$ $Cl{-}PtCl_4{-}OH_2^-$ $\rightarrow$ $Cl{-}PtCl_4{-}Cl^{2-}$	Cl^-	$PtCl_4^{2-}$	$k=(k'+k''[Cl^-])[PtCl_4^{2-}]$	$k'/s^{-1}M^{-1}$ 4.5×10^{-1} (50°) $k''/s^{-1}M^{-2}$ 1.5×10^{-1} (50°)	10
(C)	$Cl{-}PtBr_4{-}OH_2^-$ $\rightarrow$ $Cl{-}PtBr_4{-}Br^{2-}$ $\rightarrow$ $Br{-}PtBr_4{-}Br^{2-}$	Br^-	Br^-	$k=k'[Br^-]^2+k''[Br^-]$	$k'/s^{-1}M^{-2}$ 4.2×10^{-4} (50°) $\sim3\times10^{-5}$ (25°) $k''/s^{-1}M^{-1}$ 5.8×10^{-4} (50°)	this paper
(D)	$Cl{-}Pt(CN)_4{-}OH_2^- \rightarrow Cl{-}Pt(CN)_4{-}Cl^{2-}$	Cl^-	$Pt(CN)_4^{2-}$	$k=f([Cl^-])+\frac{k''[Cl^-]}{1+k'''[Cl^-]}[Pt(CN)_4^{2-}]$	$f([Cl^-])/s^{-1}$ 3×10^{-3} ($[Cl^-]=0.500M$) $k''/s^{-1}M^{-2}$ 47 k'''/M^{-1} 7.6×10^{-1}	9
(E)	$Cl{-}Pt(CN)_4{-}OH_2$ $\rightarrow$ $Br{-}Pt(CN)_4{-}Br^{2-}$ $\rightarrow$ $Cl{-}Pt(CN)_4{-}Br^{2-}$	Br^-	$Br^-, Pt(CN)_4^{2-}$	$k=k'[Br^-]+k''[Br^-][Pt(CN)_4^{2-}]$	$k'/s^{-1}M^{-1}$ 5.37 $k''/s^{-1}M^{-2}$ $\sim2\times10^2$	7
(F)	$Cl{-}Pt(NH_3)_4{-}OH_2^{3+} \rightarrow Cl{-}Pt(NH_3)_4{-}Cl^{2+}$	Cl^-	$Pt(NH_3)_4^{2+}$	$k=k''[H^+][Cl^-][Pt(NH_3)_4^{2+}]$	$k''/s^{-1}M^{-3}$ 1.7×10^3	13
(G)	$Cl{-}Pt(en)_2{-}OH_2^{3+} \rightarrow Cl{-}Pt(en)_2{-}Cl^{2+}$	Cl^-	$Pt(en)_2^{2+}$	$k=k''[H^+][Cl^-][Pt(en)_2^{2+}]$	$k''/s^{-1}M^{-3}$ 1.4×10^3	13
(H)	$Br{-}PtCl_4{-}OH_2^- \rightarrow Br{-}PtCl_4{-}Cl^{2-}$	Cl^-	Br^-, Cl^-	$k=k'[Br^-][Cl^-]+k''[Cl^-]^2$	$k'/s^{-1}M^{-2}$ 2.7 (50°) $\sim2\times10^{-1}$ (25°) $k''/s^{-1}M^{-2}$ 2.95×10^{-3} (50°) $\sim2\times10^{-4}$ (25°)	this paper
(K)	$Br{-}PtCl_4{-}OH_2^- \rightarrow Br{-}PtCl_4{-}Br^{2-}$	Br^-	Br^-	$k=k'[Br^-]^2$	$k'/s^{-1}M^{-2}$ 4.3×10^{-1}	this paper
(L)	$Br{-}PtBr_4{-}OH_2^- \rightarrow Br{-}PtBr_4{-}Cl^{2-}$	Cl^-	Br^- Cl^-	$k=k'[Br^-][Cl^-]+k''[Cl^-]^2$	$k'/s^{-1}M^{-2}$ 4.7×10^{-1} (50°) $\sim4\times10^{-2}$ (25°) $k''/s^{-1}M^{-2}$ 7.6×10^{-4} (50°) $\sim6\times10^{-5}$ (25°)	this paper
(M)	$Br{-}PtBr_4{-}OH_2^- \rightarrow Br{-}PtBr_4{-}Br^{2-}$	Br^-	$Br^-, PtBr_4^{2-}$	$k=k'[Br^-]^2+\frac{k''[Br^-]}{1+k'''[Br^-]}[PtBr_4^{2-}]$	$k'/s^{-1}M^{-2}$ 6.4×10^{-2} $k''/s^{-1}M^{-2}$ 1.05×10^2 k'''/M^{-1} 3.5	8
(N)	$Br{-}PtBr_3H_2O{-}OH_2 \rightarrow Br{-}PtBr_3H_2O{-}Br^-$	Br^-	Br^-	$k=k'[Br^-]^2$	$k'/s^{-1}M^{-2}$ 8.9×10^{-1}	8
(O)	$Br{-}PtBr_2(H_2O)_2{-}Br$ (trans) $\rightarrow$ $Br{-}PtBr_4{-}OH_2^-$ $\rightarrow$ $Br{-}PtBr_4{-}Br^{2-}$	Br^-	$PtBr_4^{2-}$	$k=(k'+k''[Br^-])[PtBr_4^{2-}]$	$k'/s^{-1}M^{-1}$ 3.5 $k''/s^{-1}M^{-2}$ 2.04×10^2	8
(P)	$Br{-}Pt(CN)_4{-}OH_2^- \rightarrow Br{-}Pt(CN)_4{-}Cl^{2-}$	Cl^-	Br^-, Cl^-	$k=k'[Br^-][Cl^-]+k''[Cl^-]^2$	$k'/s^{-1}M^{-2}$ 7.4×10^4 $k''/s^{-1}M^{-2}$ 2.2×10^1	7
(Q)	$Br{-}Pt(CN)_4{-}OH_2^- \rightarrow Br{-}Pt(CN)_4{-}Br^{2-}$	Br^-	$Br^-, Pt(CN)_4^{2-}$	$k=k'[Br^-]^2+k''[Br^-][Pt(CN)_4^{2-}]$	$k'/s^{-1}M^{-2}$ 1.6×10^5 $k''/s^{-1}M^{-2}$ 6.2×10^5	7, 4b
(R)	$Br{-}Pt(NH_3)_4{-}OH_2^{3+} \rightarrow Br{-}Pt(NH_3)_4{-}Br^{2+}$	Br^-	$Br^-, Pt(NH_3)_4^{2+}$	$k=\frac{k'}{K_a}[H^+][Br^-]^2+\frac{k''}{K_a}[H^+][Br^-][Pt(NH_3)_4^{2+}]$	$\frac{k'}{K_a}/s^{-1}M^{-3}$ 5.2×10^1 $\frac{k''}{K_a}/s^{-1}M^{-3}$ 8.0×10^6	4b,5
(S)	$Br{-}Pt(en)_2{-}OH_2^{3+} \rightarrow Br{-}Pt(en)_2{-}Br^{2+}$	Br^-	$Pt(en)_2^{2+}$	$k=k''[H^+][Br^-][Pt(en)_2^{2+}]$	$k''/s^{-1}M^{-3}$ 4.2×10^6	4b

