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A Kinetic Study of the Hydrolysis of Acetonitrile Co-ordinated to Platinum, Yielding Platinblau

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When aqueous solutions containing tetrachloroplatinate(II) and acetonitrile are warmed in the presence of oxygen, a blue product is formed. This product is shown to be the same platinblau as that reported elsewhere. During the reaction acid is liberated and oxygen consumed. The rates of acid release and colour development have both been studied, leading to the postulation of a mechanism. Initially a series of substitution reactions occurs, yielding $[PtCl(OH)_2(H_2O)]^-$ *and* $[PtCl(OH)_3]^{2-}$ *in equilibrium with each other. These complexes react with oxygen in the presence of acetonitrile to produce platinum(IV) complexes containing acetonitrile ligands. These ligands are then attacked by hydroxide ions to yield the acetamidato ligands of platinblau. Equilibrium and rate constants are quoted for several steps within the overall reaction sequence.*

Introduction

When the complex *cis*-$[PtCl_2(NCCH_3)_2]$ is treated with silver salts in aqueous media, a blue colouration is produced [1], usually referred to as 'platinblau'. Although various attempts [2–4] have been made to identify this material, the characterisation is still not complete. There is general agreement that the product prepared in this manner contains hydrolysis products of acetonitrile, and does not contain chloride. The studies of Brown *et al.* [4], on the related compounds derived from trimethylacetamide suggest that platinblau is a 6 co-ordinate complex of platinum(IV), specifically *trans*-dihydroxybis(acetamidato)platinate(IV). Other tautomeric forms occur for the trimethylacetamide derivatives, and so such forms must be regarded as feasible for the parent 'platinblau'. In this paper we describe the results of kinetic studies on the formation of a 'platinblau' from aqueous solutions of potassium tetrachloroplatinate(II) and acetonitrile. Since our preparative route differs from that of Hoffmann and Bugge, we refer to our product as 'blau' rather than 'platinblau'.

The chemical literature [5–7] shows that studies of the amminolysis of acetonitrile in the complex *cis*-$[PtCl_2(NCCH_3)_2]$ have posed similar problems to those of platinblau. Again X-ray crystallographic studies [8] have helped to characterise the product, which contains *trans*-diamminobis(acetamido) platinum(II), a 4 co-ordinate complex of platinum(II), analogous to one of the forms proposed by Brown *et al.* [4].

The hydrolysis of ligands containing either co-ordinated [9–13] or free [14–17] nitrile groups has attracted considerable attention. In all cases known to us, the reactions involve the attack of hydroxide on the nitrile group. When the nitrile group is directly attached to the metal a dramatic increase in the rate of hydrolysis may be observed [13]. The rate of hydrolysis may also be enhanced [14, 15] when the metal is attached to a different part of the ligand molecule, if it can interact with and stabilise the transition state.

Results

Initially we attempted to study the formation of 'platinblau' by the reaction [1, 2] of silver salts and chloro complexes in aqueous media. The precipitation of silver chloride occurs continuously during the development of the blue colour, and we were unable to devise a satisfactory procedure for its removal. When this reaction is carried out under oxygen free conditions, some metallic silver is also produced, an observation supporting the suggestion that the oxidation state of platinum in 'platinblau' is IV and not II. When potassium tetrachloroplatinate(II) is heated in an aqueous solution of acetonitrile for several hours, a blue colour is produced, but only if oxygen is present. This blue colour is rapidly discharged upon the addition of the reducing agent, sodium dithionite. Since the reaction does not involve the formation of any precipitate until the later stages of the reaction, when a blue solid sometimes begins to separate out, we decided to study this reaction.

Samples of the blue solid, prepared under the conditions used for kinetic experiments, have been investigated. That is, the solid was prepared at pH = 7, maintained by the addition of suitable quantities of base. Data from elemental analyses vary from sample to sample. There are, however, certain consistent features within the sets of data. The molar ratio of platinum to nitrogen remains at 1:2, while the potassium:chlorine ratio remains close to 1:1. One such set of data is quoted in the experimental section. These data strongly suggest that the solid isolated is a mixture of a platinum compound and potassium chloride. When organic solvents such as ethanol are used during the preparation, some solvent is also retained in the solid. Other workers have also experienced problems with impure products when preparing platinblau [2].

