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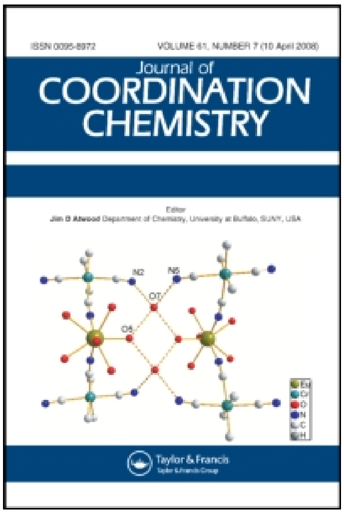

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OXIDATIVE ADDITION REACTIONS OF d^8 COMPLEXES. I. CHLORINE OXIDATION OF TETRACHOLOROPALLADATE (II)

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The reaction of Na_2PdCl_4 with chlorine in aqueous acid solution proceeds in two stages: oxidation of the complex to a Pd(IV) species followed by a slower substitution reaction. The oxidation reaction is first order in complex and first order in chlorine. At high chloride concentration, a six-coordinate palladium(II) intermediate is formed, which is oxidised via an outer-sphere type mechanism. Oxidation of the chloroaquopalladium(II) species present at low chloride concentration occurs via a different mechanism, probably involving coordination of the oxidant in a "quasi-inner-sphere" mechanism.

INTRODUCTION

In recent years oxidative addition reactions of d^8 metal complexes have been extensively studied,[1-10] primarily in the context of the synthesis of organometallic complexes of rhodium(I) and iridium(I). Much of this interest derives from the fact that many d^8 complexes catalyse organic reactions of considerable importance,[4-6] and one of the key steps in the catalytic mechanism is frequently an oxidative addition process.

The kinetics of oxidative addition have been studied for various rhodium(I) and iridium(I) systems,[7-10] but very few mechanistic studies have been reported for platinum(II) complexes, probably because of the rapidity of the reactions involved. Mason[11] showed that the oxidation of $Pt(CN)_4{}^{2-}$ and $Pt(NH_3)_4{}^{2+}$ by bromine proceeds in two stages, the first fast stage corresponding to oxidative formation of a bromoaquo complex which then undergoes slow anation. However, only the substitution process was studied. Jones and Morgan[12] reported the oxidation of $PtCl_4{}^{2-}$ by chlorine but their results have recently been criticised by Elding and Gustafson,[13] who showed that this reaction is first order in both oxidant and complex. The latter workers also investigated the iodine oxidation of $Pt(CN)_4{}^{2-}$ and found first order behaviour with respect to complex, iodine and iodide. A mechanism was suggested in which the species being oxidised is either a five-coordinate adduct formed between the mother complex and free halide ion, or a five coordinate species in which the fifth ligand is a solvent molecule.

Complexes of palladium(IV) are considerably less stable than their platinum(IV) analogues, and only a few such compounds are known.[14] These palladium (IV) complexes are formed by the oxidative addition of two ligands to palladium(II) precursors, but there appear to have been no kinetic studies of the process to date. This paper reports a mechanistic investigation of the oxidation of Na_2PdCl_4 by chlorine.

EXPERIMENTAL

Sodium tetrachloropalladate(II) was purchased from Ventron, Alfa Products, Beverley, Mass., U.S.A., and dried at 383K before use. Other chemicals were analytical reagent grade. Triply distilled water was used throughout. Hexachloropalladate(IV) was prepared by bubbling chlorine through an aqueous acid (c. 0.5 M HCl) solution of Na_2PdCl_4, and isolated as its potassium salt by addition of a large excess of KCl. The product was characterised by its infrared spectrum.[15]

The tetraaquocomplex, $Pd(H_2O)_4{}^{2+}$, was prepared by a method similar to that of Elding.[16] Palladium powder (0.25 g) was dissolved in a minimum amount of concentrated nitric acid, and the solution repeatedly evaporated with concentrated perchloric acid to

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remove nitrates. The solution was adjusted to standard volume, with addition of sufficient perchloric acid (if necessary) to give the required hydrogen ion concentration. Palladium was determined gravimetrically with dimethylglyoxime.[17a] Other palladium solutions were prepared by dissolving the desired amount of Na_2PdCl_4 in solutions of NaCl and HCl of the required concentration. Ionic strength was maintained constant throughout at 2 M with $HClO_4$ or $NaClO_4$. Solutions of $NaClO_4$ were standardised by passage through a cation exchange column in the hydrogen form, and titration of the eluate with standard KOH.

