Kinetics and Mechanism of Reaction of Platinum(II) Complexes. Part I. Ethene and Tetrachloroplatinate(II)

By **Michael Green** * and **Christopher J. Wilson**, Department of Chemistry, University of York, Heslington, York YO1 5DD

The kinetics have been investigated of the reaction of ethene with $[PtCl_4]^{2-}$, $[PtCl_3(OH_2)]^-$, and $[PtCl_2(OH_2)_2]$ in equilibrium in water at 25.0 °C, giving second-order rate constants of $(2.06 \pm 0.06) \times 10^{-3}$, $(9.1 \pm 1.1) \times 10^{-3}$, and $(8.3 \pm 3.0) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} respectively. The overall reaction is irreversible and the products are monoplatinum mono-olefin complexes such as $[PtCl_3(C_2H_4)]^-$ and $[PtCl_2(C_2H_4)(OH_2)]$. The validity of the assumption of steady-state conditions has been investigated and found in this instance to be justified.

THE rate equation for substitution in the majority of platinum(II) complexes is of the form[1] (A) (L = the incoming ligand, Pt = the platinum complex). However, Milburn and Venanzi[2] observed in the reactions of $[PtCl_4]^{2-}$ and the substituted olefins $CH_2{=}CHCH_2Z$ ($Z = [NH_3]^+$, OH, or $[SO_3]^-$) an absence of a $k_{\rm I}$ term, in addition to other unusual features which will be mentioned later.

$$\text{Rate} = k_{\rm I}[\text{Pt}] + k_{\rm II}[\text{Pt}][\text{L}] \tag{A}$$

Here an investigation is made of the reaction between $[PtCl_4]^{2-}$ and the parent olefin, ethene, to look for similar anomalies in the kinetics. (The activation parameters found by Milburn and Venanzi[2] indicate that the substituents, Z, through which co-ordination could occur, appear to play no major role in the ligand-exchange process.) Reaction products are $[PtCl_3(C_2H_4)]^-$ and $[PtCl_2(C_2H_4)(OH_2)]$. We will see if the reaction of ethene and $[PtCl_4]^{2-}$ can be explained in terms of the normal mechanism invoked for substitution in platinum(II) complexes, namely a first path involving direct replacement of outgoing by incoming ligand, *viz.* reaction (1), and a second in which the solvent participates, *viz.* reactions (2) and (3).

$$[PtCl_4]^{2-} + C_2H_4 \longrightarrow [PtCl_3(C_2H_4)]^- + Cl^- \tag{1}$$

$$[PtCl_4]^{2-} + H_2O \rightleftharpoons [PtCl_3(OH_2)]^- + Cl^- \tag{2}$$

$$\begin{aligned}[PtCl_3(OH_2)]^- + C_2H_4 &\longrightarrow [PtCl_3(C_2H_4)]^- + H_2O \\ \text{or} &\longrightarrow [PtCl_2(C_2H_4)(OH_2)] + Cl^-\end{aligned} \tag{3}$$

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[1] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' Wiley, New York, 1967.

[2] R. M. Milburn and L. M. Venanzi, *Inorg. Chim. Acta*, 1968, **2**, 97.

In the present case a steady-state treatment depends on d$[PtCl_3(OH_2)^-]$/dt being *ca.* 0. If, in addition, reaction (3) is fast so that $[PtCl_3(OH_2)^-]$ is small, as is usually the case in platinum(II) kinetics, equation (B) follows. Then if $k_{-2}[Cl^-] \ll k_3[C_2H_4]$, (B) reduces to

$$\frac{-\mathrm{d}[PtCl_4{}^{2-}]}{\mathrm{d}t} = \frac{-\mathrm{d}[C_2H_4]}{\mathrm{d}t} = \frac{k_3k_2[PtCl_4{}^{2-}][C_2H_4]}{k_{-2}[Cl^-] + k_3[C_2H_4]} + k_1[PtCl_4{}^{2-}][C_2H_4] \quad \text{(B)}$$

