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The Nature of the Solvent Path in Substitution Reactions of Square Planar Complexes. The Non-Reactivity of Thiocyanate Ion with Trichloroaquoplatinum(II)

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The kinetics of reaction of the thiocyanate ion with equilibrium mixtures of $[PtCl_4]^{2-}$ *and* $[PtCl_3(H_2O)]^-$ *have been investigated. It is shown that the latter complex does not react with the thiocyanate ion; this is discussed in the light of currently held theories about the two-path mechanism of substitution reactions at square planar substrates.*

Introduction

Substitution reactions of square planar complexes are characterised by the well-established two-term rate law[1–3],

$$k_{obs} = k_1 + k_2\,[Y] \qquad (1)$$

in which the term independent of the incoming ligand concentration is attributed to rate-determining formation of a solvocomplex. This latter species is considered to be highly reactive and rapidly gives the product.

$$\begin{tikzcd} MA_3X + S \arrow[rr, shift left, "k_1"] \arrow[dr, "k_2(+Y{,}-X)"'] & & MA_3S + X \arrow[ll, shift left, "k_{-1}"] \arrow[dl, "k_3{,}\ \mathrm{fast}\ (+Y{,}-S)"] \\ & MA_3Y & \end{tikzcd} \qquad (2)$$

In the event that k_{-1} is insignificant and k_3 large, the rate law (1) follows directly from the suggested mechanism (2). In a number of instances, one or another of the terms of (1) is not observed. Thus, for example, the exchange reaction of $^*Cl^-$ with $[PtCl_4]^{2-}$ is accounted for entirely by the solvent path[4], whereas substitution reactions of thioethers with a variety of square planar substrates have been shown to proceed without apparent participation of solvocomplexes[5,6].

Louw and Robb[7] and Belluco *et al.,*[8] have applied the steady-state treatment to the solvospecies and derived a fuller equation that can be generalised[9] to:

$$k_{obs} = [k_2 + \frac{k_1k_3}{k_{-1}[X] + k_3[Y]}][Y] \qquad (3)$$

This expression reduces to (1) when $k_{-1}[X] \ll k_3[Y]$, *i.e.* at large excess of incoming ligand. Under the opposite limiting conditions, the solvent path is eliminated, and only the second term of (1) is obtained. The rate laws obtained for the reactions of polyamines with gold(III) and palladium(II) complexes[7,10] have been interpreted on this basis, and the solvopaths in these reactions well characterised.

However, little use has been made of equilibrated solutions of platinum complexes to study directly the reactions of solvospecies with other ligands. This paper reports a detailed study of the reaction of thiocyanate ion with tetrachloroplatinate(II). This reaction was chosen in the light of certain unusual kinetic features observed in this laboratory for the reactions of the platinum substrate with sulphur-containing ligands[11]. Furthermore, Cattalini *et al.,*[12] have reported the existence of a solvent path for this reaction.

Experimental

Solutions of K_2PtCl_4 containing the appropriate amounts of sodium chloride and buffer were made up to constant ionic strength ($\mu = 2.0$) with sodium perchlorate. Sodium thiocyanate solutions contained identical amounts of sodium chloride and buffer as the solutions with which they were reacted, and were adjusted to the same ionic strength with sodium perchlorate. The reaction was initiated by mixing appropriate volumes of complex and thiocyanate solutions in a stoppered cell. A Cary 17 spectrophotometer fitted with a thermostatted sample chamber was used to follow the reaction. Temperature control was ± 0.1 K. Measurements were made at 310 nm, where a reasonably large change in absorbance occurs without interference from other species present in solution.

The pH was controlled by sodium acetate–acetic acid or sodium dihydrogen phosphate–sodium hydroxide buffers, and was measured on a Beckman Zeromatic pH meter. Experiments in which the solutions contained different amounts of buffering material, but in the same ratios of the two components, revealed no change in the measured rates, thus eliminating possible active involvement of these species in the reaction kinetics. All reagents were analytical grade, and sodium perchlorate, thiocyanate and chloride were recrystallised from triply distilled water, which was used throughout. The complex, $K_2Pt(SCN)_4$ was prepared by the method of de Stefano and Burmeister[13]. Spectra obtained after completion of the kinetic runs were identical with spectra obtained from fresh solutions of $K_2[Pt(SCN)_4]$ of the same concentration.

Plots of $\log(D_\infty - D_t)$ against time were curved in the early stages, but gave straight lines at extended times. Rate constants for the two stages of the reaction were obtained by the same process used by Cattalini for this reaction[12]. For the faster reactions, $0.25 \leq [SCN^-] \leq 0.10$, values of the rate constant for the second reaction were obtained from the slope of the linear part of the curve. Extrapolation of the linear part of the curve to zero time gave a value, D_∞', of the optical density corresponding to completion of the first reaction. Values of the first rate constant were then obtained from the slopes of plots of $\log(D_\infty' - D)$ against time. For the slower reactions, $[SCN^-] < 0.04$, the second stage was too slow to follow accurately by the spectrophotometric technique, and was not measured. The rate of the first stage was measured as above, using the mean value of D_∞' obtained above, for the plot of $\log(D_\infty' - D_t)$. Plots of k_{obs} against $[SCN^-]$ were linear and passed through the origin for both reactions. Least squares analysis of the data revealed no intercept (see below). Values of k_{SCN^-} were calculated from the slopes of these lines and are also listed in Table I. Activation parameters (Table V) were determined from the best straight line plots of log k against 1/T.

