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Solvent Paths for Square-Planar Substitutions. Part 2.* Reactions between Aqua Chloroplatinates(II) and Ethene

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The kinetics for the reactions between the complexes $PtCl_n(H_2O)_{4-n}^{2-n}$, $n = 0,1,2,3,4$ *(including* cis- *and* trans-*isomers for* $n = 2$*) and ethene have been studied. In the case of* trans-$PtCl_2(H_2O)_2$, *product analysis shows that both the chloride ligand and the aqua ligand are substituted by ethene in two parallel paths, differing in rate by a factor of only 1.5. The experiments show that ethene, and probably olefins in general, are inefficient entering ligands, similar to dimethyl sulphoxide. Steric reasons might be responsible. Changes in relative* cis- *and* trans-*effects are compatible with an associative mechanism. The aqua complexes are sufficiently reactive with ethene to be steady-state intermediates in associative solvent paths. Reaction models and rate laws for associative square-planar substitutions are discussed, with special reference to reported non-reactivity of solvento intermediates in some previously studied systems.*

Introduction

Aqua complexes appear as intermediates in square-planar substitution reactions in aqueous solution, if an associative mechanism for the solvent path is operative. In general terms, the mechanism can be written as scheme (1), S = solvent:

$$\begin{tikzcd}
ML_3X \arrow[r, shift left, "k_2"] \arrow[d, shift right, "k_1"'] & ML_3Y \arrow[l, shift left, "k_{-2}"] \arrow[dl, shift left, "k_{-3}"] \\
ML_3S \arrow[u, shift right, "k_{-1}"'] \arrow[ur, shift left, "k_3"] &
\end{tikzcd} \qquad (1)$$

For excess X and Y compared to substrate complex this mechanism gives the pseudo first-order rate constant (2)

$$k_{exp} = \frac{k_1 + \dfrac{k_1k_{-2}[X]}{k_2[Y]}}{1 + \dfrac{k_{-1}[X]}{k_3[Y]}} + k_{-2}[X] + k_2[Y] \qquad (2)$$

if the solvento intermediate ML_3S is assumed to be present in steady-state concentrations and if the condition $(k_2/k_{-2}) = (k_1/k_{-1})(k_3/k_{-3})$ is used. If the reverse reactions described by k_{-2} and k_{-3} are negligible, scheme (1) simplifies to (3),

$$\begin{tikzcd}
ML_3X \arrow[r, "k_2"] \arrow[d, shift right, "k_1"'] & ML_3Y \\
ML_3S \arrow[u, shift right, "k_{-1}"'] \arrow[ur, "k_3"'] &
\end{tikzcd} \qquad (3)$$

with the rate constant (4), in which the first term describes the contribution from the solvent path *via* ML_3S.

$$k_{exp} = \frac{k_1}{1 + \dfrac{k_{-1}[X]}{k_3[Y]}} + k_2[Y] \qquad (4)$$

The special case of a rapid equilibrium between the parent complex ML_3X and the solvento intermediate ML_3S for excess X gives the rate constant (5)

$$k_{exp} = \frac{k_2 + k_3K/[X]}{1 + K/[X]} \cdot [R] \qquad (5)$$

where $K = k_1/k_{-1}$ and R is the excess reactant (Y or complex).

When no extra leaving ligand is added in the experiments *i.e.* $k_{-1}[X] \ll k_3[Y]$, eqn. (4) is reduced to the well-known expression (6).

$$k_{exp} = k_1 + k_2[Y] \qquad (6)$$

A necessary condition for rate laws (2), (4) and (6) is that the solvento intermediates are sufficiently reactive to satisfy the steady-state approximation. Information on their reactivities is therefore relevant in this context.

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*Part 1: Ref. 1.

We have recently reported kinetic data for the reactions between the complexes $PtCl_n(H_2O)_{4-n}^{2-n}$; n = 0,1,2,3,4 and the nucleophiles Y = Cl^-, Br^-, I^-, SCN^- and DMSO [1]. The experiments supported scheme (3) and gave rate constants of the forms (4) and (6). We will here report supplementary data for ethene as entering ligand in these complexes. We have studied reactions (7) to (12):

$$PtCl_4^{2-} + C_2H_4 \rightarrow PtCl_3(C_2H_4)^- + Cl^- \qquad (7)$$

$$PtCl_3H_2O^- + C_2H_4 \rightarrow PtCl_3(C_2H_4)^- + H_2O \underset{\pm Cl}{\overset{\text{Fast}}{\rightleftharpoons}} \textit{trans}\text{-}PtCl_2(C_2H_4)H_2O \qquad (8)$$

$$\begin{tikzcd} & \textit{trans}\text{-}PtCl_2(C_2H_4)H_2O + H_2O \underset{\pm Cl^-}{\overset{\text{Fast}}{\rightleftharpoons}} PtCl_3(C_2H_4)^- \quad (9a) \\ \textit{trans}\text{-}PtCl_2(H_2O)_2 + C_2H_4 \arrow[ur] \arrow[dr] & \\ & \textit{trans}\text{-}PtCl(C_2H_4)(H_2O)_2^+ + Cl^- \quad (9b) \end{tikzcd}$$