(A), the well known relation given earlier ($k_\mathrm{I} \equiv k_2$ and $k_\mathrm{II} \equiv k_1$). If reaction (3) is not fast, it may still be possible to derive an analytical expression for the rate, by modifying the experimental procedure so that the platinum-containing species, $[PtCl_4]^{2-}$ and $[PtCl_3(OH_2)]^-$, come to equilibrium before the olefin is introduced. Then providing d$[PtCl_3(OH_2)^-]$d$t = 0$, (C) is obtained,

$$\frac{-\mathrm{d}[Pt]_\mathrm{T}}{\mathrm{d}t} = \frac{-\mathrm{d}[C_2H_4]}{\mathrm{d}t} = \frac{[Pt]_\mathrm{T}[C_2H_4]\ (1 + \{k_3k_2/(k_{-2}[Cl^-] + k_3[C_2H_4])\})}{1 + (K_2/[Cl^-])} \quad \text{(C)}$$

$$[Pt]_\mathrm{T} = [PtCl_4{}^{2-}] + [PtCl_3(OH_2)^-] \quad \text{(D)}$$

and if $k_{-2}[Cl^-] \gg k_3[C_2H_4]$, equation (E) follows which incidentally has no k_1 term.

$$\frac{-\mathrm{d}[Pt]_\mathrm{T}}{\mathrm{d}t} = \frac{-\mathrm{d}[C_2H_4]}{\mathrm{d}t} = \frac{[Pt]_\mathrm{T}[C_2H_4]\{1 + (k_3K_2/[Cl^-])\}}{1 + (K_2/[Cl^-])} \quad \text{(E)}$$

RESULTS

The rate of reaction of ethene with the solutions made up from $K_2[PtCl_4]$ was studied by following the uptake of gas with time. The rate of stirring was rapid enough to ensure that the rate of reaction of the ethene was slow compared with its transfer across the gas–liquid interface. This uptake of ethene was monitored either by following its change of pressure at constant volume or by measuring the amount of it that had to be admitted to the system to maintain constant pressure. For both modes of operation, a linear response with time was observed for several minutes at the beginning of a run which enabled a precise determination to be made of initial rates of reaction. These were not significantly dependent on which mode was used. All the runs were at 25.0 ± 0.1 °C, the solvent being water throughout. Ionic strength was maintained at 1.0 mol dm^{-3} using $HClO_4$, except where stated otherwise.

During some initial runs made both with freshly prepared solutions of $K_2[PtCl_4]$ and with solutions which had been allowed to stand overnight, it became clear that the rate of reaction of ethene is comparable to that of reaction (2). As ethene can react through reaction (1) and/or (3) in principle, it is not safe to assume that (3) is fast, as is necessary for equations (B) and (A) to apply. In order to simplify the problem, therefore, systematic work was confined to 'aged' solutions of $K_2[PtCl_4]$ which had been allowed to stand for 10—15 h at 25.0 ± 0.1 °C, in order for $[PtCl_4]^{2-}$ to come to equilibrium with aqua-complexes such as $[PtCl_3(OH_2)]^-$, so that (C) and related equations might be applicable. To take account of the aqua-complexes, the term $[Pt]_\mathrm{T}$ will be used in connection with work on the aged solutions to denote total platinum content. Thus $[PtCl_4{}^{2-}]$ for a fresh solution = $[Pt]_\mathrm{T}$ for an aged one. Runs were made over the concentration ranges:* $1 \times 10^{-3} < [Pt]_\mathrm{T} < 1 \times 10^{-2}$, $1 \times 10^{-3} < [C_2H_4] < 4 \times 10^{-3}$, and $0 < [Cl^-] < 1.0$ mol dm^{-3}.

Typical results for the aged solutions are given in Figures 1—3.

(*i*) When $[Cl^-] = 0$, initial rates are directly proportional to both $[Pt]_\mathrm{T}$ and $[C_2H_4]$, *e.g.* Figures 1 and 2 respectively. Least-squares fitting of data to Rate = $k[Pt]_\mathrm{T}$-$[C_2H_4]$ gave values of k of 7.4×10^{-3} and 7.1×10^{-3} dm^3 mol^{-1} s^{-1} for runs in which $[C_2H_4]$ and $[Pt]_\mathrm{T}$ are respectively kept constant. It is notable that there is no evidence for a ligand–independent, k_I, path, *cf.* equation (E).

(*ii*) The ion $[PtCl_3(C_2H_4)]^-$ is produced during the reaction and a possible impurity in $K_2[PtCl_4]$ is $K_2[PtCl_6]$. However, solutions made up initially 3.1×10^{-3} mol dm^{-3} in $K[PtCl_3(C_2H_4)]$ or 2.1×10^{-3} mol dm^{-3} in $K_2[PtCl_6]$ did not react at significantly different rates from those to which neither substance had been added.

