Reactions of Platinum(II) Complexes. Part 2.[1] Catalysis of the Aquation of Tetrachloroplatinate(II) Ion by Trichloro(η-ethylene)platinate(II) (Zeise's Anion)

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The reaction $[PtCl_4]^{2-} + H_2O \longrightarrow [PtCl_3(OH_2)]^- + Cl^-$ proceeds faster in the presence of $[PtCl_3(C_2H_4)]^-$, although the effect tends to be nullified gradually by increasing concentration of chloride ion. The actual catalyst is considered to be *trans*-$[PtCl_2(C_2H_4)(OH_2)]$ since the increase in rate is proportional tc the concentration of this complex.

IN the course of studying the kinetics of the reaction $[PtCl_4]^{2-} + C_2H_4 \longrightarrow [PtCl_3(C_2H_4)]^- + Cl^-$ we observed that $K[PtCl_3(C_2H_4)]$, or some species readily derived from it, perhaps catalysed the substitution processes (1) and (−1). Details of the catalysis are reported here.

$$[PtCl_4]^{2-} + H_2O \rightleftharpoons [PtCl_3(OH_2)]^- + Cl^- \quad (1)$$

RESULTS AND DISCUSSION

The rate of reaction (1) at 25.0 °C was followed spectrophotometrically in the absence and presence of $K[PtCl_3(C_2H_4)]$, in the concentration ranges $1 \times 10^{-3} \leqslant [K_2PtCl_4] \leqslant 1 \times 10^{-2}$ mol dm^{-3} and $1 \times 10^{-4} \leqslant [KPtCl_3(C_2H_4)] \leqslant 1.5 \times 10^{-3}$ mol dm^{-3}. Ionic strength was maintained at 0.5 mol dm^{-3} using $HClO_4$ and HCl, the latter being used to vary $[Cl^-]$. The relation between time and concentration for a reversible reaction, pseudo-first order in the forward direction and second order in the reverse direction, is given by (2), an equation which is not easy to handle in this context. Where t = time,

$$t = (1/a) \ln [(bx_t - a)x_0/(bx_0 - a)x_t] \quad (2)$$

e denotes equilibrium, $x = [PtCl_4^{2-}]_t - [PtCl_4^{2-}]_e$, $b = k_{-1}$, $a = k_1 + k_{-1}\{[PtCl_3(OH_2)^-]_e + [PtCl_4^{2-}]_e\}$, and $k_{-1} = K_1k_1$. Therefore values of k_1 were obtained from gradients of rate curves extrapolated to zero time. Taking[2,3] K_1 as 1.26×10^{-2} mol dm^{-3}, we substituted the values so obtained in equation (2) and were able to verify that it applies to within 10% when $[Cl^-] \geqslant 10^{-2}$ mol dm^{-3}. The poorer agreement below this chloride concentration is not surprising as reactions (3) and (−3)

$$[PtCl_3(OH_2)]^- + H_2O \rightleftharpoons [PtCl_2(OH_2)_2] + Cl^- \quad (3)$$

are known, K_3 being[2,3] 1.4×10^{-3} mol dm^{-3}. Unfortunately, the catalytic activity of $K[PtCl_3(C_2H_4)]$ is small when $[Cl^-] \geqslant 10^{-2}$ mol dm^{-3}, so, while initial gradients in this range are justified as a means of obtaining rates, we were forced to use those at lower chloride-ion concentration without rigorous validation. Because of serious possible complications due to (3), the lowest $[Cl^-]$ used was 2×10^{-3} mol dm^{-3}, thus, in effect, $2 \times 10^{-3} \leqslant [Cl^-] \leqslant 2 \times 10^{-2}$ mol dm^{-3}.

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[1] Part 1, M. Green and C. J. Wilson, *J.C.S. Dalton*, **1977**, 2302.

[2] L. I. Elding and I. Leden, *Acta Chem. Scand.*, 1966, **20**, 706.

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

The rate of reaction (1) increases with increasing concentration of K$[PtCl_3(C_2H_4)]$, but is inversely related to chloride-ion concentration. This suggests that it is not $[PtCl_3(C_2H_4)]^-$ itself which catalyses the reaction, but a derivative. Equilibrium (4) is known to be established very rapidly; the inverse relation in $[Cl^-]$