$$\textit{cis}\text{-}PtCl_2(H_2O)_2 + C_2H_4 \rightarrow \textit{cis}\text{-}PtCl_2(C_2H_4)H_2O + H_2O \xrightarrow[-Cl^-]{\text{Fast}} \textit{cis}\text{-}PtCl(C_2H_4)(H_2O)_2^+ \qquad (10)$$

$$PtCl(H_2O)_3^+ + C_2H_4 \rightarrow \textit{trans}\text{-}PtCl(C_2H_4)(H_2O)_2 + H_2O \xrightarrow[-Cl^-]{\text{Fast}} Pt(C_2H_4)(H_2O)_3^{2+} \qquad (11)$$

$$Pt(H_2O)_4^{2+} + C_2H_4 \rightarrow Pt(C_2H_4)(H_2O)_3^{2+} + H_2O \qquad (12)$$

We have found only two quantitative studies of olefins as entering ligands for square-planar complexes in the literature [2, 3]. The conclusions in these papers are discordant. Milburn and Venanzi [2] in their study of some $PtCl_4^{2-}$–olefin reactions, explained the absence of an observable solvent path in terms of a lower reactivity between the olefin and $PtCl_3H_2O^-$ compared to $PtCl_4^{2-}$, whereas Green and Wilson [3] found that $PtCl_3H_2O^-$ reacts readily with ethene. Other cases of non-reactivity of aqua species have also been suggested [4] (*vide infra*).

Experimental

Chemicals and Solutions

Potassium tetrachloroplatinate(II) from Johnson and Matthey was used directly. Solutions (1 to 13 m*M*) of the complexes $Pt(H_2O)_4^{2+}$, $PtCl(H_2O)_3^+$, *cis*- and *trans*-$PtCl_2(H_2O)_2$ in 1.00 *M* perchloric acid were prepared as described previously [1]. Zeise's salt, $KPtCl_3(C_2H_4)$, was prepared according to Chatt and Searle [5]. The ethene was C.P. grade from Matheson Gas Products. Ethene stock solutions (*ca.* 5 m*M*) were prepared by saturation of aqueous perchloric acid (1.00 *M*) or perchloric/hydrochloric acid (1.00 *M*) with gas for 3 h at 25 °C and atmospheric pressure using the apparatus described in Ref. 5. The solutions were analyzed for ethene by addition of excess bromine and subsequent determination of the residual free bromine by addition of iodide and spectrophotometric analysis for I_3^- at 353 nm; $\epsilon_{I_3^-} = 26400$ cm^{-1} M^{-1}.

Kinetics

In the experiments with excess ethene, the kinetics for reactions (7), (9), (10), (11) and (12) were started by rapidly mixing 1 ml of platinum complex solution with 100 ml of ethene–chloride or ethene solution at 25.00 °C. For reaction (8), 10 ml of a pre-equilibrated platinum complex solution (C_{Pt} = 0.10 m*M*, C_{Cl} = 0.020 *M*, giving 61% $PtCl_4^{2-}$ and 39% $PtCl_3H_2O^-$ at equilibrium, *cf.* Ref. 9) was mixed with 90 ml of an ethene–chloride solution.

In the experiments on reaction (7) with excess complex, 10 ml of ethene stock solution and 90 ml of $PtCl_4^{2-}$ solution were mixed. A sample of the reacting solution was transferred to a cell in the thermostated holder of a Zeiss PMQ II spectrophotometer, kept at (25.00 ± 0.02) °C, whereupon the cell was stoppered. The ionic strength and hydrogen ion concentration were 1.00 *M*, supported by perchloric acid. Excess chloride was added to the ethene solutions as hydrochloric acid in the experiments with $PtCl_4^{2-}$ and *trans*-$PtCl_2(H_2O)_2$. Excess ethene or complex gave pseudo first-order kinetics. Reverse reactions were negligible because of the high stability of the ethene complexes formed. For the low concentrations of ethene used (0.5 to 5 m*M*) there was no indication of formation of complexes containing more than one ethene ligand. Rate constants were calculated directly from the absorbance *vs.* time plots using a least-squares program. Table I reviews the experiments.

TABLE I. Rate Constants for the Reactions Between $PtCl_n(H_2O)_{4-n}^{2-n}$, n = 0,1,2,3,4, and Ethene at 25.0 °C and 1.00 *M* Perchloric Acid Medium.