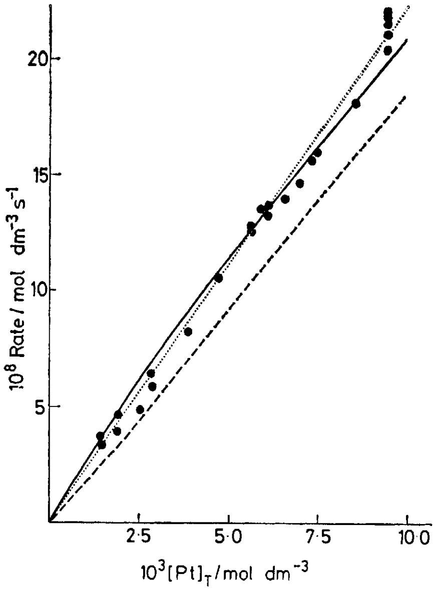

FIGURE 1 Relations between the rate of reaction and $[Pt]_\mathrm{T}$ for an aged solution in which the concentration of dissolved C_2H_4 was 3.1×10^{-3} mol dm^{-3}, I = 1.0 mol dm^{-3} (using $HClO_4$), and no Cl^- was added. (· · · ·), Empirical relation, rate = 7.4×10^{-3} $[Pt]_\mathrm{T}[C_2H_4]$ mol dm^{-3} s^{-1}; (– – – –) and (——), steady- and non-steady-state treatments with $k_5 = 0$ and 8.3×10^{-3} dm^3 mol^{-1} s^{-1} respectively

(*iii*) Sets of runs were performed at various $[Cl^-]$ using HCl, ionic strength and $[H^+]$ being maintained at 1.0 mol dm^{-3}. Figure 3 illustrates that rate is proportional to $1/[Cl^-]$ at low values of $1/[Cl^-]$. A least-squares linear

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* The coexistence of $[PtCl_4]^{2-}$, $[PtCl_3(OH_2)]^-$, and other aqua-species such as $[PtCl_2(OH_2)_2]$ means that if ethene reacts with one of these species at a rate very different from the others, even in an aged solution, steady-state conditions could be upset during later stages of a run. Thus rate constants based on initial rates should be more appropriate. However, in each case, data obtained using the constant-pressure mode of operation led to graphs of log{$[Pt]_\mathrm{T}$ − (the number of moles of ethene consumed/volume of solution)} against time which were linear, and moreover the ensuing rate constants agreed to within 5% of those obtained from initial rates using either the constant-volume or constant-pressure mode.

correlation of these and other initial rates with $1/[Cl^-]$, as in equation (F), over the range $1.0 < 1/[Cl^-] < 5.0$ dm^3 mol^{-1} gave a rate constant of $(2.06 \pm 0.06) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} at the intercept, c, where $1/[Cl^-] = 0$, and a gradient, m, of $(1.15 \pm 0.05) \times 10^{-4}$ s^{-1}.

$$k_{obs.} = c + (m/[Cl^-]) \qquad (F)$$

$$k_{obs.}[Pt]_T[C_2H_4] = -d[C_2H_4]/dt \text{ in this context} \qquad (G)$$

Milburn and Venanzi [2] commented that in the reactions of $CH_2{=}CHCH_2Z$ there is no dependence on $[Cl^-]$. However, over the range through which they varied this parameter it is not clear that we would have detected any unequivocal dependence either.

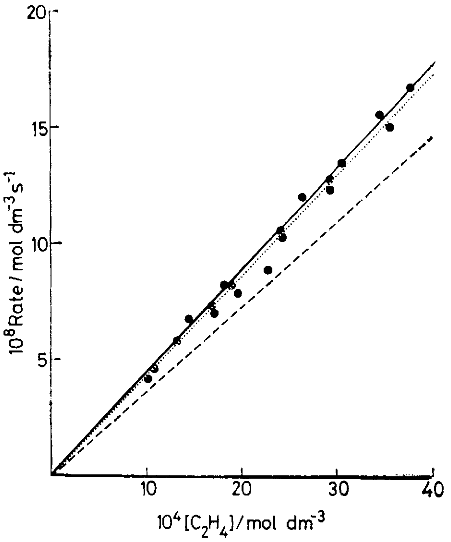

FIGURE 2 Relations between the rate of reaction and $[C_2H_4]$ for an aged solution in which $[Pt]_T = 6.14 \times 10^{-3}$ mol dm^{-3}, $[C_2H_4]$ refers to dissolved ethene, $I = 1.0$ mol dm^{-3} (using $HClO_4$), and no Cl^- was added. (· · · ·), Empirical relation, rate $= 7.1 \times 10^{-3}$ $[Pt]_T[C_2H_4]$ mol dm^{-3} s^{-1}; (– – – –) and (——), as in Figure 1