Chlorine solutions were prepared by bubbling chlorine gas into water and diluting appropriately into previously prepared solutions of the required chloride and hydrogen ion composition. Chlorine was determined iodometrically.[17b] The volatility of chlorine constitutes an important experimental problem as discussed by Cornelius and Gordon.[18] For rate and spectral measurements the problem was minimised by bringing the chlorine solutions to thermal equilibrium and determining the chlorine concentration immediately before use. Individual rate measurements were reproducible to within 10% (usually considerably less), while spectral determinations were sometimes subject to slightly greater error because of the more protracted nature of the measurements, as reflected in the large standard deviations found for the equilibrium constants (Table I).

Spectral and equilibrium constant measurements were made on a Perkin-Elmer 402 visible-uv spectrophotometer equipped with a thermostatted sample holder that facilitated temperature control to ±0.1 K. Kinetic measurements were performed on a Durrum D110 stopped-flow spectrophotometer. The output signal was stored in a Biomation 805 digital waveform recorder, and displayed on an oscilloscope. A permanent record of the absorbance change was obtained by plotting the stored signal on a Telrad chart recorder.

TABLE I
Equilibrium constants for the oxidation of Pd(II) to Pd(IV) by Cl_2

Temperature/K	Equil. Const: 10^{-3} K/mol^{-1}dm^3
288	2.6 ± 0.5
298	1.3 ± 0.5
308	0.2 ± 0.3

$\Delta H° = -101.4$ kJ mol^{-1}

RESULTS

When solutions of chlorine and $PdCl_4^{2-}$ in hydrochloric acid are mixed, the following spectral changes are observed: an intense peak with maximum at 340 nm develops rapidly, followed by a very much slower change in which the absorption maximum shifts slightly and the intensity decreases (Figure 1). The fast change is too rapid to follow using classical methods, and was monitored by the stopped-flow technique. During the second (slow) process, a well-defined isosbestic point develops at 303 nm, indicating the presence of two absorbing species. As discussed in more detail below, the fast reaction is attributed to oxidation of $PdCl_4^{2-}$ to a palladium(IV) species which subsequently undergoes a slow substitution reaction. Equilibrium constants for the oxidation represented by the fast reaction were estimated by the method of Benesi and Hildebrand[19] using the following readily derived expression,

$$\frac{\epsilon_{eff} - \epsilon_{Pd(II)}}{[Cl_2]} = \epsilon_{Pd(IV)}K - \epsilon_{eff}K \qquad (1)$$

where the ϵ's are extinction coefficients and K is the equilibrium constant for the reaction represented

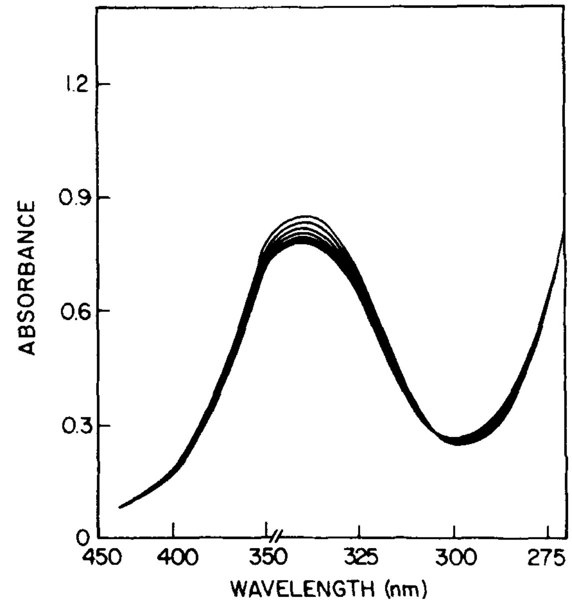

FIGURE 1 Spectral changes on mixing solutions of $PdCl_4^{2-}$ and Cl_2 in 2 M HCl. Top spectrum at 340 nm: immediately after mixing. Successive spectra at intervals of c. 1 min.