Reaction	10^3 $[C_2H_4]/M$	10^3 $[Cl^-]_{added}/M$	10^4 C_{Pt}/M	λ/nm	10^5 k_{exp}/s^{-1}
(7)	0.5	50	0.5	218	0.148 ± 0.020
	1.0	100	0.5	218	0.180 ± 0.020
	1.5	150	0.5	218	0.265 ± 0.020
	2.0	200	0.5	218	0.291 ± 0.025
	3.0	300	0.5	218	0.476 ± 0.035
	4.0	400	0.5	218	0.549 ± 0.020
	4.5	450	0.5	218	0.589 ± 0.020
	0.1	900	10.0	218	0.102 ± 0.015
	0.2	900	20.0	218	0.214 ± 0.020
	0.3	900	30.1	218	0.319 ± 0.025
	0.5	900	50.2	218	0.537 ± 0.025
	0.5	900	70.2	218	0.779 ± 0.039
	0.5	900	100.0	218	1.13 ± 0.05
(8)	1.0	20	1.0	287	0.34 ± 0.02
	2.0	20	1.0	287	0.66 ± 0.03
	3.0	20	1.0	287	0.97 ± 0.07
	4.0	20	1.0	287	1.31 ± 0.04
	4.4	20	1.0	287	1.45 ± 0.03
(9)	1.0	10	0.64	250	1.09 ± 0.12
	2.0	20	0.64	250	2.16 ± 0.15
	3.0	30	0.64	250	3.08 ± 0.16
	4.0	40	0.64	250	3.89 ± 0.18
	5.0	50	0.64	250	4.97 ± 0.11
(10)	1	–	0.2	250	3.6 ± 0.5
	3	–	0.2	250	10.7 ± 0.6
	5	–	0.2	250	18.1 ± 1.0
(11)	1.7	–	0.1	250	5.9 ± 0.3
	3.0	–	0.1	250	10.1 ± 0.7
	4.0	–	0.1	250	13.8 ± 1.0
	5.0	–	0.1	250	17.4 ± 1.0
(12)	0.98	–	1.32	220	0.94 ± 0.05
	2.0	–	1.0	220	2.03 ± 0.2
	2.45	–	1.32	220	2.6 ± 0.2
	3.0	–	1.0	220	3.0 ± 0.2
	3.92	–	1.32	220	3.9 ± 0.3
	4.0	–	1.0	220	4.0 ± 0.3
	4.90	–	1.32	220	5.0 ± 0.3
	5.0	–	1.0	220	5.0 ± 0.3

Side Reactions

Ethene–chloro–aqua complexes decompose slowly in aqueous solution, the ethene probably being oxidized to acetaldehyde [6]. These processes are slow and kinetically well separated from the ligand substitution reactions studied here. The least stable complex appears to be *cis*-$PtCl(C_2H_4)(H_2O)_2^+$, formed in reaction (10), whereas the platinum–ethene–aqua complex $Pt(C_2H_4)(H_2O)_3^{2+}$ is stable in aqueous perchloric acid solution for several months.

Spectra

The absorption spectra given in Fig. 1 were recorded at 25.0 °C using a Beckman Model 25 recording spectrophotometer. The spectrum of $PtCl_3(C_2H_4)^-$ was recorded using a solution with C_{Pt} = 0.1 m*M* and C_{Cl} 0.050 *M* or 1.00 *M* and that of *trans*-$PtCl_2(C_2H_4)(H_2O)$ using a 0.1 m*M* solution of Zeise's salt in 1.00 *M* perchloric acid. No extra chloride was added. The latter solution contains more than 97% of the platinum as *trans*-$PtCl_2(C_2H_4)H_2O$, *cf.* reaction (13).

TABLE II. Second-order Rate Constants at 25.0 °C and a 1.00 M Perchlorate Medium for Reactions of Ethene with $PtCl_n(H_2O)_{4-n}^{2-n}$, n = 0,1,2,3,4. Rate constants for dimethyl sulphoxide from Ref. 1 have also been included. Values of $k/(nQ^q)$ calculated as described in Ref. 1.

Reaction	Substrate Complex	Leaving Ligand	$k/M^{-1}\ s^{-1}$		$(k/nQ^q)/M^{-1}\ s^{-1}$	
			C_2H_4	DMSO [1]	C_2H_4	DMSO [1]
(7)	$PtCl_4^{2-}$	Cl^-	$(1.1 \pm 0.1) \times 10^{-3\,a}$	3.2×10^{-3}	2.8×10^{-4}	9.0×10^{-5}
(8)	$PtCl_3H_2O^-$	H_2O	$(9.1 \pm 0.8) \times 10^{-3\,a}$	2.79×10^{-2}	9.1×10^{-3}	9.3×10^{-5}
(9a)	*trans*-$PtCl_2(H_2O)_2$	H_2O	$(4.0 \pm 0.4) \times 10^{-3}$	–	2.0×10^{-3}	–
(9b)	*trans*-$PtCl_2(H_2O)_2$	Cl^-	$(5.9 \pm 0.4) \times 10^{-3}$	1.42×10^{-3}	3.0×10^{-3}	7.0×10^{-3}
(10)	*cis*-$PtCl_2(H_2O)_2^+$	H_2O	$(3.6 \pm 0.5) \times 10^{-2}$	2.53×10^{-2}	1.8×10^{-2}	1.3×10^{-2}
(11)	$PtCl(H_2O)_3^+$	*trans*-H_2O	$(3.5 \pm 0.3) \times 10^{-2}$	1.2×10^{-2}	3.5×10^{-2}	3.6×10^{-2}
(12)	$Pt(H_2O)_4^{2+}$	H_2O	$(1.0 \pm 0.1) \times 10^{-2}$	8.4×10^{-5}	2.5×10^{-3}	1.9×10^{-4}

[a] Green and Wilson [3] obtained $(2.06 \pm 0.06) \times 10^{-3}\ M^{-1}\ s^{-1}$, $(9.1 \pm 1.1) \times 10^{-3}\ M^{-1}\ s^{-1}$ for reactions (7) and (8), respectively.