(*iv*) Some runs performed in 2.0 mol dm^{-3} HCl (and no $HClO_4$) with 9.67×10^{-3} mol dm^{-3} $K_2[PtCl_4]$ and $0.68 \times 10^{-3} < [C_2H_4] < 3.68 \times 10^{-3}$ mol dm^{-3} gave a linear relation between rate and $[C_2H_4]$ and a rate constant of $(2.13 \pm 0.05) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}, a value which is very close to that obtained for c in equation (F).

DISCUSSION

We will now see whether our results (based on data from aged solutions) can be interpreted using reactions (1), (2), (−2), and (3) and whether it is fair to assume that a steady state exists, *i.e.* is equation (C) applicable?

Steady-state Conditions.—For conditions where $K_2/[Cl^-] \ll 1$, (E) can be simplified to (H), noting (G). As [3]

$$k_{obs.} = k_1 + (k_3K_2/[Cl^-]) \qquad (H)$$

K_2 equals $(1.26 \pm 0.09) \times 10^{-2}$ mol dm^{-3}, this is true if $1/[Cl^-] < 1.0$ dm^3 mol^{-1}, one of the conditions under which the parameters of equation (F) were derived. The correspondence of (F) and (H) supports the treatment so far; thus $k_1 \equiv c = (2.06 \pm 0.06) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} and $k_3K_2 = m$ so $k_3 = (9.12 \pm 1.04) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}, using Elding's value [3] of K_2 just quoted.

The value of 2.06×10^{-3} dm^3 mol^{-1} s^{-1} just obtained for k_1 ($I = 1.0$ mol dm^{-3}) agrees with the rate constant of 2.13×10^{-3} dm^3 mol^{-1} s^{-1} obtained from the runs in 2.0 mol dm^{-3} HCl. At this $[Cl^-]$, 99.3% of the total platinum is present as $[PtCl_4]^{2-}$, so that (3) is eliminated and the observed rate constant is that of reaction (1). Admittedly the ionic strengths are different for the two sets of runs, *viz.* 1.0 and 2.0 mol dm^{-3}, but as one of the species reacting in (1) is neutral the comparison is legitimate and further supports the treatment adopted.

To return to data in which $1/[Cl^-] < 1.0$ dm^3 mol^{-1}, equations (E) and (H) can be rearranged to (I), without the restriction $K_2/[Cl^-] \ll 1$. In order to test (I), the data

$$k_{obs.}\{1 + (K_2/[Cl^-])\} = k_1 + (k_3K_2/[Cl^-]) \qquad (I)$$

of Figure 3 and other initial rates were replotted in the form $k_{obs.}\{1 + (K_2/[Cl^-])\}$ against $1/[Cl^-]$. A good straight line was observed over the range $1 < 1/[Cl^-] \leqslant 200$ dm^3 mol^{-1}, which enabled a linear regression to be carried out giving $k_1 = (2.08 \pm 0.21) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} and $k_3 = (9.08 \pm 0.91) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}, again using Elding's value [3] of K_2. This linear relation together with the nice agreement between these values for k_1 and k_3 with those obtained using equation (F) might tempt one to think that the reaction of ethene with aged solutions of $[PtCl_4]^{2-}$ could be fully explained using equations (1), (2), (−2), (3), and (C).