TABLE I. Thiocyanate Dependence for the Reaction of $[PtCl_4]^{2-}$ with SCN^- : a = fast reaction, b = slow reaction.

$[Cl^-]/(M)$	$[SCN^-]/(M)$	$10^4\ k_{obs,a}/(sec)^{-1}$	$10^4\ k_{obs,b}/(sec)^{-1}$
0.8	0.40	58.2	4.95
0.8	0.30	40.3	3.76
0.8	0.25	35.2	3.35
0.8	0.20	30.2	2.58
0.8	0.10	13.2	1.28
0.8	0.04	6.25	–
0.8	0.012	1.80	–
0.8	0.008	1.10	–
0.8	0.004	0.60	–
0	0.04	6.45	–
0	0.012	1.80	–
0	0.008	1.23	–
0	0.004	0.56	–

$[PtCl_4^{2-}] = 2 \times 10^{-4} M$; pH = 4.62; T = 25° C.

In order to investigate the action of thiocyanate on $[PtCl_3(H_2O)]^-$ in the absence of $[PtCl_4]^{2-}$, the aquocomplex was prepared by adding an equimolar amount of $AgNO_3$ to a $2 \times 10^{-3} M$ solution of K_2PtCl_4. When the reaction was complete, the solution was filtered. These solutions were then mixed with sodium thiocyanate solutions, containing buffer and sodium perchlorate in such ratios that the same values of ionic strength and concentrations were obtained as for the other kinetic runs.

Results and Discussion

The reaction between $[PtCl_4]^{2-}$ and thiocyanate proceeds in two steps which are ascribed to the replacement of the first and third chlorides, respectively, with the substitution of the third chloride an order of magnitude slower than that of the first. Because of the high *trans* effect of thiocyanate, the substitution of the second and fourth chlorides is fast, and these steps are not observed. Cattalini *et al.*,[12] have previously reported data for the first observed substitution reactions of $[PtCl_4]^{2-}$ with thiocyanate. The factor of seven difference between their value and the result reported here for the ligand path of the first reaction must be ascribed to the different ionic media employed.

Cattalini *et al.*,[12] reported that this reaction obeyed the two-term rate law (1), but in the present study, no evidence could be found for an intercept in the k_{obs} *vs.* $[SCN^-]$ plot, for either of the two reactions, using fresh as well as equilibrated solutions of $[PtCl_4]^{2-}$. For the equilibrated solutions, the value of the (negative) least-squares intercept obtained over a concentration range of two orders of magnitude, was of the same order of magnitude as the 95% confidence limit for this value. However, if the results for fresh solutions of complex are considered (Table I), the least squares intercept obtained is $-0.002 \times 10^{-4}\ sec^{-1}$. Only a relatively limited ligand concentration range was employed here in order to check the question of the existence of the intercept, the lower limit being determined by the need to maintain pseudo-first order conditions without reducing the complex concentration below values that gave reasonably measurable rates. Nonetheless, the results clearly show that the intercept of the line does not give the rate constant for the hydrolysis of $[PtCl_4]^{2-}$, *viz.* $0.4 \times 10^{-4}\ sec^{-1}$. Catalini's claim[12] that the reaction obeys the two-term rate law must therefore be viewed with some caution. The non-existence of the intercept is consistent with other data discussed below.

If mechanism (2) operates, with k_3 larger than k_{-1}, not only would a solvent path be expected, but as the equilibrium concentration of the aquospecies is increased, the relative contribution of the solvent path to the overall rate would also be expected to increase. The equilibrium concentration of aquotrichloroplati-

TABLE II. Chloride Dependence for the Reaction of $[PtCl_4]^{2-}$ with SCN^-; a = fast reaction, b = slow reaction.

$[Cl^-]/(M)$	$10^3\ k_{obs,a}/(sec)^{-1}$	$10^4\ k_{obs,b}/(sec)^{-1}$	$100\,\frac{[PtCl_3H_2O^-]}{[PtCl_4^{2-}]}$
0.80	3.52	3.35	1.625
0.40	3.45	3.24	3.25
0.20	3.59	3.08	6.5
0.10	3.45	3.68	13.0
0.05	3.43	3.04	26.0
0.00^c	3.44	3.34	–
Mean	3.48	3.28	–

$[PtCl_4^{2-}] = 2 \times 10^{-4}M$; $[SCN^-] = 0.25M$; pH = 4.62; T = 25° C; c = freshly prepared solution without added chloride.

num(II) can easily be changed by varying the chloride ion concentration. However, as can be seen from Table II, this has no effect on the rate over a range of chloride concentrations such that up to 26% of the nominal complex concentration is the solvocomplex (higher concentrations of $[PtCl_3(H_2O)]^-$ could not be attained without introducing the complication of significant amounts of higher aquospecies). In fact, the rates of reaction of freshly prepared (non-equilibrated) solutions of complex without added chloride are indistinguishable from the rates in equilibrated chloride-containing media (Table I).