schematically

$$\text{"Pd(II)"} + Cl_2 \overset{K}{\rightleftharpoons} \text{"Pd(IV)"} \qquad (2)$$

The slope of plots of the left hand side of (1) against ϵ_{eff} gives the equilibrium constant. Values so obtained are subject to a measure of uncertainty because of the spectral change associated with the second reaction. However, from the values listed in Table I, it can be seen that the equilibrium constant is sufficiently large that under the conditions of the kinetic experiments, the oxidation reaction proceeds to completion.

The value of $10^{3.11}$ at 298 K is to be compared with a literature value[20] of $10^{3.62}$ but this latter value does not appear to have taken cognisance of the two-stage nature of the oxidation and refers to the overall process including the substitution reaction, as described below. Similar considerations apply to the enthalpy of reaction of -101.4 kJ mol^{-1} obtained from the temperature dependence of the equilibrium constant.

TABLE II
Dependence of k_{obs} on initial palladium(II) concentration, and on chlorine concentration

10^4 [Pd(II)]$_0$/mol dm^{-3}	10^3 [Cl$_2$]/mol dm^{-3}	k_{obs}/sec^{-1}
0.44	4.00	97
0.88	4.00	93
1.75	4.00	86
2.50	4.00	91
1.75	8.60	195
1.75	5.80	126
1.75	2.75	48

T = 288 K; λ = 400 nm; μ = [H$^+$] = [Cl$^-$] = 2 mol dm^{-3}

The kinetic data obtained for the fast reaction were treated by plotting $\log(A_\infty - A_t)$ against time, where A is the absorbance. From the slopes of the straight lines so obtained, values of the pseudo-first-order rate constant, k_{obs}, were obtained. The rate constant is independent of the initial palladium(II) concentration and linear in chlorine concentration with a negligible (negative) intercept (Table II). The dependence of the rate constant on the chloride concentration in the range 0.2 mol dm^{-3} $\leqslant$ [Cl$^-$] $\leqslant$ 2 mol dm^{-3} (Table III) is shown in Figure 2, and can be described mathematically by the expression

$$\frac{1}{k_{obs}/[Cl_2]} = a + \frac{b}{[Cl^-]^2} \qquad (3a)$$

or

$$k_{obs} = \frac{[Cl^-]^2}{a[Cl^-]^2 + b}[Cl_2] \qquad (3b)$$

The reaction was shown to be approximately independent of the hydrogen ion concentration by determining the values of the parameters a and b at different acidities (Table IV).

The form of Eq. (3) implies that in the absence of chloride ion, palladium(II) is not oxidised by chlorine. As this suggestion is highly improbable, the reaction was investigated at low chloride concentrations (ratio of total chloride to total palladium between 1–20) using solutions prepared by addition of appropriate amounts of NaCl to solutions of $Pd(H_2O)_4{}^{2+}$. For these reactions, plots of $\log(A_\infty - A_t)$ against time are curved in the initial

TABLE III
Variation of k_{obs} with chloride ion concentration

High chloride region		Low chloride region		k_{obs}/sec^{-1}	
[Cl$^-$]/mol dm^{-3}	k_{obs}/sec^{-1}	10^3 [Cl$^-$]$_t^a$/mol dm^{-3}	10^3 [Cl$^-$]$_f^b$/mol dm^{-3}	Fast reaction	Slow reaction
2.00	85	4.11	3.61	1.9	0.14
1.75	79	3.08	2.61	1.3	0.13
1.50	70	2.06	1.63	0.93	0.11
1.00	49	1.23	0.87	0.71	0.14
0.50	35	0.822	0.51	0.63	0.12
0.346	21	0.411	0.18	0.33	0.12
0.283	17	0.205	0.06	0.12	
0.250	14				

a. Total chloride.
b. Free chloride calculated from formation constants for chloroaquocomplexes, $PdCl_n(H_2O)_{4-n}^{-n+2}$, $1 \leqslant n \leqslant 4$).