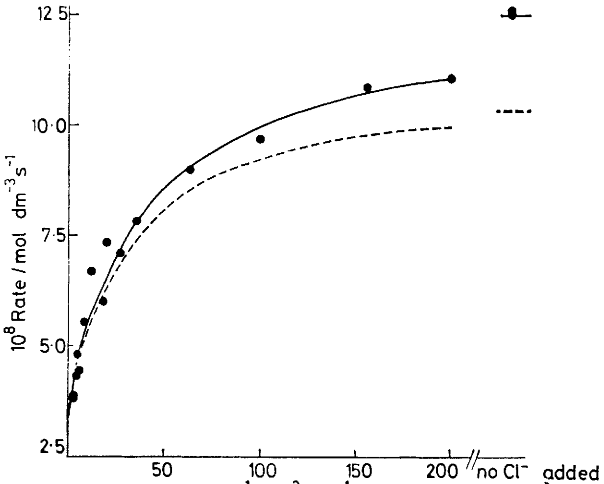

FIGURE 3 Relations between the rate of reaction and $1/[Cl^-]$ for an aged solution in which $[Pt]_T = 5.67 \times 10^{-3}$ mol dm^{-3}, $[C_2H_4] = 3.08 \times 10^{-3}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3} (using $HClO_4$), and Cl^- was added as HCl. (– – – –) and (——), as in Figure 1

Unfortunately, however, equilibrium (4) is known to occur, K_4 being of a significant size in this context, namely [3] $(1.4 \pm 0.1) \times 10^{-3}$ mol dm^{-3}; hence reaction

$$[PtCl_3(OH_2)]^- + H_2O \rightleftharpoons [PtCl_2(OH_2)_2] + Cl^- \qquad (4)$$

(5) could be significant. Inclusion of reactions (4), (−4),

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[3] L. I. Elding, *Acta Chem. Scand.*, 1970, **24**, 1331 and refs. therein.

and (5), a further steady-state approximation, $d[PtCl_2(OH_2)_2]/dt = 0$, and the assumption, $k_{-4}[Cl^-] \gg k_5[C_2H_4]$, in the treatment leading to (E) results in it being superseded by equation (J).

Reactions (6) and (7) have been ignored, because in all the runs the value [3] of K_6 indicates that $[PtCl(OH_2)_3^+]/[Pt]_T <$ 1%, and because the low stability of cationic platinum–olefin complexes hints that k_7 is probably very small.

$$[PtCl_2(OH_2)_2] + C_2H_4 \longrightarrow [PtCl_2(C_2H_4)(OH_2)] + H_2O \text{ or } [PtCl(C_2H_4)(OH_2)_2]^+ + Cl^- \quad (5)$$

$$-\frac{d[Pt]_T}{dt} = \frac{-d[C_2H_4]}{dt} = \frac{[Pt]_T[C_2H_4]\{k_1 + (k_3K_2/[Cl^-]) + (k_5K_2K_4/[Cl^-]^2)\}}{1 + (K_2/[Cl^-]) + (K_2K_4/[Cl^-]^2)} \quad (J)$$

$$[Pt]_T = [PtCl_4{}^{2-}] + [PtCl_3(OH_2)^-] + [PtCl_2(OH_2)_2] \quad (K)$$

Equation (J) was tested using our rate constants just obtained, $k_1 = 2.1 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}, and the values of K_2 and K_4 already quoted.[3] Incidentally, K_4 does not distinguish between the *cis* and *trans* isomers of $[PtCl_2(OH_2)_2]$. The broken lines in Figure 3 illustrate an attempt to replicate data using equation (J) with $k_5 = 0$.† The fact that in the range $50 \leqslant 1/[Cl^-] \leqslant 100$ dm^3 mol^{-1} they are not very successful in spite of the linearity of the plot based on (I), the more simple equation, suggests that there must be some mutually cancelling effect between the $K_2K_4/[Cl^-]^2$ terms in the numerator and denominator of (J). At low $[Cl^-]$ this can be shown to occur when $k_5 = k_4$. In fact, over the whole range of $[Cl^-]$ the best fit is obtained with $k_5 = (8.3 \pm 2.0) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}. This was obtained using all our data in a quadratic regression based on (J) in which the rate and k_5 were the only variables.†

$$[PtCl_2(OH_2)_2] + H_2O \rightleftharpoons [PtCl(OH_2)_3]^+ + Cl^- \quad (6)$$

$$[PtCl(OH_2)_3]^+ + C_2H_4 \longrightarrow [PtCl(C_2H_4)(OH_2)_2]^+ + H_2O \text{ or } [Pt(C_2H_4)(OH_2)_3]^{2+} + Cl^- \quad (7)$$