The effects of entering and bridging ligands for the platinum(II)-dependent anations in Table V are of the same magnitude as those obtained for the halide assisted reactions – *cf.* Table VI. The relative efficacy of various platinum(II) complexes is $Pt(CN)_4^{2-} < PtCl_4^{2-} < PtBr_4^{2-} < Pt(NH_3)_4^{2+}$ (1:20:200:5 × 10^4). This order can be estimated from comparisons of the third-order rate constants for the bromide-assisted

TABLE VI. Reactivity Correlations for the Halide Anations in Table V.

Halide Assisted Anations		
Assistant ligand, Y	$Cl^- < Br^-$	$\sim 1{:}10^3$
Bridging ligand, Z	$Cl^- < Br^-$	$\sim 1{:}10^3$
Cis-ligands in Pt(IV), L	$Br^- < Cl^- < NH_3 < CN^-$	$\sim 1{:}5{:}?{:}10^6$
Entering ligand, X	$Cl^- < Br^-$	$\sim 1{:}2$
REOA Anations		
Cis-ligands in Pt(IV), L	$Br^- < CN^-$	
Platinum(II) Dependent Anations		
Pt(II) complex	$Pt(CN)_4^{2-} < PtCl_4^{2-} < PtBr_4^{2-} <$ $< Pt(NH_3)_4^{2+}$	$\sim 1{:}20{:}200{:}5 \times 10^4$
Bridging ligand, Z	$Cl^- < Br^-$	$\sim 1{:}10^3$
Cis-ligands in Pt(IV), L	$Br^- < Cl^- < CN^-$	$\sim 1{:}20{:}10^6$
Entering ligand, X	$Cl^- < Br^-$	$\sim 1{:}4$

and the platinum(II)-dependent reaction paths for (A) [18], (M), (Q) and (R) which give the efficiency of the various platinum(II) complexes relative to bromide.