There is no evidence, in the infra-red spectrum of our product, of a symmetric Pt–Cl stretch around 342 cm^{-1}, such as one would expect [4] if co-ordinated chloride were present. In contrast, we do observe a strong band at 343 cm^{-1} in the spectrum of *cis*-[PtCl$_2$(NCCH$_3$)$_2$]. There are, in the spectrum of the 'blau', bands which we assign to O–H (3430 m), N–H (3335 m) and C=O (1570 s). This latter band corresponds to that observed for metal acetates [18], and may indicate co-ordination through a C=O group, probably with chelation. Our product does not melt, but decomposes above 250 °C, and so one can not expect a parent ion peak in the mass spectrum. Major peaks are seen at 58, 43 and 42 Daltons, assigned to CH$_3$CONH, CH$_3$CO and CH$_3$CNH respectively, indicating the presence of the acetamido group. The only feature observed in the proton magnetic resonance spectrum in deuteriated dimethylsulphoxide is a singlet at 6.6 τ, exceptionally low for a methyl group. The proposed structure could result in extensive deshielding by the nearby Pt^{IV}.

When our 'blau' is prepared in dilute aqueous solution at pH = 7, a broad absorption maximum centred on 612 nm. is observed in the visible region. The position of the maximum varies with pH, as reported by Gillard and Wilkinson [2] for their dihydroxo product. We find that these dilute solutions obey Beer's law. When the isolated blau is redissolved in water, the broad absorption band is found to have moved to 632 nm. This may be due to some degree of polymerisation when solutions are concentrated [4]. One additional observation is worth recording. In an attempt to separate the KCl from the platinum product, we ran solutions down various ion exchange columns, in H$^+$ and subsequently OH$^-$ forms. In all cases we observe that the majority of the blue colour is retained at the top of the cation column, while the remainder of the column has a reasonably uniform blue colouration, leaving only a pale blue eluent. We believe this to show that the major component in a blau solution can be protonated, yielding a cation which is held at the top of the column, followed by a slowly achieved equilibrium which accounts for the continuous blue colouration.

In short, our product is not completely identified. However the major, if not sole, component present in dilute aqueous solutions is almost certainly *trans*-[dihydroxybis(acetamidato)platinate(IV)], and its concentration may be followed spectrophotometrically.