The full lines in Figures 1—3 are based on this value of k_5 and agreement is good. The full line in Figure 2 where $[C_2H_4]$ is varied at constant $[Pt]_T$ is linear. What is surprising is the slight curvature in Figure 1 where constant and variable quantities are reversed. Scrutiny of this graph indicates that accurate data in the range $0.004 < [Pt]_T < 0.01$ mol dm^{-3} might be described empirically by a straight line with finite intercept, of a form unknown in platinum(II) chemistry, *viz.* equation (L).

$$\text{Rate} = k_{II}[Pt^{II}][C_2H_4] + k_{III}[C_2H_4] \quad (L)$$

To summarize so far, the results can be interpreted in terms of ethene attacking $[PtCl_4]^{2-}$, $[PtCl_3(OH_2)]^-$, and $[PtCl_2(OH_2)_2]$ in simultaneous parallel reactions; the assumption of steady state appears to be justified.

Non-steady-state Conditions.—The agreement between the experimental data and equation (J) is good, but it could be fortuitous {as is equation (I) when $1/[Cl^-] = 100$ dm^3 mol^{-1}}. In addition to assuming steady-state conditions in deriving (J), two simplifications were made based on the inequalities $k_{-2}[Cl^-] \gg k_3[C_2H_4]$ and $k_{-4}[Cl^-] \gg k_5[C_2H_4]$. As $k_{-2} = 2.8 \times 10^{-3}$ dm^3 mol^{-1} s^{-1} and $k_{-4} = 7.5 \times 10^{-2}$ dm^3 mol^{-1} s^{-1} (see below), the first of these simplification is not justified for solutions to which no HCl has been added.*

Therefore a non-steady-state treatment was carried out, full details of which are given in the Mathematical section. At zero time, it was assumed (as in the steady-state treatment) that the solution had aged so that $[PtCl_4]^{2-}$, $[PtCl_3(OH_2)]^-$, and $[PtCl_2(OH_2)_2]$ were in equilibrium. As the reaction proceeded the following quantities were calculated at intervals of 1 min: the concentrations of $[PtCl_4]^{2-}$, $[PtCl_3(OH_2)]^-$, $[PtCl_2(OH_2)_2]$, and Cl^-, the rates of reactions (1), (3), and (5), and the overall rate as defined by (Q) in the Mathematical section. The rate constants k_2, k_3, and k_5 were given the values just obtained in the steady-state treatment, namely 2.1×10^{-3}, 9.1×10^{-3}, and 8.3×10^{-3} dm^3 mol^{-1} s^{-1} respectively; k_2 and k_{-2} were taken as 3.7×10^{-5} s^{-1} and 2.8×10^{-3} dm^3 mol^{-1} s^{-1} respectively.[4] The complex $[PtCl_2(OH_2)_2]$ consists of two isomers, but in this context k_{4trans} and $k_{-4trans}$ are insignificant,[4] so k_4 and k_{-4} were put equal to k_{4cis} and k_{-4cis}, namely 6×10^{-5} s^{-1} and 7.5×10^{-2} dm^3 mol^{-1} s^{-1} respectively.[4] However, in evaluating $[PtCl_2(OH_2)_2]$, K_4 was taken as 1.4×10^{-3} mol dm^{-3}, the value which does not distinguish between isomers.

The overall calculated rate constant does vary with time and convergence towards a constant rate is very slow. Nevertheless, in runs where the effect is greatest, namely where added $[Cl^-] = 0.01-0.02$ mol dm^{-3}, the change in overall rate constant is less than 1 and 3% in the first hour and first three hours respectively, which accords with the apparent steady state seen experimentally (see footnote*). To some extent, however, this near constancy of overall rate arises from cancelling of rival effects: the relative concentrations of $[PtCl_4]^{2-}$, $[PtCl_3(OH_2)]^-$, and $[PtCl_2(OH_2)_2]$ do change with time, *e.g.* for $[Cl^-] = 1.33 \times 10^{-2}$, $[Pt]_T = 5.67 \times 10^{-3}$, and $[C_2H_4] = 3.08 \times 10^{-3}$ mol dm^{-3} the ratios are $1 : 0.78 : 0.07$ and $1 : 0.81 : 0.03$ at $t = 0$ and $t = 1$ h respectively, but the relative amount of the two aqua-species (whose rates of reaction with ethene, k_3 and k_5, are almost equal) remains at 0.84 ± 0.01.