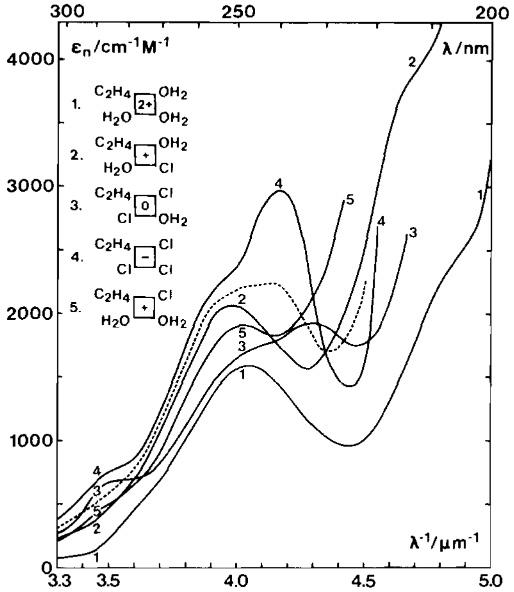


Fig. 1. Spectra of the complexes: 1) $Pt(C_2H_4)(H_2O)_3^{2+}$; 2) *trans*-$PtCl(C_2H_4)(H_2O)_2^+$; 3) *trans*-$PtCl_2(C_2H_4)(H_2O)$; 4) $PtCl_3(C_2H_4)^-$ and 5) *cis*-$PtCl(C_2H_4)(H_2O)_2^+$. The dashed spectrum was recorded using an equilibrated solution of reaction (9) with $C_{Pt} = 1.09 \times 10^{-4}$ M, $[C_2H_4] = 5.0$ mM, and $[Cl^-] = 50$ mM. It is a superposition of spectra 2 and 4 in the ratio (1.5 ± 0.2):1.

Calculations and Results

Reaction Products

The chloride ligands *trans* to the olefin are labile due to the large *trans*-effect of ethene. The following rapid aquation equilibria must be considered in the product analysis:

$$PtCl_3(C_2H_4)^- + H_2O \rightleftarrows trans\text{-}PtCl_2(C_2H_4)H_2O + Cl^- \qquad (13)$$

$$trans\text{-}PtCl(C_2H_4)(H_2O)_2^+ + H_2O \rightleftarrows Pt(C_2H_4)(H_2O)_3^{2+} + Cl^- \qquad (14)$$

$$cis\text{-}PtCl_2(C_2H_4)(H_2O) + H_2O \rightleftarrows cis\text{-}PtCl(C_2H_4)(H_2O)_2^+ + Cl^- \qquad (15)$$

The acid hydrolysis equilibrium constants are $K_{(13)} = 3 \times 10^{-3}$ M, $K_{(14)} \sim 1 \times 10^{-4}$ M, and $K_{(15)} \sim 1 \times 10^{-3}$ M. $K_{(13)}$ has been measured by Leden and Chatt [7], whereas the values for $K_{(14)}$ and $K_{(15)}$ can be estimated from an analogy with the constants for the corresponding Pt(II)–DMSO–Cl^-–H_2O complexes [8]. Thus, for the experimental concentrations of chloride given in Table I, $PtCl_3(C_2H_4)^-$ will be the sole reaction product in reaction (7), *trans*-$PtCl(C_2H_4)(H_2O)_2^+$ in reaction (9b), *cis*-$PtCl(C_2H_4)(H_2O)_2^+$ in reaction (10) and $Pt(C_2H_4)(H_2O)_3^{2+}$ in reactions (11) and (12). Reactions (8) and (9a) will give equilibrium mixtures of *trans*-$PtCl_2(C_2H_4)H_2O$ and $PtCl_3(C_2H_4)^-$ as the reaction products, except for the highest concentration of chloride used in reaction (9a) (50 mM), where more then 95% of the platinum will be present as Zeise's anion.

The reaction product for reaction (7) was identified by a comparison of the spectrum for the equilibrated solution with the independently recorded spectrum for $PtCl_3(C_2H_4)^-$ in Fig. 1.

Absorption spectra for the reaction products of reactions (10) – *cis*-$PtCl(C_2H_4)(H_2O)_2^+$ – and (11) and (12) with and without addition of excess chloride – *trans*-$PtCl(C_2H_4)(H_2O)_2^+$ and $Pt(C_2H_4)(H_2O)_3^{2+}$ – are also included in the Figure. The dashed line in Fig. 1 represents the spectrum of the equilibrated solution formed in reaction (9) for $[Cl^-] = 50$ mM. This spectrum is a superposition of the spectra for *trans*-$PtCl(C_2H_4)(H_2O)_2^+$ and $PtCl_3(C_2H_4)^-$ in the ratio (1.5 ± 0.2):1 which directly gives the ratio between the two over-all rate constants for the parallel paths (9b) and (9a) (*vide infra*).