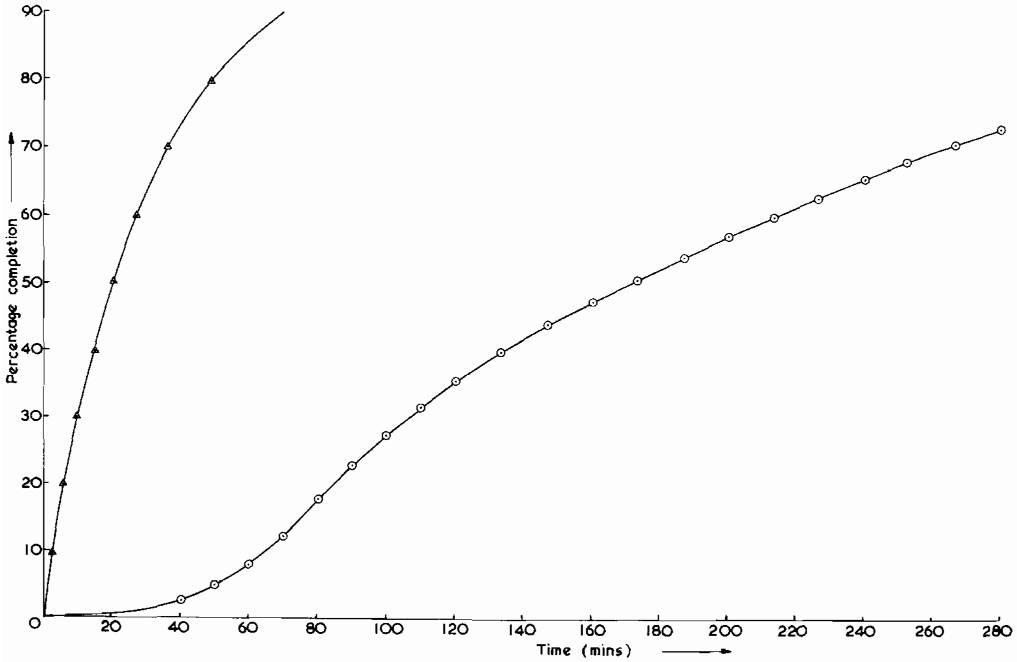

Figure 1. Typical reaction profile for liberation of acid (Δ) and development of colour (O) during a kinetic run. Data for [PtCl$_4^{2-}$] = 4 × 10^{-4}*M*, [CH$_3$CN] = 0.10*M*, pH = 7.0, T = 64.0 °C.

When aqueous solutions containing both acetonitrile and potassium tetrachloroplatinite(II) are warmed together, the pH drops over a period of approximately an hour, and a blue colouration develops more slowly. The time scales of these processes may be judged from the visual presentation of Figure 1. In the range $4 < pH < 9$, the quantity of acid produced varies from 2 to 3 protons per platinum. Although various buffering agents may be employed to maintain a reasonable constancy in pH, their use in this instance is unacceptable. For example the spectrophotometrically determined reaction profile at pH = 6 differs for each of the buffers [19] based on phosphate, succinate, phthalate, acetate and citrate, and differs from that obtained when the acid produced is continuously neutralised by the addition of base. We therefore chose this latter method for the maintenance of constant pH. It offers the added advantage that the rate of acid production can be determined. Figure 1 shows the titration and spectrophotometric profiles produced in this way. We find that the generalised reactions (i) and (ii) describe the acid production. In these equations A, B and C

$$A \xrightarrow{k_a} B + xH^+ \qquad (i)$$

$$B \xrightarrow{k_b} C + yH^+ \qquad (ii)$$

represent platinum containing species; k_a and k_b are composite rate constants; and x and y are numbers which vary with pH. Thus B and C represent families of compounds, within which rapid equilibria occur. The rate at which alkali must be added to maintain a constant pH during these reactions is then described by

$$[OH^-]_t = [OH^-]_\infty x \left\{1 + \frac{(xk_a - yk_b)e^{-k_at} + (y - x)k_ae^{-k_bt}}{y(k_b - k_a)}\right\} \qquad (iii)$$

Equation (iii) satisfactorily describes all the sets of data obtained by us. An iterative least squares computer program was used to find the best values of k_a, k_b and x for each run. The value of y is determined from a knowledge of $[OH]_\infty$, the total quantity of base added to maintain constant pH. The resulting values are quoted in Table I to IV. These tables illustrate the effect of pH, acetonitrile concentration and temperature on the rate parameters. Data are also quoted for runs during which argon or oxygen was bubbled through the reaction solution, as distinct from the normal exposure to air. In the tables of data, further columns of numbers are quoted, headed k_c, k_d, and D_{inf}. These data refer to the fitting of the spectrophotometric curves obtained for these same kinetic runs.

As Figure 1 shows, the release of acid is complete long before the blue colour is fully developed. This is so under all conditions studied by us. Optical density measurements show a pronounced induction period indicating that the 'blau' is produced at the end of a series of consecutive reactions. The problems associated with fitting the spectrophotometric data are obviously more severe than those with the titration data. There must be additional rate constants; also the onset of precipitation sometimes prevents the measurement of the final optical density. The spectrophotometric data have been successfully fitted to a sequence of successive pseudo-first order reactions, by setting the values of k_a and k_b as those determined for the same run from the independant titration data; and by finding best values for either one or two additional constants k_c and k_d, and for the final optical density if that could not be measured accurately. Examination of the tabulated results shows that the data are adequately described by three rate constants when the fourth, k_d, becomes much larger than k_c.

The general equation describing the appearance of a product (Z) formed at the end of a series of n first order reactions described by the rate constants k_1, k_2, ... k_n is stated as equation (iv). In order to simplify the statement of this equation, the constants k_{n+i} are defined as in equation (v).