Reactions (A), (D) and (M), (P) give the reactivity order $Br^- < Cl^- < CN^-$ ($1{:}20{:}10^6$) for the non-labile *cis*-ligands L in the platinum(IV) complex, if the efficiency of various platinum(II) complexes is taken into account. The relative rates are approximately of the same magnitude as those calculated for the halide assisted anations in Table VI. Obviously, the order of increasing reactivity for the L_4-ligands of the platinum(IV) complex, $Br^- < Cl^- < CN^-$, is the reverse compared to the order when these ligands are coordinated to platinum(II). A comparison with redox potentials from Refs. 19, 20, and 21 shows that the reactivity increases with increasing reducing properties of the platinum(II) complex and with increasing oxidizing properties of the platinum(IV) complex. This is also valid for the halide assisted anations, where the reactivity increases with the reducing ability of the assistant halide, $Cl^- < Br^-$.

Ammonia is an exception to this rule. The rate compared to chloride and bromide complexes is increased both when ammonia is coordinated to platinum(II) and to platinum(IV). This might be due to an effect of ionic charge similar to that proposed to explain the enhanced reactivity of *cis*-$PtBr_4(H_2O)_2$ compared to $PtBr_5H_2O^-$.

The correlations in Table VI are of the same magnitude for the halide assisted and platinum(II)-dependent anations. This fact and the similar dependence of the reactions on the redox properties of the assistant halide Y, the platinum(II) complex and the platinum(IV) substrate support the suggested mechanistic analogy between these two types of reaction. In both cases, electron displacement towards the platinum(IV) centre in the intermediates might labilize the ligands in the platinum(IV) complex, especially the ligand in *trans*-position to the bridging Z.

The formation of the platinum(IV) complex Z–Pt(IV)–X *via* the path k_1, k_3, k_5 in Figures 1b and 1c involves a replacement of the aqua ligand coordinated to platinum(II) in the intermediates and gives a central-ion exchange. But, if there is a labilization of especially the terminal *trans*-ligand at the platinum(IV) side of the intermediate, a substitution of that ligand cannot be excluded. In that case substitution might take place without central-ion exchange. The mechanistic rôle of the platinum(II) complex would then be analogous to that of the assistant halide Y in the halide assisted anations in Figure 1a. This can be visualized by Figure 1c for Y = H_2O as a reaction *via* path k_8, k_3, k_5 for anations and *via* k_6, k_4, k_7 for acid hydrolyses of platinum(IV) complexes. Obviously, further study of the rate of central-ion exchange for reactions of this type is desirable.

The reactivity correlations in Table VI can be used to predict approximate rates and mechanisms for other reactions. For instance, a platinum(II)-independent reaction path for reactions (A), (D), (F), (G) and (S) should be halide assisted since the REOA-process will give no net reaction for Z = Y. For reaction (A) the rate constant for a chloride assisted path can be estimated to be 3×10^{-6} $s^{-1}M^{-2}$, for instance by comparison with the rate constant for the chloride assisted reaction path of reaction (H). This agrees satisfactorily with the experimental value for k_o (1×10^{-5} s^{-1}, $[Cl^-] \sim 1.00\,M$) if the experimental errors and the difference in ionic strength are considered. The third-order rate constant for a chloride assisted reaction path of (D) can be estimated to be 2×10^{-2} $s^{-1}M^{-2}$, using the rate constant for the chloride assisted path of reaction (P). The value agrees with the experimental value of 3×10^{-3} s^{-1} for $[Cl^-] = 0.500\ M$. Since the efficiency of $Pt(NH_3)_4^{2+}$ and $Pt(en)_2^{2+}$ to promote reaction is much larger than that of chloride or bromide, platinum(II)-independent paths for reactions (F), (G) and (S) will be negligibly slow compared to the platinum(II)-dependent paths, but they can probably take place under suitable conditions.

For reactions (B) and (O) to occur, on the other hand, the presence of $PtCl_4^{2-}$ and $PtBr_4^{2-}$, respectively, is required. Since water is a bad bridging ligand the formation of $PtCl_5H_2O^-$ and $PtBr_5H_2O^-$ cannot proceed *via* an REOA or a halide assisted process according to the model in Figure 1a, which requires an effective bridging ligand in *trans*-position to the replaced aqua ligand. In these reactions the reducing agents, $PtCl_4^{2-}$ and $PtBr_4^{2-}$, probably attack a halide ligand in *cis*-position to the aqua ligands. Oxidation of the reductants gives the observed products. The difference in reactivity between *cis*- and *trans*-$PtBr_4(H_2O)_2$ gives a further illustration to the importance of the geometrical arrangement of the ligands in the platinum(IV) complex. *Cis*-$PtBr_4(H_2O)_2$ reacts readily with bromide ions in a bromide assisted anation (N) but *trans*-$PtBr_4(H_2O)_2$ is stable towards bromide attack. Only when platinum(II) is present does a reaction (O) occur, but as mentioned above the *trans*-$PtBr_4(H_2O)_2$ in this case reacts as an oxidant and not as a substrate for an anation.

Acknowledgments

Our thanks are due to professor Ido Leden for valuable comments, to Fil. Mag. Ingegerd Lind for experimental assistance, and to the *Swedish Natural Science Research Council for* financial support.

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