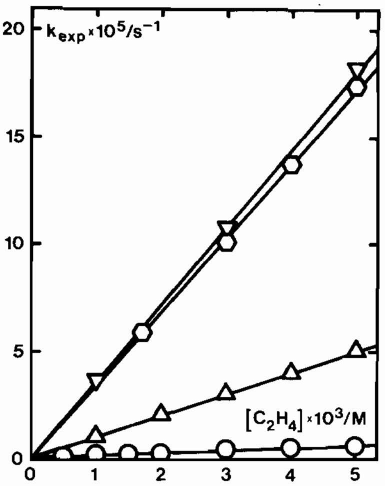


Fig. 2. Observed rate constants for reactions (7) –○; (10) –△; (11) –○ and (12) –▽ *vs.* the concentration of excess ethene.

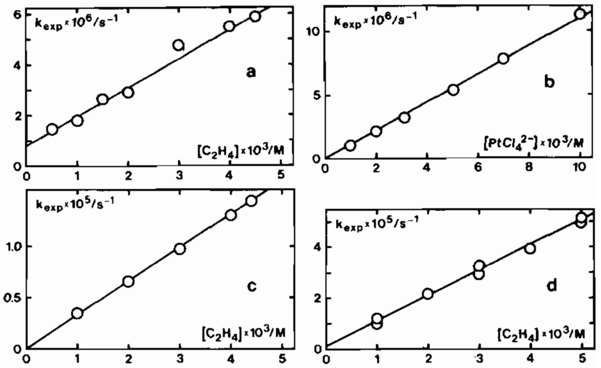


Fig. 3. Observed rate constants for reactions (7), (8) and (9) *vs.* concentration of excess reactant, (a) reaction (7) for excess ethene; (b) reaction (7) for excess tetrachloroplatinate(II); (c) reaction (8) for excess ethene and (d) reaction (9) for excess ethene.

Kinetics

Reactions (10), (11) and (12) are simple substitutions of aqua ligands by ethene. Fig. 2 shows plots of the observed rate constants *vs.* the concentration of excess ethene and Table II gives the rate constants obtained from the slopes of these plots.

Reaction (7) was studied using excess of chloride and $PtCl_4^{2-}$ or ethene. Reaction (8) was studied using excess of chloride and ethene and a pre-equilibrated solution of $PtCl_4^{2-}$ (*ca.* 61%) and $PtCl_3(H_2O)^-$ (*ca.* 39%), *cf.* Table I. Scheme (3) takes the form (16) for these reactions.

$$\begin{tikzcd}
PtCl_4^{2-} \arrow[r, "k_2"] \arrow[d, shift right, "k_1"'] & PtCl_3(C_2H_4)^- \\
PtCl_3(H_2O)^- \arrow[u, shift right, "k_{-1}"'] \arrow[ur, "k_3"] &
\end{tikzcd} \qquad (16)$$

For reaction (7), the observed rate constant for excess ethene is described by eqn. (4) where the ratio $[X]/[Y] = [Cl^-]/[C_2H_4] = 100$ was kept constant in all experiments, *cf.* Table I. Figure 3a shows a plot according to eqn. (4). Introducing $k_{-1} = (5.2 \pm 0.2) \times 10^{-3}\ M^{-1}\ s^{-1}$ from Ref. 9 and $k_3 = (9.1 \pm 0.8) \times 10^{-3}\ M^{-1}\ s^{-1}$ from Table II, the intercept of Fig. 3a $(0.80 \pm 0.11) \times 10^{-6}\ s^{-1}$ gives $k_1 = (4.7 \pm 0.5) \times 10^{-5}\ s^{-1}$, in good agreement with previously determined values [9] for the acid hydrolysis rate constant of $PtCl_4^{2-}$ $(4.0 \pm 0.2) \times 10^{-5}\ s^{-1}$. The slope of the plot in Fig. 3a gives $k_2 = (1.1 \pm 0.1) \times 10^{-3}\ M^{-1}\ s^{-1}$.

For excess tetrachloroplatinate(II) compared to ethene, all experiments on reaction (7) were performed using a constant, large excess of leaving ligand ($[Cl^-] = 0.900\ M$), which determines the distribution of platinum between $PtCl_4^{2-}$ and $PtCl_3(H_2O)^-$ in rapid equilibrium with each other, *cf.* scheme (16). The equilibrium mixture of $PtCl_4^{2-}$ and $PtCl_3H_2O^-$ reacts *via* the two parallel, slow paths denoted by k_2 and k_3 to the common product $PtCl_3(C_2H_4)^-$. The observed pseudo first-order rate constant is described by eqn. (5) where $[R] = C_{Pt}$ denotes the total concentration of platinum and K is the equilibrium constant [9] $k_1/k_{-1} = 7.7 \times 10^{-3}\ M$. For the high concentration of leaving ligand used, the term $K/[X] \ll 1$ and eqn. (5) can be simplified to (17). Fig. 3b