TABLE I. The Effect of Varying the pH of the Reaction Solution on the Kinetic Parameters for the Reaction between K_2PtCl_4 and CH_3CN in Water. Initially the concentrations are $4 \times 10^{-4}M$ and $0.10M$ respectively. T = 64.0 °C.

pH	$10^2k_a/min^{-1}$	$10^2k_b/min^{-1}$	x	y	$10^3k_c/min^{-1}$	$10^2k_d/min^{-1}$	D_{inf}
6.0	6.00	6.34	0.223	2.03	6.13	2.91	1.12
6.3	6.00	5.75	0.388	2.06	6.04	5.09	1.26
6.7	6.00	5.10	0.665	2.14	5.86	8.25	1.22
7.0	6.05	4.32	0.978	2.25	5.57[a]		1.34
7.2	6.01	3.93	1.16	2.28	5.71[a]		1.24
7.7	6.02	3.12	1.58	2.50	5.95[a]		1.39
8.0	5.91	1.66	1.80	2.68	[b]		

[a] Later part of spectrophotometric data treated as simple first order fit since effect of k_d is negligible. [b] Behaviour of solution prevents accurate determination of data.

TABLE II. The Variation of Rate Parameters with Acetonitrile Concentration, at 64.0 °C and $[PtCl_4^{2-}] = 4 \times 10^{-4}M$.

pH	$[CH_3CN]/M$	10^2k_a/min^{-1}	10^2k_b/min^{-1}	x	y	10^3k_c/min^{-1}	10^2k_d/min^{-1}	D_{inf}
7.0	0.02	6.03	2.58	1.15	2.28	[b]		
	0.04	5.95	3.74	1.07	2.29	10.9 [a]		1.03
	0.07	6.00	4.14	1.01	2.18	6.74[a]		1.21
	0.10	6.05	4.32	0.978	2.25	5.57[a]		1.34
	0.24	6.01	5.33	0.929	2.25	5.70	3.91	0.788
	0.38	6.04	5.79	0.819	2.23	5.54	2.95	0.601
	0.50	6.00	6.33	0.688	2.26	5.17	1.85	0.555
	0.65	6.01	6.47	0.572	2.25	5.07	2.40	0.311
7.7	0.10	6.02	3.12	1.58	2.50			
	0.24	5.98	2.89	1.43	2.47			
	0.38	5.97	2.88	1.51	2.52			
	0.50	5.96	2.91	1.47	2.50			
	0.65	5.98	3.25	1.43	2.57			

[a] Later part of spectrophotometric curve treated as simple first order fit. [b] Reaction cannot be followed spectrophotometrically.

TABLE III. The Variation of Rate Parameters with Temperature. $[PtCl_4^{2-}] = 4 \times 10^{-4}M$, $[CH_3CN] = 0.10M$, pH = 7.0.

T/°C	10^2k_a/min^{-1}	10^2k_b/min^{-1}	x	y	10^3k_c/min^{-1} [a]	D_{inf}
50.0	1.43	1.22	1.15	2.09	1.77	1.33
57.0	2.88	2.32	1.14	2.05	2.92	1.38
64.0	6.05	4.32	0.978	2.25	5.57	1.34
71.0	11.0	7.71	1.13	1.98	9.38	1.29
78.0	21.0	14.3	0.980	2.06	16.3	1.08

[a] Later part of spectrophotometric curve treated as simple first order fit.

TABLE IV. The Effect of Gases[b] on Rate Parameters. $[PtCl_4^{2-}] = 4 \times 10^{-4}M$, $[CH_3CN] = 0.10M$, pH = 7.0, T = 64.0 °C.

Gas	10^2k_a/min^{-1}	10^2k_b/min^{-1}	x	y	10^3k_c/min^{-1} [a]	D_{inf}
Ar	6.01	4.22	0.971	2.00	4.85	1.18
air	6.05	4.32	0.978	2.25	5.57	1.34
O_2	6.02	4.31	0.931	1.98	10.1	1.15

[a] Later portion of spectrophotometric data fitted to simple first order equation. [b] Gas merely bubbled through reaction solution. No attempt made to rigorously degas solution.