T = 288 K; λ = 400 nm; μ = 2 mol dm^{-3} (HClO$_4$); [H$^+$] = 2 mol dm^{-3}; [Cl$_2$] = 4 x 10^{-3} mol dm^{-3}; [Pd(II)] = 1.75 x 10^{-4} mol dm^{-3} (high chloride region) or 2.06 x 10^{-4} (low chloride region).

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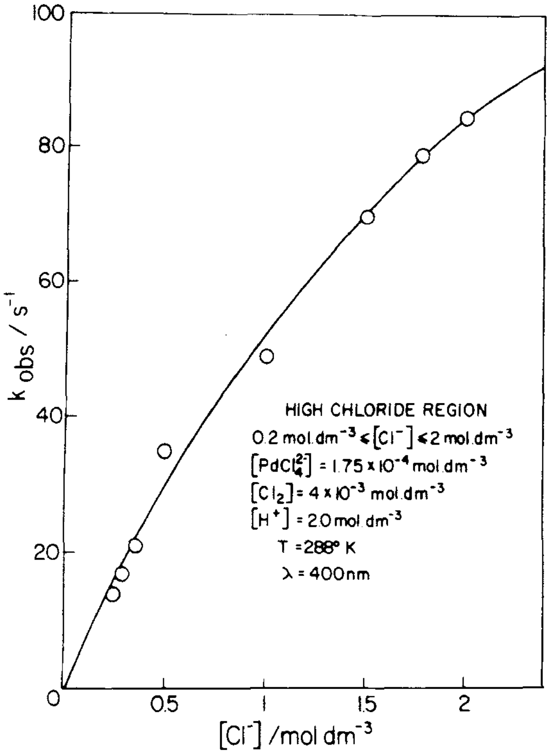


FIGURE 2 Dependence of k_{obs} on Chloride ion concentration in high chloride region (0.2 mol $dm^{-3} \leqslant [Cl^-] \leqslant$ 2 mol dm^{-3}).

stages but become linear at longer values of time. These curves were "stripped" into two component reactions by conventional methods[22] and rate constants are listed in Table III. Rate constants for the first reaction are smaller in the low chloride region than those in the high chloride region by some 2–3 orders of magnitude. The zero intercept in Figure 2 arises from the experimental difficulty of extrapolating large rate constants to a value smaller by some orders of magnitude.

The two reactions observed in the low chloride region exhibit different functional dependence on the chloride ion concentration. The slow reaction is independent of $[Cl^-]$, whereas for the fast reaction, the complex dependence is depicted in Figure 3. Values of the free chloride concentration were solved numerically from the known values[16] of the stepwise formation constants of the chloroaquocomplexes $PdCl_n(H_2O)_{4-n}^{-n+2}$ $(1 \leqslant n \leqslant 4)$. The behaviour in the low chloride region differs from that found in the high chloride region also in that no slow process is observed to accompany the development of the intense absorption peak in the region of 340 nm, on the time-scale of the spectral determination. Since the second process, whose kinetics were thus determined in the low chloride region, is ascribed to a substitution reaction, no equilibrium constants were determined in this chloride region, as they would describe a composite chemical phenomenon (see below).

