

A Kinetic Study of the Substitution Reactions of the Tetrachloroplatinate(II) Ion with Water and Acetonitrile

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Received May 5, 1975

The hydrolysis of $[\text{PtCl}_4]^{2-}$ to $[\text{PtCl}_3(\text{OH}_2)]^-$ and Cl^- , its reverse reaction, and the substitution of CH_3CN into $[\text{PtCl}_4]^{2-}$ have been studied over the temperature range 50 to 70°C. The relevant rate constants and activation parameters have been determined. At 64°C, the rate constants for the three reactions are $2.35 \times 10^{-3} \text{ s}^{-1}$, $6.85 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ and $4.83 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ respectively. The appropriate activation energies are 22.5, 17.6 and 16.2 kcal mol⁻¹. The ionization constant for $[\text{PtCl}_3(\text{OH}_2)]^-$ is found to be $(3.5 \pm 0.6) \times 10^{-7} \text{ M}$ at 64°C.

Introduction

We have recently undertaken studies of the formation of 'Platinblau', the intense blue product which can be obtained as a product of the reaction between chloro-complexes of platinum, acetonitrile and water¹⁻³. A necessary prerequisite of these studies is a knowledge of the kinetics of the reactions between the tetrachloroplatinate(II) ion and water or acetonitrile in the temperature range 50–70°C. The simple system of tetrachloroplatinate(II) in an aqueous medium has been studied at ambient temperatures⁴⁻⁸. However, we have been unable to find information in the literature for the replacement of chloride by acetonitrile. We have therefore studied both systems at temperatures between 50 and 70°C. The data described below are consistent with the data for the hydrolysis of tetrachloroplatinate(II) at lower temperatures, and with the general pattern of behaviour expected⁹ for square planar platinum(II) complexes.

Hydrolysis of $[\text{PtCl}_4]^{2-}$

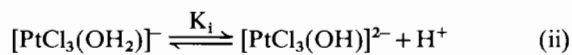
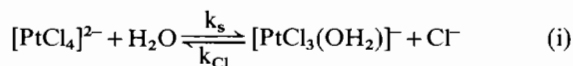
The rate of disappearance of the tetrachloroplatinate(II) ion in aqueous solutions, at known pH and chloride ion concentrations, was observed spectrophotometrically at 228 nm, a wavelength near to the maximum at 218 nm. In all experiments the chloride ion con-

centration was much greater than that of the platinum containing reagent while the pH was held constant. Under these circumstances the disappearance of tetrachloroplatinate(II) obeys a simple pseudo-first order rate equation. The rate constants evaluated, designated k_{obs} are tabulated in Table I.

The early behaviour of the $[\text{PtCl}_4]^{2-}$ ion in aqueous solution is adequately described by equations (i) and (ii):

TABLE I. Observed Rate Constants for the Hydrolysis of the Tetrachloroplatinate Ion in Aqueous Solution. The pH and the ionic strength of solutions were maintained by adding perchloric acid, lithium perchlorate and potassium hydroxide, while the initial concentration of $[\text{PtCl}_4]^{2-}$ used was $1.00 \times 10^{-4} \text{ M}$.

Temp/°C	pH	$[\text{Cl}^-]/\text{M}$	μ/M	$10^4 k_{\text{obs}}/\text{s}^{-1}$
50.0	4.00	0.005	0.1	6.70
50.0	4.00	0.010	0.1	7.72
50.0	4.00	0.015	0.1	8.80
50.0	4.00	0.020	0.1	9.97
57.0	4.00	0.005	0.1	13.6
57.0	4.00	0.010	0.1	15.3
57.0	4.00	0.015	0.1	17.3
57.0	4.00	0.020	0.1	19.5
64.0	4.00	0.005	0.1	27.2
64.0	4.00	0.010	0.1	30.7
64.0	4.00	0.015	0.1	34.0
64.0	4.00	0.020	0.1	37.2
64.0	4.00	0.030	0.1	44.8
64.0	4.00	0.040	0.1	52.2
70.0	4.00	0.005	0.1	46.2
70.0	4.00	0.010	0.1	51.5
70.0	4.00	0.015	0.1	56.3
70.0	4.00	0.020	0.1	62.3
64.0	5.00	0.010	0.1	30.2
64.0	6.00	0.010	0.1	29.3
64.0	6.30	0.010	0.1	27.3
64.0	6.60	0.010	0.1	26.3
64.0	6.85	0.010	0.1	25.5
64.0	4.00	0.010	0.05	30.7
64.0	4.00	0.010	0.01	30.7