$$Z = Z_\infty \left[1 - \sum_{i=1}^{n} \left\{ e^{-k_i t} \cdot \prod_{j=i+1}^{i+n-1} [k_j/(k_j - k_i)] \right\}\right] \quad \text{(iv)}$$

$$\text{where } k_{n+i} = k_i \quad \text{for } i = 1,2, \quad \ldots, n-1 \quad \text{(v)}$$

Again, an iterative least squares computer program was used to find the best fit of equation (iv) to our data. It should be noted that the assymetry of equation (iii) allows one to state that k_a precedes k_b; but the sequence of k_c and k_d is not determined from equation (iv). In some cases it is sufficient to treat the major part of the spectrophotometric reaction profile as obeying a first order equation. Where this has been done, the data are appropriately identified in the tables.

The cleavage of Pt–Cl bonds must be involved in some of the steps of the reaction sequence. In the absence of any added chloride ion, the reverse reactions are negligible. If chloride ion is added to the reaction medium, this mathematical simplification may become invalid and the reaction scheme more complicated. When potassium chloride is added to reaction solutions we find that equation (iii) fits less well as the chloride concentration increases, but that the total volume of base consumed remains unchanged over the range studied by us. Thus the reverse reaction of reaction ii) is still unimportant, whereas reaction i) is altered. Reaction i) can be presented in full as

$$A \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} B + Cl^- + xH^+ \quad \text{(vi)}$$

Then, towards the end of the production of acid, the rate of consumption of base, relative to a suitable arbitrary origin, will be first order with an observed rate constant given by

$$k_{obs} = K_a k_b/(K_a + [Cl^-][H^+]^x) \qquad \text{(vii)}$$

In Table V we quote values for k_{obs} at added chloride concentrations between 0.024*M* and 0.050*M*. At lower concentrations the data are described well by equation (iii) and so k_b is quoted. That is, below 0.024*M* chloride the reverse of reaction i) is relatively unimportant and reaction i) does not reach equilibrium. The major portion of the curves for optical density against time, for these kinetic runs, can also be described by a first order equation.

TABLE V. The Variation of Rate Parameters with Concentration of Added KCl. $[PtCl_4]^{2-} = 4 \times 10^{-4}$ *M*, $[CH_3CN] = 0.10$*M*, pH = 7.0, T = 64.0 °C.

$[Cl^-]/M$	$10^2 k_{obs}/min^{-1}$ [a]	Y	$10^3 k_c/min^{-1}$ [b]	D_{inf}
0.002	3.65	2.11	5.25	1.17
0.010	2.85	2.15	5.30	1.24
0.024	2.25	2.14	4.71	1.13
0.038	1.67	2.18	5.33	0.963
0.050	1.43	2.16	4.56	0.853

[a] Later portion of titration data fitted to first order equation, see equation (vii). [b] Later portion of spectrophotometric data similarly fitted.

Proposed Reaction Scheme

$$\begin{tikzcd}
{[PtCl_4]^{2-}} \arrow[rr, "+CH_3CN"] \arrow[dr, "+H_2O"'] & & {[PtCl_3(CH_3CN)]^- + Cl^-} \\
& {[PtCl_3(H_2O)]^-} \arrow[ur, "+CH_3CN"'] &
\end{tikzcd} \qquad \text{(viii)}$$

$$[PtCl_3(CH_3CN)]^- + H_2O \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} [PtCl_2(CH_3CN)(H_2O)] + Cl^- \qquad \text{(ix)}$$

$$[PtCl_2(CH_3CN)_2] + 2H_2O \overset{K_3}{\rightleftharpoons} [PtCl_2(H_2O)_2] + 2CH_3CN \qquad \text{(x)}$$

$$[PtCl_2(H_2O)_2] \overset{K_4}{\rightleftharpoons} [PtCl_2(OH)(H_2O)]^- + H^+ \qquad \text{(xi)}$$

$$[PtCl_2(OH)(H_2O)]^- \overset{K_5}{\rightleftharpoons} [PtCl_2(OH)_2]^{2-} + H^+ \qquad \text{(xii)}$$

$$[PtCl_2L_2] + H_2O \xrightarrow{k_b'} [PtCl_2(OH)_2(H_2O)]^-, \ L = CH_3CN, H_2O \text{ or } OH^- \qquad \text{(xiii)}$$