$$k_{exp} = (k_2 + k_3K[Cl^-]^{-1})C_{Pt} \qquad (17)$$

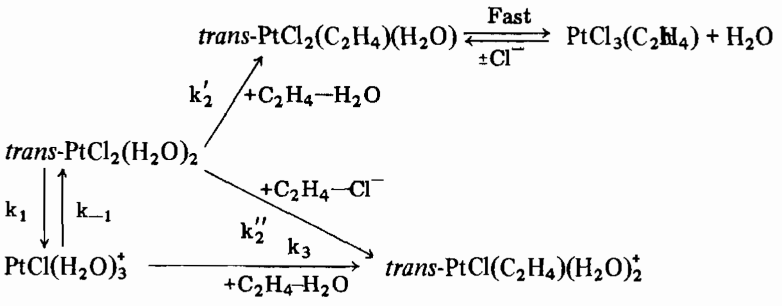
shows a plot according to eqn. (17). The slope $(1.17 \pm 0.03) \times 10^{-3}\ M^{-1}\ s^{-1}$ and the value of $k_3K[Cl^-]^{-1} = (7.8 \pm 2.0) \times 10^{-5}\ M^{-1}\ s^{-1}$ (using the k_3 value in Table II) give $k_2 = (1.09 \pm 0.05) \times 10^{-3}\ M^{-1}\ s^{-1}$, in good agreement with the determination in Fig. 3a from the experiments with excess ethene.

For reaction (8), the aqua intermediate $PtCl_3(H_2O)^-$ and the parent complex, $PtCl_4^{2-}$ can also be considered to be in rapid equilibrium with each other, and the observed first-order rate constant is described by eqn. (5) with $R = C_2H_4$. Fig. 3c shows a plot according to eqn. (5). From the slope, $(3.3 \pm 0.1) \times 10^{-3}\ M^{-1}\ s^{-1}$ and the values [9] of $K = 7.7 \times 10^{-3}\ M$ and $k_2 = (1.1 \pm 0.1) \times 10^{-3}\ s^{-1}$ (Table II), we obtain $k_3 = (9.1 \pm 0.8) \times 10^{-3}\ M^{-1}\ s^{-1}$.

Reaction (9) was also studied using excess chloride and ethene. The product analysis shows that the reaction between ethene and *trans*-$PtCl_2(H_2O)_2$ takes place via the two parallel paths denoted (9a) and (9b). Thus, reaction (9) can be described by scheme (18). Steady-state conditions for the aqua intermediate $PtCl(H_2O)_3^+$ give the observed pseudo

TABLE III. Second-order Rate Constants for Reaction of $PtCl_4^{2-}$ with Various Olefins at 25 °C.

Olefin	$k_2 \times 10^3/M^{-1}\ s^{-1}$	Ionic Medium	Ref.
CH_2CH_2	1.1 ± 0.1	1 M ClO_4^-	This paper
$CH_2{:}CH{\cdot}CH_2OH$	1.30 ± 0.02	2 M Cl^-	2
$CH_2{:}CH{\cdot}CH_2NH_3^+$	1.86 ± 0.02	2 M Cl^-	2
$CH_2{:}CH{\cdot}CH_2SO_3^-$	0.83 ± 0.02	2 M Cl^-	2



(18)

first-order rate constant for excess ethene of eqn. (19). The ratio $[Cl^-]/[C_2H_4] = 10$ was constant in all experiments, *cf.* Table I. Fig. 3d shows a plot

$$k_{exp} = \frac{k_1}{1 + k_{-1}[Cl^-]/k_3[C_2H_4]} + (k_2' + k_2'')[C_2H_4] \qquad (19)$$

according to eqn. (19). The first term in eqn. (19) corresponds to the small intercept, which is approximately $(1.0 \pm 0.2) \times 10^{-6}\ s^{-1}$. Introducing the rate constants $k_{-1} = 0.46\ M^{-1}\ s^{-1}$ from Ref. 10 and $k_3 = 3.5 \times 10^{-2}\ M^{-1}\ s^{-1}$ from Table I we find that k_1 is approximately $(1.3 \pm 0.3) \times 10^{-4}\ s^{-1}$, in satisfactory agreement with the separately determined [10] acid hydrolysis rate constant for *trans*-$PtCl_2(H_2O)_2$ $(1 \times 10^{-4}\ s^{-1})$.

The product analysis gives $k_2''/k_2' = 1.5 \pm 0.2$, since the first term in eqn. (19) can be neglected compared to $k_2''[C_2H_4]$. The slope of the plot in Fig. 3d gives the sum of the rate constants, $k_2' + k_2'' = (9.9 \pm 0.7) \times 10^{-3}\ M^{-1}\ s^{-1}$. Thus, we obtain the values $k_2' = (4.0 \pm 0.4) \times 10^{-3}\ M^{-1}\ s^{-1}$ and $k_2'' = (5.9 \pm 0.5) \times 10^{-3}\ M^{-1}\ s^{-1}$ given in Table II.

Discussion

Table II gives a review of the rate constants. For comparison, corresponding values for dimethyl sulphoxide [1] have been included. We have also listed values of $k/(nQ^q)$ calculated as described previously [1].

Our rate constants for reactions (7) and (8) agree relatively well with those determined by Green and Wilson [3]. G & W had to use complicated expressions to evaluate their constants from the rate of absorption of gaseous ethene by aqueous solutions of $PtCl_4^{2-}$, $PtCl_3H_2O^-$ and (probably *cis*-) $PtCl_2(H_2O)_2$ in equilibrium with each other. A comparison with Milburn's and Venanzi's [2] previous data is given in Table III.