Our observations, see below, support the conclusion^{4,7} that the replacement of a second chloride ion is much slower than the replacement of the first, while direct substitution by hydroxide ion may be neglected since this ion exhibits^{5,6} a low nucleophilicity for platinum (II), and our studies are in acidic media. From these equations one may deduce that

$$k_{\text{obs}} = k_s + k_{\text{Cl}}[\text{Cl}^-][\text{H}^+]/(K_i + [\text{H}^+]) \quad (\text{iii})$$

The ionization constant, K_i , has been estimated⁴ to have a value of *ca.* $10^{-7} M$ at 25°C ; therefore at low pH values equation (iii) reduces to

$$k_{\text{obs}} = k_s + k_{\text{Cl}}[\text{Cl}^-] \quad (\text{iv})$$

while no acid will be produced as a result of the hydrolysis. This deduction is confirmed by our observation that base must be added to maintain a constant pH, only at pH values above 5.

Evaluation of k_s and k_{Cl} from the data of Table I leads to the data given in Table II. The activation energies of k_s and k_{Cl} are (22.5 ± 0.4) and (17.6 ± 0.4) kcal mol⁻¹ respectively. Equation (iii) shows that the observed rate constant for a reaction will vary with the hydrogen ion concentration. However, the variation will be significant only over a narrow pH range, while the extent of the variation will be determined by the chloride ion concentration. Unfortunately, the greater the chloride ion concentration, the greater is the fraction of platinum species remaining as $[\text{PtCl}_4]^{2-}$. Thus it is difficult to study accurately the variation with hydrogen ion concentration. Table I contains data of our attempts to determine K_i kinetically, by varying pH. From these data we deduce that, at 64.0°C

$$K_i = (3.5 \pm 0.6) \times 10^{-7} M$$

This result is in reasonable agreement with the estimate made by Grantham, Ellemann and Martin⁴ at 25°C .

Finally, the data of Table I shows that, under our experimental conditions the observed rate constant appears to be independent of ionic strength. This finding reflects the minor importance of the k_{Cl} term in the equation for k_{obs} .

TABLE II. Rate Constants^a, k_s and k_{Cl} , at pH = 4.0 and $\mu = 0.1 M$.

Temp/ $^\circ \text{C}$	$10^4 k_s / \text{s}^{-1}$	$10^2 k_{\text{Cl}} / M^{-1} \text{s}^{-1}$
50.0	5.58	2.17
57.0	11.4	3.95
64.0	23.5	6.85
70.0	40.7	10.6

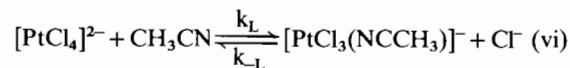
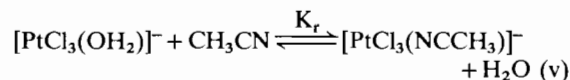
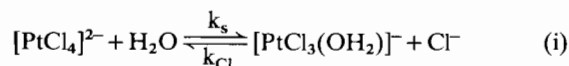
^a The standard deviations of these values are less than 4%.