$$[PtCl(OH)_2(H_2O)]^- \overset{K_6}{\rightleftharpoons} [PtCl(OH)_3]^{2-} + H^+ \qquad \text{(xiv)}$$

$$[PtCl(OH)_2(H_2O)]^- + O_2 + CH_3CN \overset{K_7}{\rightleftharpoons} [PtCl(OH)_2(CH_3CN)(O_2)(H_2O)]^- \qquad \text{(xv)}$$

$$[PtCl(OH)_2(CH_3CN)(O_2)(H_2O)]^- \xrightarrow{k_8} [Pt^{IV}Cl(OH)_3(O_2H)CH_3CN)] \qquad \text{(xvi)}$$

$$[PtCl(OH)_2(H_2O)]^- \xrightarrow{k_9} \text{side reaction products} \qquad \text{(xvii)}$$

$$[Pt^{IV}Cl(OH)_3(O_2H)(CH_3CN)]^- + [PtCl(OH)_2(H_2O)]^- + CH_3CN \xrightarrow[\text{fast}]{k_{10}} 2[Pt^{IV}Cl(OH)_4(CH_3CN)]^- \qquad \text{(xviii)}$$

$$[Pt^{IV}Cl(OH)_4(CH_3CN)]^- + OH^- \xrightarrow{k_{11}} [Pt^{IV}Cl(OH)_4(CH_3CONH)]^{2-} \qquad \text{(xix)}$$

$$[Pt^{IV}Cl(OH)_4(CH_3CONH)]^{2-} + CH_3CN \xrightarrow[\text{fast}]{k_{12}} \text{trans-}[Pt^{IV}(CH_3CONH)_2(OH)_2] + Cl^- + OH^- \qquad \text{(xx)}$$

Discussion

In an earlier paper [20] we have shown that the conversion of $[PtCl_4]^{2-}$ to $[PtCl_3(CH_3CN)]^-$, reaction viii, under the conditions of the present experiments, is much more rapid than is the rate of production of acid. Therefore the mono-acetonitrile complex can be regarded as the initial reagent in the present case. The rate of the first reaction studied here, described by k_a, is independent of pH, acetonitrile concentration and of the gaseous atmosphere. It shows a reverse reaction in the presence of added chloride ion.

The activation enthalpy for k_a is (87.4 ± 2) kJ mol^{-1}, while the entropy of activation is –78 J deg^{-1} mol^{-1}. From a comparison with known data [20], it is clear that k_a describes the attack of water on $[PtCl_3(CH_3CN)]^-$, reaction ix. It is surprising that the major pathway from $[PtCl_4]^{2-}$ to $[PtCl_3CN]^-$ under these conditions [20] is the direct replacement of Cl^- by CH_3CN, whereas the loss of the next chloride ligand involves only the initial replacement by water molecules. From the data of table V, we find that k_{-a} = (1.67 ± 0.13) litre mol^{-1} min^{-1} at 64.0 °C and pH = 7.0.

There is obviously a set of equilibria, involving various dichloro species, which accounts for the value of x, the number of protons released per platinum for these dichloro species. Some of the likely equilibria are shown in reactions (x) to (xii). Additionally one can postulate further equilibria involving dichloromonoacetonitrilo complexes. From the variation of x with pH and acetonitrile concentration it is possible to evaluate the relevant equilibrium constants. There is a great variation of x over the pH range described in table I, whereas table II shows a less pronounced variation over the acetonitrile concentrations studied. We are able to obtain a reasonable fit to the data only if we assume that the concentration of dichloromonoacetonitrilo species is negligible, and that reactions (x) to (xii) are operative. Given this assumption we find that at 64 °C $K_3 = 0.114\ mol^2\ litre^{-2}$, $K_4 = 2.9 \times 10^{-7}$ mol $litre^{-1}$ and $K_5 = 3.5 \times 10^{-8}$ mol $litre^{-1}$. The values of K_4 and K_5 seem very reasonable for the acidity of coordinated water, compare $(3.5 \pm 0.6) \times 10^{-7}$ mol $litre^{-1}$ for the equivalent equilibrium [20] involving $[PtCl_3(H_2O)]^-$.