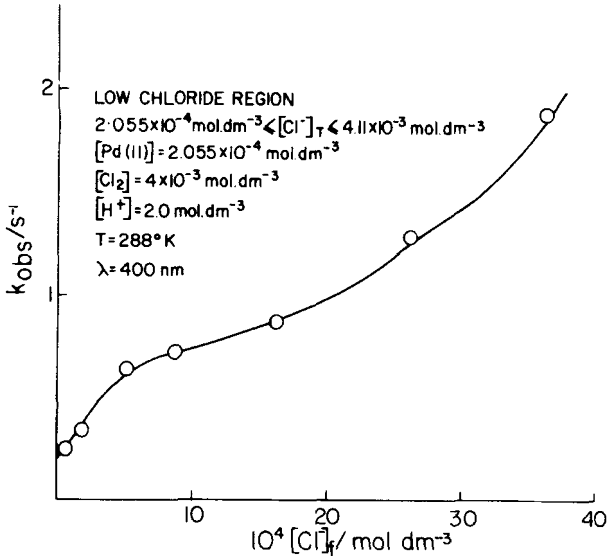


FIGURE 3 Dependence of k_{obs} on free chloride ion concentration in low chloride region $(0{\cdot}5 \leqslant [Cl^-]_t/[Pd]_t \leqslant 20)$.

DISCUSSION

The kinetics and equilibria of the interconversion of the chloroaquopalladium(II) complexes $PdCl_n(H_2O)_{4-n}^{-n+2}$ have been thoroughly investigated by Elding.[16,22] The formation constants of the chloro species are large and no aquo or mixed chloroaquo complexes are present at chloride concentrations above 10^{-1} mol dm^{-3} and palladium concentration of the order of 10^{-4} mol dm^{-3}. For convenience, the results for the high chloride region (no aquo species) will be discussed separately from the low chloride region where significant amounts of various members of the chloroaquo series are found.

The kinetics for the high chloride region, described by Eq. (3), can be accounted for by the following simple mechanism:

$$Pd^{II}Cl_4{}^{2-} + 2Cl^- \overset{K_{46}}{\rightleftharpoons} Pd^{II}Cl_6{}^{4-} \quad (4)$$

$$Pd^{II}Cl_6{}^{4-} + Cl_2 \xrightarrow{k_6} Pd^{IV}Cl_6{}^{2-} + 2Cl^- \quad (5)$$

TABLE IV
Hydrogen ion dependence of kinetic parameters of high chloride region mechanism

$[H^+]$/mol dm^{-3}	10^2a/mol dm^{-3} sec	10^3b/mol^{3}dm^{-9} sec	10^{-4}k$_6$/mol^{-1}dm^{3}sec^{-1}	K$_{46}$/mol^{-2}dm^6
2.00	1.36 ± 0.17	3.55 ± 0.17	1.84 ± 0.23	3.8 ± 0.6
1.00	1.04 ± 0.16	4.11 ± 0.20	2.41 ± 0.37	2.5 ± 0.5
0.50	1.14 ± 0.13	4.40 ± 0.16	2.19 ± 0.25	2.6 ± 0.4
0.20	1.37 ± 0.35	3.70 ± 0.36	1.83 ± 0.46	3.7 ± 1.3

$T = 288$ K; $\mu = 2.0$ mol dm^{-3} ($NaClO_4$); $[Cl_2] = 4\times10^{-3}$ mol dm^{-3}; $[Pd(II)] = 1.75\times10^{-4}$ mol dm^{-3}. Error limits are one standard deviation.

This yields the rate expression

$$k_{obs} = \frac{k_6K_{46}[Cl^-]^2}{1+K_{46}[Cl^-]^2}[Cl_2] \qquad (6)$$

which is equivalent to (3) with

$$a = 1/k_6 \qquad (7a)$$

$$b = 1/k_6K_{46} \qquad (7b)$$

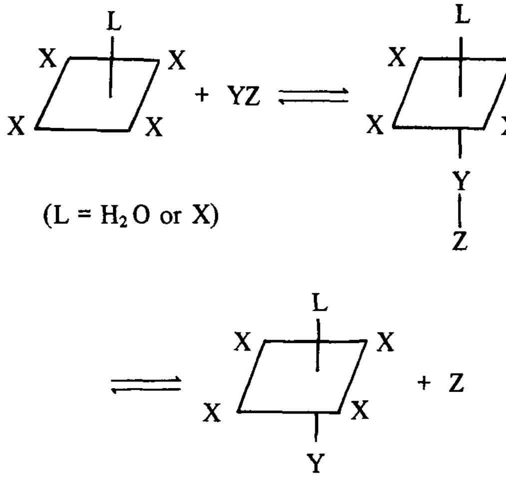
Values of k_6 and K_{46} are listed in Table IV.