The following conclusions can be drawn from the values in Tables II and III:

(*i*). Ethene behaves like an uncharged entering ligand, *i.e.* the ionic charge of the substrate complex has no influence on the rates (Q = 1.0 ± 0.1). M & V's data in Table III show similarly that allyl alcohol reacts with the same rate as ethene with $PtCl_4^{2-}$, whereas the rate increases slightly for the allylammonium ion and decreases for the allylsulphonate ion. The variations in rate with the substituents on the olefin are very small, which is reasonable, since the charged parts of the olefins are relatively far from the reaction centre.

(*ii*). Ethene, and probably olefins in general, *cf.* Table III, are inefficient entering ligands, like dimethyl sulphoxide. We can put forward the following approximate sequence for entering-ligand-efficiency in these simple platinum(II)–chloro–aqua complexes, water being the leaving group, *cf.* Ref. 1:

$$\begin{array}{ccccccc} H_2O & < DMSO & \approx C_2H_4 & < Cl^- & < Br^- & < SCN^- & < I^- \\ \sim 10^{-3} & 0.3 & 0.4 & 1 & 4 & 40 & 100 \end{array}$$

Specific steric requirements for the formation of the transition state might be responsible for the low efficiency of DMSO and ethene as nucleophiles.

TABLE IV. Comparison between the Reactivity of the Aqua Complexes $PtCl_3(H_2O)^-$ and $PtCl(H_2O)_3^+$ and the Corresponding Chloro Complexes, $PtCl_4^{2-}$ and *trans*-$PtCl_2(H_2O)_2$, respectively, for Various Entering Ligands (rate constants from Ref. 1 and the present study).

Substrate Complex	Leaving Ligand	$k/M^{-1}\ s^{-1}$					
		Cl^-	Br^-	I^-	SCN^-	DMSO	C_2H_4
$PtCl_4^{2-}$	Cl^-	$\sim 1 \times 10^{-5}$	4.8×10^{-5}	2.0×10^{-2}	0.010	3.2×10^{-3}	1.1×10^{-3}
$PtCl_3H_2O^-$	H_2O	5.2×10^{-3}	2.1×10^{-2}	0.38	0.10	2.8×10^{-2}	9.1×10^{-3}
trans-$PtCl_2(H_2O)_2$	Cl^-	–	6.7×10^{-3}	0.31	0.30	1.42×10^{-3}	5.9×10^{-3}
$PtCl(H_2O)_3^+$	*trans*-H_2O	0.46	1.7	39	16	1.2×10^{-2}	3.5×10^{-2}

(*iii*). We observed previously [1] that the relative *trans*-effect Cl^-/H_2O, which is 350 for chloride as entering ligand, varies with the nature of the entering nucleophiles. We can now include ethene in this series

$$Cl^- > Br^- \approx SCN^- > I^- > DMSO > C_2H_4$$

350 200 200 80 50 10

and conclude that the relative *trans*-effect Cl^-/H_2O decreases, when the *trans*-effect of the entering nucleophile increases. The relative *cis*-effect $Cl^-/H_2O = 0.5 \pm 0.2$, on the other hand, is independent of the nature of the entering nucleophile, including ethene. Both observations are in accord with a trigonal bipyramidal transition state, where there is a strong interaction between entering, leaving and *trans*-ligands, whereas the *cis*-ligands are much less involved. In agreement with this, the relative efficiency of leaving ligands also varies with the nature of the entering nucleophile, but this dependence is less regular.

Reaction Mechanisms

The present results give further support to reaction scheme (3). Thus, the values of k_1 obtained by extrapolation of the plots in Fig. 3a and 3d agree within the limits of error with the separately determined acid hydrolysis rate constants for $PtCl_4^{2-}$ and *trans*-$PtCl_2(H_2O)_2$.

Table IV compares the rate constants for the substitution of an aqua ligand in the complexes $PtCl_3H_2O^-$ and $PtCl(H_2O)_3^+$ with those for the substitution of a chloride in the corresponding parent chloro complexes $PtCl_4^{2-}$ and *trans*-$PtCl_2(H_2O)_2$ for various entering nucleophiles. The difference in reactivity between aqua complex and chloro complex is large (*ca.* 500) for entering ligands of low *trans*-effect like chloride and bromide, whereas the difference is much smaller (about 10) for nucleophiles high in the *trans*-effect series like iodide, thiocyanate, DMSO and ethene. In all cases studied, however, the aqua complexes are sufficiently reactive to function as steady-state intermediates in a solvent path according to schemes (3), (16) and (18).

One obvious reason for the non-appearance of one of the terms in the rate laws (2), (4) or (6) is the trivial fact that in some systems $k_1 \ll k_2[Y]$ and in others $k_1 \gg k_2[Y]$. For instance, the nature of the entering group is much more important for the reactions of gold(III) substrates than for those of palladium(II) or platinum(II). Therefore, the stepwise halide substitutions in the $AuCl_4^-$–Br^- system [11] take place without any significant contribution by the solvent path in the bromide concentration range necessary for the experiments*. The reverse is true for the analogous $PtCl_4^{2-}$–Br^- reactions [9], where the solvent path is predominant and it is necessary to increase the bromide concentration to very large values in order to observe the small contribution from the $k_2[Y]$ term in eqn. (2).