An average rate based on the first 15 min of reaction was used for comparison with the experimental data. What is particularly interesting is that in each case the rates obtained using the non-steady-state treatment were within 1% of those obtained assuming a steady state, and thus equally well represented by the full lines in the Figures. Thus there is no need to modify the values of k_1, k_3, and k_5 already obtained. However, the errors should be increased slightly to the values given in the Abstract.

At this stage it might be argued that the non-steady-state treatment was pointless. However, we have found that, by adjusting the values of the k terms in this non-steady-state treatment, it is possible to obtain variations in the overall rate constant with time of as much as 10%. If these values are averaged and substituted into an equation analogous to (I) a straight line is still produced but with distorted values corresponding to k_1 and k_3.

Products, etc.—Visible–u.v. spectra indicate that the products are $[PtCl_3(C_2H_4)]^-$ and *trans*-$[PtCl_2(C_2H_4)(OH_2)]$. However, as these two species equilibrate rapidly, because of the *trans* effect of ethene, it is impossible to say which is the initial product in reaction (3). The instability of cationic

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† The chloride-ion concentrations quoted in the text and Figures represent that based on the amount of HCl added to the solutions. They do not include that produced on ageing by reactions (2) and (5), which have to be included in testing equation (J), particularly when ' $[Cl^-] = 0$.'

[4] L. I. Elding, *Acta Chem. Scand.*, 1970, **24**, 1527 and refs. therein.

platinum-olefin complexes[5] suggests that the product of (5) is *trans*-$[PtCl_2(C_2H_4)(OH_2)]$. There is no evidence, spectroscopic, kinetic, or stoicheiometric, for the formation of species such as *cis*- or *trans*-$[PtCl_2(C_2H_4)_2]$ or $[(C_2H_4)ClPtCl_2PtCl(C_2H_4)]$ which are unstable in water at room temperature. No ethene was evolved from solutions of $K[PtCl_3(C_2H_4)]$ after 72 h, from which it was concluded that the reactions involving ethene were irreversible.

It is interesting that the rates of reaction of $[PtCl_4]^{2-}$, $[PtCl_3(OH_2)]^-$, and $[PtCl_2(OH_2)_2]$ with ethene are approximately equal (in a kinetic context). One could speculate that ethene is behaving as a weak nucleophile such as water where the rate of reaction is not seriously dependent on the charge of the complex.[6] However, it seems more likely that ethene is biphilic,[7] and that the equality in the rates is due to a coincidental balancing of σ donation and π acceptance by the ligand.

EXPERIMENTAL

The salt $K_2[PtCl_4]$, supplied by Johnson, Mathey, was recrystallized twice before use, washed with distilled water under a nitrogen atmosphere, and dried *in vacuo* for 12 h.

Potassium Trichloro(ethene)platinate(II).—The salt $K_2[PtCl_4]$ (10 g) was dissolved in 2.0 mol dm^{-3} hydrochloric acid (100 cm^3), placed in a glass autoclave liner and several sapphire balls were added to the solution. This vessel was placed in a high-pressure autoclave which was charged with ethylene at 1 000 lbf in^{-2}.* The autoclave was shaken at room temperature for 24 h. The resulting yellow solution was reduced in volume at the water pump. The product was recrystallized from a solution of potassium chloride (0.1 mol dm^{-3}) immediately prior to use, washed with distilled water, and dried in a desiccator. Analysis showed the product to be the monohydrate. Further drying for 4 h on an oil-pump gave the anhydrous product, yield 80—85%.

Ethene was of C.P. grade for which a typical analysis is 99.72% ethene, 0.12% propene and butene, and 0.16% propane and butanes. The apparatus for studying the uptake of ethene could be operated at either constant volume or constant pressure. The constant-volume mode, which is much simpler mechanically, involved merely following the decrease in pressure of ethene in a gas reservoir using a pressure transducer. The constant-pressure mode, which will be described fully elsewhere,[8] utilized a throttling valve and an electrically operated valve, in that order, between a large gas reservoir and the reaction vessel. The electrically operated valve was normally closed, but opened when a potential was applied to it. Pressure in the reaction vessel was measured by a transducer attached to a recording instrument. A magnet on the pen of the recorder activated reed switches which caused the potential to be applied to and disconnected from the electrically operated valve, thus opening and closing it and maintaining pressure constant to within 5 mmHg. Application of the potential also started a clock which recorded the time for which the valve was open. The number of moles of ethene consumed in the time recorded by the clock can be calculated from the increase in pressure during the ' topping-up ' with gas and from the volume of the reaction vessel. The apparatus was enclosed in an air thermostat in which fluctuations and gradients in temperature were less than 0.1 °C.