The rate dependence on the square of the chloride concentration is unusual, and mathematically no distinction can be made between mechanism (4)–(5) and an analogous mechanism involving reaction between $PdCl_4{}^{2-}$ and a species formed by the interaction between chlorine and two chloride ions. For reasons discussed below, the formulation (4)–(5) is preferred. It should be noted that the observed form of the rate Eq. (3) cannot be accounted for by mechanisms involving pre-equilibrium formation of $PdCl_5{}^{3-}$ and $Cl_3{}^-$.

The ability of square-planar d^8 complexes to add additional ligands and attain higher coordination geometries is well known, and a vast amount of data testify to the associative nature of substitution reactions of such complexes.[23] Stable five-coordinate palladium(II) complexes have been described[24] and kinetic evidence for five-coordinate intermediate palladium(II) species has been reported.[25] Hexacoordination is less common for d^8 systems, but recently six-coordinate species have been proposed to be formed in rapid preequilibrium stages in the reactions of both platinum(II)[26] and gold(III)[27,28] complexes.

The question of the nature of the palladium species present in chloride media has been studied by various authors,[29] and there is general agreement that in concentrations up to 1 M chloride, complexes higher than $PdCl_4{}^{2-}$ are not observed by spectroscopic techniques. However, in more concentrated chloride media there are conflicting reports: the quantitative spectral data of Harris *et al.*[30] disagree with those of Elding.[16] In the light of the magnitude found for K_{46}, it would be expected that equilibrium (4) could be studied independently. Small but definite spectral changes were in fact observed in the range 2–12 M HCl, which testify to the formation of higher complexes at these concentrations, but the intensity variations were too small for quantitative estimation of the stability constant(s) involved. It should be remembered that the additive interaction between square-planar species and extra ligands perpendicular to the square plane is likely to be weak, and particularly for two ligands of not vastly differing ligand fields, Cl^- and H_2O, insufficient change in the ligand field at the metal ion may be experienced for the spectrum to be sensibly altered. The high lability of palladium(II) systems prevents study of equilibrium (4) by more direct separation techniques.

Elding and Gustafson[13] have summarised the sparse information that has accumulated to date concerning the mechanism of oxidative addition to classical complexes of the type $PtX_4{}^{n+}$. In general the mechanism requires coordination of the oxidant YZ to a five-coordinate species, as follows



(8)

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Since this mechanism involves coordination of the oxidant in the incipient coordination shell of the product, it may be appropriately described as a quasi-inner sphere mechanism. However, in the reaction of $PdCl_4^{2-}$ with Cl_2, the six-coordinate intermediate, $Pd^{II}Cl_6^{4-}$, produced in the pre-equilibrium stage, differs from the product only in the fine details of the octahedral geometry. An outer sphere electron transfer mechanism thus seems highly logical, and the much greater reactivity at high chloride concentrations, where the six-coordinate intermediate is present in appreciable concentrations, than at low chloride concentration, where four-coordinate complexes are found, appears to support this contention.

Many workers[11-13,31] have noted that if $L = H_2O$ in mechanism (8) the subsequent anation reaction is slow since the d^6 octahedral system can be expected to be inert. In the present case since the immediate product of the oxidation is $Pd^{IV}Cl_6^{2-}$, the subsequent slow substitution must be the hydrolysis of one of the coordinated chloride ligands. This assignment is supported by the spectral behaviour observed when chloride is added to solutions in which the final equilibrium position, i.e. after both observed stages are completed, has been reached. The spectrum is shifted towards the spectrum obtained immediately after the fast oxidation step but before the slow second process is complete. Similarly if a solution that has ceased reacting is diluted with respect to chloride, spectral changes begin anew in the same direction as depicted in Figure 1. Because of the small optical density changes involved, quantitative evaluation of the kinetics of the second reaction was not attempted.