The solvent path can also be quenched by the presence of large concentrations of leaving ligand, compare reaction schemes (1) and (3). The leaving group X and the entering group Y compete for the solvento intermediate. If the concentration of leaving ligand is increased, the first term in eqns. (2) and (4) will decrease and will sometimes become negligible compared to other terms in the rate equation.

Milburn's and Venanzi's investigation [2], performed using a large excess of leaving ligand, gives an example of such behaviour. M & V observed that the reaction path *via* $PtCl_3(H_2O)^-$ was negligible, but their conclusion that the aqua complex is less reactive towards olefins than $PtCl_4^{2-}$ is obviously not in agreement with our present results, nor with Green's and Wilson's observations [3].

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*This does not imply, of course, that aqua complexes of Au(III) react slowly with nucleophiles. Compare, for instance, the rate constant [12] for the $AuCl_3H_2O$–Cl^- reaction ($2.3 \times 10^3\ M^{-1}\ s^{-1}$) with that for the $AuCl_4^-$–Cl^- isotopic exchange [13] ($1.5\ M^{-1}\ s^{-1}$).

The discrepancy can be explained, if M & V's experimental design is considered. Using scheme (16) and their notations for the rate constants, we can estimate† $k_1 \equiv k' = 4 \times 10^{-5}$ s^{-1}, $k_{-1} \equiv k'' = 8 \times 10^{-3}$ M^{-1} s^{-1}, $k_3 \equiv k''' = 1 \times 10^{-2}$ M^{-1} s^{-1}. k_2 is given by M & V as 1.86×10^{-3} M^{-1} s^{-1}. These values of the rate constants indicate that the first term in eqn. (4) will never amount to more than about 1% of the second term for the large concentrations of chloride used (1 *M* or 2 *M*). Thus, the experimental results of M & V can be explained by the general rate law (4), without any special assumptions about a non-reactivity of the solvento intermediate.

In this context it is interesting to examine other experimental studies [4], suggesting that solvento intermediates react slowly (or not all) with the entering nucleophile, Y. For instance, Bekker and Robb [14] have reported studies of the reactions between $PdCl_4^{2-}$ and a series of substituted thioureas. Their experimental design was similar to that of M & V in that a large excess of leaving ligand was used. Linear plots through the origin of k_{exp} *vs.* [Y] with slope k_2 were obtained for all values of [Y] and [X]. To explain the absence of the solvent path in this particular case, the authors assumed that $k_3 \approx k_2$ using the notation in scheme (3). However, the steady-state conditions were fulfilled only for the highest concentrations of chloride used (2 *M*), and in these experiments, the solvent path was effectively quenched, *i.e.* $k_1k_3/(k_3[Y] + k_{-1}[X]) \ll k_2$, even if $k_3 \gg k_2$. For $[Cl^-] = 0.100$ *M* neither of the two conditions steady-state for $PdCl_3H_2O^-$ or a rapid equilibrium between $PdCl_4^{2-}$ and $PdCl_3H_2O^-$ leading to eqn. (5) – were fulfilled, so the rate expressions used were not applicable. Independent studies of the $PdCl_3H_2O^-$–thiourea reaction have not been performed. Mureinik [15] has suggested that thiocyanate is unreactive towards aqua complexes of platinum(II), *viz.* $PtCl_3H_2O$, but new experiments [1] have disproved this conclusion.

In cases where both terms of eqns. (2) and (4) contribute to the over-all reaction, a necessary condition for linear relationships of k_{exp} *vs.* [Y] is obviously that the series of experiments are performed using constants ratios [X]/[Y], both X and Y being present in excess compared to the substrate complex. Examples of such plots are given by the $PtCl_4^{2-}$–iodide and DMSO reactions [1], the $PtCl_4^{2-}$–ethene and *trans*-$PtCl_2(H_2O)_2$–ethene reactions in the present report and by the $PtCl_4^{2-}$–bromide and $PtBr_4^{2-}$–chloride reactions [9].

If the condition [X]/[Y] = constant is not fulfilled, curved plots of k_{exp} *vs.* [X] and k_{exp} *vs.* [Y] will be obtained, as has recently been pointed out by de Waal and Robb [16]. This case is illustrated by Seguin's and Zador's study [17] of the $PtdienBr^+$–inosine reaction, which conforms to scheme (1) and where iteration methods were used for the evaluation of the rate constants.

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†The value of $k_3 \equiv 1 \times 10^{-2}$ M^{-1} s^{-1} for the $PtCl_3H_2O^-$ olefin reactions in general seems reasonable, since $PtCl_3H_2O^-$ reacts with ethene with a rate constant of 1.1×10^{-2} M^{-1} s^{-1} (Table II) and there is no significant difference in reactivity between the various olefins (Table III). The acid hydrolysis rate constant k_1 is approximately independent of ionic strength [9] whereas the chloride anation rate constant k_{-1} has been extrapolated to the ionic strength 2 *M* from values at 0.5 *M* and 1.0 *M* ionic strength [9].