Hydrolysis of $[\text{PtCl}_3(\text{OH}_2)]^-$

The experimental arrangement used by us incorporates a pH-stat to enable the pH of a reaction solution to be maintained automatically. Above pH = 5, base must be added to maintain a constant pH. If equations (i) and (ii) were a complete representation of the reaction under study, the volume of added base would obey a first order equation, governed by the same rate constant as that determined spectrophotometrically. Also, the addition of base should cease when the reaction studied spectrophotometrically is complete, with the total volume of added base corresponding to the relevant values of k_s , k_{Cl} and K_i . Thus at 64°C and pH = 7, 0.78 mol of base per mol of $[\text{PtCl}_4]^{2-}$ would be required. Plots of added base against time at pH > 5 do not conform to this pattern. In the early stages of the reaction, the generation of acid does indeed appear to be first order. But acid continues to be slowly produced after the first hydrolysis step is complete. Ultimately more than two protons per platinum are released and a grey precipitate develops. Therefore $[\text{PtCl}_3(\text{OH}_2)]^-$ must be undergoing slow subsequent hydrolysis reactions. We have been unable to extract from the data numerical values for these subsequent hydrolysis reactions. A plausible estimate of the value of the rate constant for the second hydrolysis at pH = 7 and 64.0°C is circa $4 \times 10^{-4} \text{s}^{-1}$. This estimate is based on the observation that the time of half reaction for the generation of additional acid is approximately 30 minutes, under these conditions. Therefore the ratio of rate constants for the replacement of the first and second chloride ligands by water is in the region of 6:1.

The Substitution of CH_3CN for Cl^- in $[\text{PtCl}_4]^{2-}$

The ligand substitution reactions of square planar platinum(II) complexes in water proceed through two parallel routes⁹. The first involves the reaction described above by k_2 , followed by a rapid replacement of water by the incoming ligand. The second involves direct substitution of the leaving group by the incoming ligand. Thus the substitution of acetonitrile for chloride in $[\text{PtCl}_4]^{2-}$ should be described by equations (i), (ii), (v) and (vi). Below pH = 5, equation (ii) will be unimportant and so the complete reaction scheme should be



In the absence of added chloride ion, the back reactions of equations (i) and (vi) will also be unimportant, and so the disappearance of tetrachloroplatinate(II) will obey first order kinetics with a measured rate constant, k_{meas} , described by equation (vii) irrespective of the value of K_r :

$$k_{meas} = k_s + k_L[CH_3CN] \quad (vii)$$

The replacement of chloride by acetonitrile was followed at pH = 4, and an ionic strength of 0.1M, in an analogous manner to the hydrolysis studied above. There is an additional experimental problem in this system, since a species is produced which has a weak absorption at the wavelength used. This product arises slowly, and only affects optical density measurements of the final few per cent of reaction, and the infinity reading. The behaviour of the measured optical density shows that this absorbing species must be the product of a subsequent reaction, and that it is not a trichloro complex. The first 75% of reaction is well described by a first order equation, and the values of k_{meas} quoted in Table III are derived from this portion of the reaction profile. In order to obtain accurate values of k_{meas} , the data was computed using an iterative least squares program which treated both the rate constant and the final optical density as unknown constants to be evaluated. In all cases the computed final optical density agreed well with the approximate value which can be estimated by inspection of the reaction profile. In addition to the values of k_{meas} , the value of k_s derived above is a valid point for the determination of k_L from these experiments. Hence

TABLE III. Rate Data at pH = 4 and an Ionic Strength of 0.1M for the Replacement of Chloride by Acetonitrile in $[PtCl_4]^{2-}$, in Aqueous Solution.

Temp/°C	$[CH_3CN]/M$	$10^4 k_{meas}/s^{-1}$	$10^2 k_L/M^{-1} s^{-1}$
50.5	0.01	7.45	
50.5	0.02	9.15	
50.5	0.03	11.05	
50.5	0.04	12.8	
57.0	0.01	14.1	2.73 ± 0.05
57.0	0.02	16.8	
57.0	0.03	19.7	
57.0	0.04	22.3	
64.0	0.01	29.3	4.83 ± 0.14
64.0	0.02	33.7	
64.0	0.03	38.3	
64.0	0.04	43.5	
64.0	0.05	48.7	
64.0	0.06	53.5	
70.0	0.01	47.7	7.30 ± 0.20
70.0	0.02	54.7	
70.0	0.03	62.2	
70.0	0.04	70.0	

the activation energy is found to be (16.2 ± 0.7) kcal mol^{-1} . It is worth noting here that our unpublished studies of the subsequent reactions in these solutions show that the main product of the reaction described here is $[PtCl_3(NCCH_3)]^-$. This product undergoes further replacement of chloride by H_2O only, and the observed rate constant is independent of pH in the range 6.0 to 8.0. If the trichloro-species contained water as the fourth ligand, the next rate constant would be pH dependant. Thus, although acetonitrile is not a good ligand for platinum(II), in this instance it seems to be preferable to water.