In the low chloride region, the mechanism is considerably less well defined, and complex dependence of the rate on the chloride ion concentration is observed (Figure 3). Not unexpectedly, plots of log k_{obs} vs. log $[Cl^-]$ are not linear. In the low chloride region, all the members of the chloroaquo series $PdCl_n(H_2O)_{4-n}^{-n+2}$ $(0 \leqslant n \leqslant 4)$ are present in amounts dependent on the chloride concentration. The simplest mechanism that can be suggested may be formulated as composed of five parallel reactions

$$Pd^{II}Cl_n(H_2O)_{4-n}^{-n+2} + Cl_2 \xrightarrow{k_n} Pd^{IV}Cl_{n+2}(H_2O)_{4-n}^{-n+2} \qquad (0 \leqslant n \leqslant 4)$$

Each such path would contribute a rate term

$$R_n = k_n[Pd^{II}Cl_n(H_2O)_{4-n}^{-n+2}][Cl_2]$$

leading to the overall rate expression

$$R = k_{obs}[Pd]_t[Cl_2]$$

where

$$k_{obs} = \frac{\sum_0^4 k_n\beta_n[Cl^-]_f^n}{\sum_0^4 \beta_n[Cl^-]^n} \qquad (9)$$

where β_n is the nth cumulative formation constant and $[Cl^-]_f$ is the free chloride concentration calculated from the known equilibrium constants. Only the rate constants k_n are unknown in (9) and an attempt was made to solve sets of Eq. (9) using a computer program that solves the k_n vector of the matrix equation that results when (9) is cast in matrix form. The results so obtained were not self-consistent and on occasion even led to negative values for some of the rate constants. The primary reason was found to be the inherent uncertainty in the measured rate constant, which were reproducible at times to no better than 10%, while the measured rate changed by a factor of only about 20 in the low chloride region. In order to investigate the importance of the experimental uncertainty, we solved (9) using values of k_{obs} incorporating the reproducibility limits.[18] This had the effect of drastically changing the values of the various constants even on occasion to the extent of changing its sign. The value of k_4 was usually found to be significantly larger than the other constants, perhaps suggesting that $PdCl_4^{2-}$ is the species most susceptible to oxidation in the aquochloro series.

In a detailed discussion of the low chloride region, consideration should be taken of the hydrolysis equilibrium[32-34]

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

since up to 10% of the total chlorine is present as HOCl. The hydrolysis product HOCl has been shown to be more reactive than Cl_2 towards iron(II)[33] and vanadium(IV),[34] although the reactivity order is inverted towards vanadium(III).[18] In principle HOCl can contribute to the observed rate by reaction with all or any of the $PdCl_n(H_2O)_{4-n}^{-n+2}$ species. Since this would introduce (up to) another five parameters into a model which for reasons of experimental accuracy cannot cope with five rate constants, the low chloride region was not pursued further.

It would seem most likely, however, that in the region in which chloroaquo complexes of various composition occur all of these undergo oxidative addition by the quasi inner sphere mechanism described above. The mechanism is likely to differ from that applying in the high chloride region because of the more open square-planar structure and the availability of vacant z-axis coordination sites to the oxidant molecule.