The second experimentally observed rate constant, k_b, presumably relates to the conversion of dichloro species to monochloro complexes. Inspection of the tabulated data shows that k_b increases slightly as the pH of the reaction solution drops, or as the acetonitrile concentration rises. At pH = 7.7, the major dichloro species is $[PtCl_2(OH)_2]^{2-}$ and k_b is independent of the acetonitrile concentration. Therefore this complex is attacked solely by water at a rate comparable to the overall constant k_b at this pH. The insensitivity of k_b to the pH and acetonitrile concentration precludes the separation of individual rate constants from k_b. The apparent activation energy for this composite constant is (83 ± 2) kJ mol^{-1} as compared to (91 ± 2) kJ mol^{-1} for k_a. It seems that the closely related family of square planar platinum(II) complexes with two chloride ligands undergo substitution reactions at very similar rates, with water behaving as the main or sole substituent for chloride. The various reactions observed as k_b are summarised in reaction (xiii).

The total acid release per mol of platinum, y, is accounted for by equilibrium (xiv), with $K_6 = (3.5 \pm 0.5) \times 10^{-8}$ mol $litre^{-1}$. In the original preparative routes to 'platinblau' the complex $[PtCl_2(NCCH_3)_2]$ is treated with a silver salt in the presence of water. If the major role of the silver ion is to remove chloride, then our findings subsequent to k_b can be related to the mechanism of the original reaction.

Perhaps the most surprising feature of the whole reaction sequence leading to 'blau' is that no further acid is released or consumed, when once the monochloro derivatives of equilibrium (xiv) have been produced. Therefore, from this point onwards, kinetic data can only be obtained from a spectrophotometric study of the formation of the final product. The sequence of subsequent rate constants cannot be unequivocally identified purely from this kinetic study. Of necessity one must resort to argument to assign the sequence.

We could not detect any acetamide formation over the period of acid release. This observation suggests that the conversion of acetonitrile to acetamide does not occur on platinum(II). In the introduction we pointed out that the hydrolysis of coordinated nitriles involves attack by hydroxide ions. Therefore we deduce that the oxygen sensitive rate constant k_c describes the oxidation of platinum (II) to platinum(IV), and precedes all attack on coordinated acetonitrile. The other rate constant observed by us shows a pH variation which is consistent with its assignment to a hydrolysis reaction involving hydroxide attack. On the basis of these remarks we ascribe the ordered alphabetical subscripts to the constants.

There seems to be no reason to suppose that the replacement of the last coordinated chloride on platinum(II) should occur much more rapidly than k_b. Consequently we feel that k_c follows immediately on from equilibrium (xiv). Inspection shows that k_c is independent of pH, and so both the monochloroplatinum(II) complexes must undergo oxidation at very similar rates. In all subsequent reactions, processes are shown for one monochloroplatinum(II) species. This is done for simplicity, and must be taken to be representative of both species.

The 'blau' is only produced over a limited range of acetonitrile concentrations. At concentrations below

$0.1M$, the yield of 'blau' drops markedly while k_c rises. It is difficult to maintain constant low acetonitrile concentrations under these experimental conditions. In the concentration range $0.1M$ to $0.65M$ acetonitrile, k_c varies only slowly. Beyond $0.65M$, the yield of product is small. Therefore the dependence of k_c on acetonitrile cannot be identified with certainty. Conversely there is no doubt that k_c is unaffected by the addition of excess chloride ion.

We suggest reactions (xv) to (xviii) as a plausible scheme for the overall process described by k_c. Thus

$$k_c = (2K_7k_8[O_2][CH_3CN] + k_9)/(1 + K_7[O_2][CH_3CN]) \qquad \text{(xxi)}$$

The variation of D_{inf} with acetonitrile will be governed in part by the term

$$2K_7k_8[O_2][CH_3CN]/(2K_7k_8[O_2][CH_3CN] + k_9)$$

At 64.0 °C and pH = 7, k_8 has a value of approximately 2.5×10^{-3} min^{-1} while $k_9 > 10^{-2}$ min^{-1}. The activation enthalpy for k_c is (70.5 ± 2.5) kJ mol^{-1}. Since k_c is approximately equal to $2k_8$, this value must be close to that for k_8, whose entropy of activation is then approximately -115 J mol^{-1} deg^{-1}. These values of activation parameters provide further evidence that k_c describes a reaction markedly different from k_a and k_b. Under our chosen conditions, the formation of side products is relatively unimportant, and therefore reaction (xvii) is undefined. A reasonable guess would be that this reaction is the replacement of the final chloride ligand by water.