In Table IV, the activation parameters for the three reactions, described by k_s , k_{Cl} and k_L , are listed from our results and those published elsewhere. The values from different sets of workers are in good agreement. In the case of the entropy of activation for the hydrolysis of $[PtCl_4]^{2-}$, the literature values quoted appear to have been calculated using the pseudo-first order rate constant, k_s . The value calculated from our results is obtained by converting k_s to a second order rate constant, since this value may then be compared directly with those for the other reactions. The different units of k alter the value of ΔS^\ddagger by 8 cal $deg^{-1} mol^{-1}$. The data of Table IV are in good agreement with those values often found for platinum(II) substitution reactions, which are interpreted in terms of associative mechanisms. Drougge *et al.*⁸ reported a value of 4.4 kcal mol^{-1} for the enthalpy change accompanying equation (i) over the temperature range 15°C to 35°C, and suggested that it showed a small temperature dependence. At first sight, our data would appear to support this, since we deduce a value of 4.9 kcal mol^{-1} over the range 50°C to 70°C. However, the difference between the two values is within experimental error.

Finally, since it is of relevance to our studies of the formation of 'platinblau' we note that, at temperatures in the range of 50–70°C, solutions which were initially $10^{-4} M$ in $[PtCl_4]^{2-}$ and 0.1M in acetonitrile will quickly lose $[PtCl_4]^{2-}$ concentration. The time of half reaction being of the order of one or two minutes.

TABLE IV. Activation Parameters for the Reactions Discussed Herein.

Reaction	$\Delta H^\ddagger/kcal mol^{-1}$	$\Delta S^\ddagger/cal deg^{-1} mol^{-1}$	Reference
$[PtCl_4]^{2-} + H_2O$	21	-8 ^a	4
	21.6	-6.4 ^a	8
	21.8	-14.7	Within
$[PtCl_3(OH_2)]^- + Cl^-$	15	-18	4
	17.2	-12.4	8
	16.9	-14.5	Within
$[PtCl_4]^{2-} + CH_3CN$	15.5	-19.4	Within

^a See text concerning units of rate constant used in calculation.

Experimental

Spectrophotometric studies were undertaken using a Pye Unicam SP1800 spectrophotometer. Reaction solution from an external thermostatted vessel was circulated, using a Watson Marlow peristaltic pump, type H.R.E., through a thermostatted silica flow cell within the spectrophotometer. The external reaction vessel consists of an inner vessel surrounded by an outer water jacket, through which water from a thermostat bath is pumped. The inner vessel is cylindrical in cross section and has a flat base, to enable a magnetic follower and an external rotating magnet to be used for stirring. This vessel is serviced from the top via several ground glass conical joints. The largest inlet takes the electrodes for an EIL, model 23A, pH-meter. The signal from the pH-meter is fed to a Pye autotitrator controller, cat. no. 11603. This controls a delivery unit which can deliver base from a 10 ml burette, through a second inlet, to the reaction solution. Additionally a thermometer and the outlet and return tubes of the circulation system enter from above, while a water condenser is mounted above the solution. The most satisfactory experimental conditions are those using a total solution volume of 200 ml, with a vessel capable of holding approximately 250 ml. The concentration of the base to be delivered by the pH controller is chosen so that the total volume to be added does not exceed 10 ml (a 5% volume change over the whole reaction), while one drop will not alter the pH of the reaction solution dramatically. This latter criterion avoids fluctuations in the pH due to errors in the delivery unit. Thus using 200 ml of $10^{-4}M$ K_2PtCl_4 solution, the base used to maintain pH in our experiments was normally $5 \times 10^{-3}M$ potassium hydroxide solution.

In order to commence a kinetic run with an essentially pure K_2PtCl_4 solution, solutions were freshly prepared each time kinetic studies were to be performed. These solutions were prepared in as concentrated a form as possible, and the reaction initiated by adding a portion of this concentrated solution to a solution of all the other reagents in the reaction vessel. All reagents used are standard materials which were used as purchased.

Acknowledgment

One of us (A.K.J.) wishes to thank the Science Research Council for the award of a research studentship.

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