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REFERENCES

1. J. P. Collman and W. R. Roper, *Adv. Organomet. Chem.*, 7, 53 (1968).
2. R. F. Heck, *Acc. Chem. Res.*, **2**, 10 (1969).
3. J. Halpern, *Acc. Chem. Res.*, **3**, 386 (1970).
4. L. Marko and B. Heil, *Catal. Rev.*, 8, 269 (1973).
5. R. Ugo, *Catal. Rev.*, **11**, 225 (1975).
6. G. W. Parshall, *Acc. Chem. Res.*, **8**, 113 (1975).
7. A. J. Deeming, *MTP Int. Rev. Science, Inorg. Chem., Series One*, Vol. 9, p. 117, 1972.
8. R. Brady, W. H. de Camp, B. R. Flynn, M. L. Schneider, J. D. Scott, L. Vaska and M. F. Werneke, *Inorg. Chem.*, **14**, 2669 (1975).
9. F. M. Miller and B. L. Shaw, *J. Chem. Soc. Dalton*, 480 (1974).
10. W. H. Thompson and C. T. Sears, *Inorg. Chem.*, **16**, 769 (1977).
11. W. R. Mason, *Inorg. Chem.*, **10**, 2823 (1971).
12. M. M. Jones and K. A. Morgan, *J. Inorg. Nucl. Chem.*, **34**, 259 (1972).
13. L. I. Elding and L. Gustafson, *Inorg. Chim. Acta*, **19**, 165 (1976).
14. S. E. Livingstone, in *Comprehensive Inorganic Chemistry*, Ed. A. F. Trotman Dickenson, Pergamon, N. Y., 1973, Vol. 3, Chap. 3.
15. P. J. Hendra and P. J. D. Park, *Spectrochim. Acta*, **23A**, 1635 (1967).
16. L. I. Elding, *Inorg. Chim. Acta*, **6**, 647 (1972).
17. A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, 3rd Edit., Longmans, London, 1961. a. p. 511; b. p. 343.
18. R. D. Cornelius and G. Gordon, *Inorg. Chem.*, **15**, 997 (1976).
19. H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949).
20. Stability constants of metal-ion complexes, *Chem. Soc. Spec. Publ.*, **17**, 1964; **25**, 1971.
21. E.g. G. Freidlander, J. W. Kennedy and J. M. Miller, *Nuclear and Radiochemistry*, 2nd Edit., Wiley, N. Y., 1964.
22. L. I. Elding, *Inorg. Chim. Acta*, **6**, 683 (1972).
23. E.g. M. L. Tobe, *Inorganic Reaction Mechanisms*, Nelson, London, 1972, Chap. 5; R. G. Wilkins, *The Study of Kinetics and Mechanisms of Reaction of Transition Metal Complexes*, Allen and Bacon, Boston, 1974, Chap. 4.
24. W. J. Louw, D. J. A. de Waal and G. J. Kruger, J. C. S. Dalton, 2364 (1976) and references therein.
25. E.g. A. J. Poë and D. H. Vaughan, *Inorg. Chim. Acta*, **1**, 255 (1967).
26. D. Banerjea and P. Banerjee, *Z. Anorg. Allgem. Chem.*, **393**, 295 (1972).
27. G. Annibale, L. Cattalini, A. A. El-Awady and G. Natile, *J. Chem. Soc. Dalton*, 802 (1974).
28. G. Annibale, G. Natile and L. Cattalini, *J. Chem. Soc. Dalton*, 285 (1976).
29. Ref. 16 and references therein.
30. C. M. Harris, S. E. Livingstone and I. H. Rees, *J. Chem. Soc.*, 1505 (1959).
31. K. A. Morgan and M. M. Jones, *J. Inorg. Nucl. Chem.*, **34**, 275 (1972).
32. G. Zimmerman and F. C. Strong, *J. Amer. Chem. Soc.*, **79**, 2063 (1957).
33. R. E. Connick and Y. Chia, *J. Amer. Chem. Soc.*, **81**, 1280 (1959).
34. H. W. Dodgen, A. D. Jordan and R. B. Jordan, *J. Phys. Chem.*, **77**, 2149 (1973).
35. T. J. Conocchioli, E. J. Hamilton and N. Sutin, *J. Amer. Chem. Soc.*, **87**, 926 (1965).
36. K. Dreyer and G. Gordon, *Inorg. Chem.*, **11**, 1174 (1972).

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