The solutions of $K_2[PtCl_4]$ in contact with the ethene were stirred at rates between 680 and 890 revolution min^{-1}, and it was shown that the rate of gas uptake was not dependent on the rate of stirring: this verifies that the rate-determining step is the chemical reaction and not diffusion of ethene across the gas–liquid interface.

The solubility of ethene was determined manometrically and found to be 4.29×10^{-3} mol dm^{-3} atm^{-1} in 1.0 mol dm^{-3} $HClO_4$, 1.0 mol dm^{-3} HCl, and 2.0 mol dm^{-3} HCl at 25.0 °C.

MATHEMATICAL

In the seven reactions described by equations (1), (2), (4), and (5) there are five reactants and/or intermediates: $[PtCl_4]^{2+}$, $[PtCl_3(OH_2)]^-$, $[PtCl_2(OH_2)_2]$, Cl^-, and C_2H_4. The rates of formation of these species are described by the five simultaneous differential equations (N)—(R). The overall rate, $-d[C_2H_4]/dt$, is given by (Q). As all the products contain one atom of Pt and one C_2H_4 ligand, the overall rate is equal to $-d[Pt]_T/dt$, see equation (K). {In

$$d[PtCl_4{}^{2-}]/dt = -k_1[PtCl_4{}^{2-}][C_2H_4] - k_2[PtCl_4{}^{2-}] + k_{-2}[PtCl_3(OH_2)^-][Cl^-] \quad (N)$$

$$d[PtCl_3(OH_2)^-]/dt = k_2[PtCl_4{}^{2-}] - k_{-2}[PtCl_3(OH_2)^-][Cl^-] - k_3[PtCl_3(OH_2)^-][C_2H_4] - k_4[PtCl_3(OH_2)^-] + k_{-4}[PtCl_2(OH_2)_2][Cl^-] \quad (O)$$

$$d[Cl^-]/dt = k_2[PtCl_4{}^{2-}] - k_{-2}[PtCl_3(OH_2)^-][Cl^-] + k_4[PtCl_3(OH_2)^-] - k_{-4}[PtCl_2(OH_2)_2][Cl^-] \quad (P)$$

$$-d[C_2H_4]/dt = k_1[PtCl_4{}^{2-}][C_2H_4] + k_3[PtCl_3(OH_2)^-][C_2H_4] + k_5[PtCl_2(OH_2)_2][C_2H_4] \quad (Q)$$

$$d[PtCl_2(OH_2)_2]/dt = k_4[PtCl_3(OH_2)^-] - k_{-4}[PtCl_2(OH_2)_2][Cl^-] - k_5[PtCl_2(OH_2)_2][C_2H_4] \quad (R)$$

the steady-state treatment, (O) and (R) are set equal to zero and the resulting equations substituted into (Q). Inclusion of (K), together with the assumptions $k_{-2}[Cl] \gg k_3[C_2H_4]$ and $k_{-4}[Cl] \gg k_5[C_2H_4]$, leads to (J).}

The Runge–Kutta method was used to solve the simultaneous differential equations in the non-steady-state method, the interval between solutions being 1 min, for various $[Pt]_T$, $[C_2H_4]$, and $[Cl^-]$ within the experimental range, from $t = 0$ to 15 min usually, but in some instances to 1, 3, and 10 h. The concentrations of individual species were calculated at 1-min intervals, as were the rates of reactions (1), (3), and (5), from which an overall $k_{obs.}$ was obtained. If a steady state exists the relative concentrations of $[PtCl_4]^{2-}$, $[PtCl_3(OH_2)]^-$, and $[PtCl_2(OH_2)_2]$ are constant with time as is $k_{obs.}$, so that variation of these quantities with time provides an indication of the extent of a non-steady state.

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* Throughout this paper: 1 lbf $in^{-2} \approx (9.8 \times 4.536)/6.45$ Pa; 1 mmHg $\approx 13.6 \times 9.8$ Pa; 1 atm = 101 325 Pa.

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