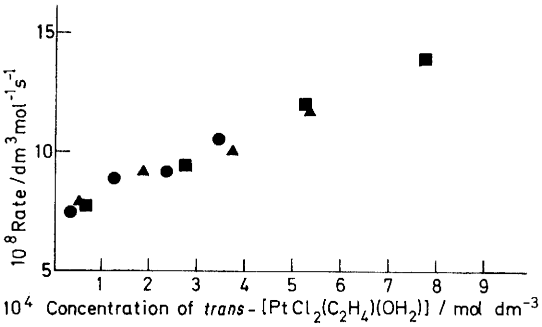
$$[PtCl_3(C_2H_4)]^- + H_2O \rightleftharpoons trans\text{-}[PtCl_2(C_2H_4)(OH_2)] + Cl^- \quad (4)$$

might be explained if the aqua(olefin) complex were the actual catalyst. This was verified by plotting graphs of rates against concentration of *trans*-$[PtCl_2(C_2H_4)(OH_2)]$ taking [4,5] K_4 as 3.0×10^{-3} mol dm^{-3}, straight lines being obtained as in the Figure. A regression analysis of all the rate constants, $k_{obs.}$, for catalysed reaction (1) gave (5) and $k_0 = (3.8 \pm 0.1) \times 10^{-5}$ s^{-1} which agrees [6] nicely with Elding's value of 3.7×10^{-5} s^{-1}

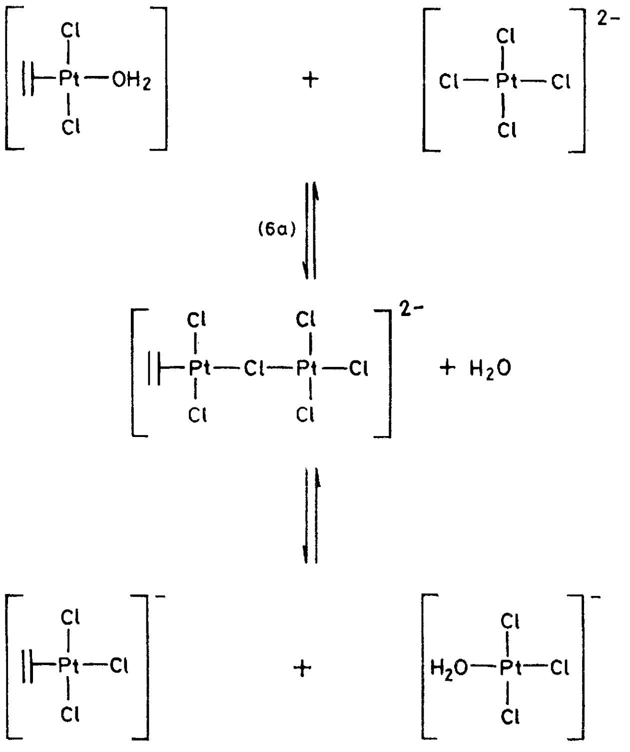
$$k_{obs.} = \{k_0 + k_{cat.}[PtCl_2(C_2H_4)(OH_2)]\}[PtCl_4^{2-}] \quad (5)$$

for k_1 in the uncatalysed process; $k_{cat.} = (4.2 \pm 0.1) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}.

Several reactions are known to involve diplatinum species [7] and it is suggested here that the scheme in (6) occurs, the chloro(olefin) and aqua(olefin) complexes being interchanged by reaction (4). Possibly, it is the lower nucleophilic character of H_2O compared with Cl^- towards Pt^{II} which enables $[PtCl_2(C_2H_4)(OH_2)]$ but not $[PtCl_3(C_2H_4)]^-$ to react with $[PtCl_4]^{2-}$. The rate-determining step in (6) is (6a), so that k_{6a} is $(4.2 \pm 0.1) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}.



Plot of rate against the concentration of *trans*-$[PtCl_2(C_2H_4)(OH_2)]$ for reaction (1): $[K_2PtCl_4] = 2 \times 10^{-3}$ mol dm^{-3}. $[Cl^-] = 2.25 \times 10^{-2}$ (■), 5.0×10^{-2} (▲), and 10.0×10^{-2} mol dm^{-3} (●)



(6)

EXPERIMENTAL

Potassium tetrachloroplatinate(II), to be used for kinetics, was recrystallised twice from 2 mol dm^{-3} HCl and dried *in vacuo*. The salt K$[PtCl_3(C_2H_4)]$ was prepared by the action of ethylene on $K_2[PtCl_4]$ in 2 mol dm^{-3} HCl at 30 atm (no catalyst being used).* It was recrystallised twice from 2 mol dm^{-3} HCl and dried under high vacuum to remove water of crystallisation.

The reaction was followed using a Cary 14 spectrophotometer. Mixtures were kept at 25.0 ± 0.1 °C in vessels from which light was excluded. Samples were removed from time to time, and their spectra were recorded at *ca.* 315 nm. Absorption coefficients for $[PtCl_4]^{2-}$ and $[PtCl_3(OH_2)]^-$ agreed with those of Elding [3] within experimental error.

[7/851 *Received*, 16*th May*, 1977]

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* 1 atm = 101 325 Pa.

[4] I. Leden and J. Chatt, *J. Chem. Soc.*, 1955, 2936.

[5] S. J. Lokken and D. S. Martin, *Inorg. Chem.*, 1963, **2**, 562.

[6] L. I. Elding, *Acta Chem. Scand.*, 1970, **24**, 1341.

[7] D. S. Martin, *Inorg. Chim. Acta Rev.*, 1967, **1**, 87.