We have only one rate constant to help in elucidating the several steps which must occur on platinum(IV). Even this constant can only be detected at the lower end of our pH range when k_c is as large as possible. Additionally, the final optical density varies with the concentration of acetonitrile or chloride. The remaining steps are believed to be (xix) and (xx). If the poorly defined observable, k_d, relates to step (xix) then

$$k_d = k_{11}[OH^-] \qquad \text{(xxii)}$$

This is consistent with the limited data of table I, and yields an estimated value of 2×10^6 litre mol^{-1} min^{-1} for k_{11}, at 64.0 °C in $0.1M$ acetonitrile. This is comparable with rate constants quoted elsewhere [11–13] for the hydrolysis of coordinated nitriles by hydroxide ion attack.

It is known [21] that substitution reactions in six coordinate platinum(IV) complexes can involve Pt(II) catalysis and conjugate base mechanisms. There still remains a significant concentration of platinum(II) in the reaction solutions while coordinated acetonitrile is being hydrolysed, also an acetamidato-ligand will have a profound effect on the substitution of other ligands. Therefore steps following reaction (xix) can be expected to be rapid. All these subsequent changes are collected together as reaction (xx).

The final optical density of reaction solutions at 612 nm varies markedly with the acetonitrile concentration. At low concentrations the effect of the factor from equation (xxi) is observed. As the concentration of acetonitrile increases the optical density passes through a maximum as a different effect becomes predominant. The addition of chloride ion causes a similar, but less marked, drop in final optical density. Since we believe the blue colour to be mainly due to the dihydroxo product, these concentration effects are ascribed to the occurrence of substitution equilibria in the product species.

The major feature of the entire reaction sequence is that acetonitrile is activated towards hydroxide attack by coordination to platinum(IV) rather then to the less polarizing platinum(II). The slower steps which we have observed merely form a necessary chain of reactions leading up to this situation.

Experimental

The details of the experimental design, and of reagents used in kinetic studies, have been given in an earlier paper [20]. Rate parameters were evaluated using iterative least squares computer programs specifically written for the problems described here.

Solid samples of our 'blau' are obtained in the following manner. Solutions of potassium tetrachloroplatinate(II) in $0.1M$ aqueous acetonitrile are prepared in the apparatus used for kinetic study, and the pH of these solutions is maintained at a value of 7 using the pH meter and autotitration unit to deliver appropriate quantities of potassium hydroxide solution. When the development of colouration is complete, the bulk of the solution is reduced by evaporation under reduced pressure until the platinum concentration is approximately $0.04M$. An equal volume of ethanol is then added and the solution filtered. An excess of diethyl ether is added to the clear blue filtrate whereon a precipitate develops. The fine, dark blue precipitate is allowed to stand for an hour before being slowly filtered off, and washed several times with ether. Finally the solid is dried *in vacuo*. A typical set of analytical results for such a product are as follows. Found 6.5%C, 0.9%H, 29.3% Cl, 35.4%K, 2.5%N, 18.0%Pt. Expected for $[Pt(CH_3CONH)(CH_3CONH_2)(OH)_2]Cl \cdot 8.9KCl \cdot C_2H_5OH$: 6.6%C, 1.4%H, 28.9%Cl, 35.4%K, 2.6%N, 17.9%Pt. Different batches of product show different ratios of KCl to Pt.

The complex *cis*-$[PtCl_2(NCCH_3)_2]$ was prepared by the literature method [22].

Physical data were obtained using a Pye Unicam SP1800 spectrophotometer, a Perkin Elmer 457 spectrometer, a Varian HA 100D spectrometer and an A.E.I. MS9 mass spectrometer. Elemental analyses were provided by Dr. F. B. Strauss of Oxford or Alfred Bernhardt of Engelskirchen, West Germany.

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