Moreover, when a freshly prepared solution of $[PtCl_3(H_2O)]^-$ was mixed with thiocyanate, no reaction was detected up to times greater than ten half-lives of the fast reaction for the same thiocyanate concentration with equilibrated complex mixtures containing $[PtCl_4]^{2-}$. This suggests that the only reactive platinum species present is the mother compound $[PtCl_4]^{2-}$, while the aquocomplex does not react with the ligand, and the behaviour of these solutions at longer times supports this proposal.

At longer times, a very slow reaction is observed in which $[Pt(SCN)_4]^{2-}$ is formed, but quantitative measurements of these kinetics cannot be made as the rate of change is too slow to follow accurately. The aquocomplex initially present in these solutions, $[PtCl_3(H_2O)]^-$, undergoes further hydrolysis to $[PtCl_2(H_2O)_2]$, and some of the chloride released during this step will anate the $[PtCl_3(H_2O)]^-$ to regenerate $[PtCl_4]^{2-}$ in significant concentration[14]. The tetrachloride thus produced will provide a reaction path to the tetrathiocyanate*: in view of the non-reactivity of $[PtCl_3(H_2O)]^-$ it is reasonable to assume that the diaquocomplex is similarly non-reactive and does not provide a route to the final product. In any event the appearance of $[Pt(SCN)_4]^{2-}$ is very much slower than the rate of the second anation measured by Elding[14].

Since in the kinetic runs between equilibrated complex solutions and thiocyanate, all the complex initially present is quantitatively converted to product, the aquocomplex must react via the anation step of the solvolysis equilibrium. This requires the product, $k_{-1}[Cl^-]$, to be greater than $k_2[SCN^-]$. The value of Elding *et al.*,[15] for k_{-1} of $(2.8 \pm 0.1) \times 10^{-3} M^{-1}\ sec^{-1}$ shows that this requirement is easily satisfied at the higher chloride concentrations. At the lowest chloride concentrations, $k_{-1}[Cl^-]$ is smaller than $k_2[SCN^-]$ by a factor of ~2. However, this can be accounted for by the fact that Elding's value refers to an ionic strength of 0.5. It is reasonable to suppose that k_{-1} would be greater by the required amount if measured at the present ionic strength.

Further indirect evidence for the non-participation of solvospecies in the thiocyanate substitution comes from the independence of the rate on hydrogen ion concentration. The aquocomplex $[PtCl_3(H_2O)]^-$ is a weak acid[16] with pK_a in the region of seven. A reasonable proportion of the complex should be present as the conjugate base at a pH of 6.80. However, once again, observed rates are indistinguishable from those at higher acidities. Because of the problems of solubility of the buffer at the ionic strength used here, measurements made at higher pH values are subject to error, and are not included in Table III. However, the observed rates at higher pH values show no marked or regular differences from the values listed.

Of interest is the fact that for the second reaction measured, *viz.*

$$[PtCl_2(SCN)_2]^{2-} + SCN^- \rightarrow [PtCl(SCN)_3]^{2-} + Cl^-$$

parallel behaviour is observed. No data are available on the aquation equilibria of the mixed complex $[PtCl_2(SCN)_2]^{2-}$, but this species, as generated in the overall reaction sequence, is not in hydrolysis equilibrium with $[PtCl(SCN)_2(H_2O)]^-$. Thus, the non-appearance of a solvent path for the slow second reaction is, in the light of the discussion below, less surprising than for the first reaction.

TABLE III. Hydrogen Ion Dependence for the Reaction of $[PtCl_4]^{2-}$ with SCN^- : a = fast reaction, b = slow reaction.

pH	$10^3\ k_{obs,a}/(sec)^{-1}$	$10^4\ k_{obs,b}/(sec)^{-1}$
3.67	3.57	3.21
4.62	3.45	3.24
5.69	3.94	3.16
6.00	3.41	3.12
6.80	3.70	3.00

$[PtCl_4^{2-}] = 2 \times 10^{-4}M$; $[SCN^-] = 0.25M$; $[Cl^-] = 0.40M$; T = 25° C.

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The non-involvement of solvospecies in the substitution reaction is very similar to the behaviour observed by Bekker[9,17] for the reaction of $[PdCl_4]^{2-}$ with thiourea. Bekker[17] notes that his kinetic observations are in accord with early work that showed that thiourea does not react with hydrolysed metal complexes. Although it is tempting to speculate that the factor responsible for this anomalous behaviour is the sulphur ligand itself, semiquantitative tests show that thiourea does anate $[PtCl_3(H_2O)]^-$ (see below). Furthermore, Teggins and Woods[19] have shown that $[PtBr_4]^{2-}$ reacts with dien independently of bromide ion concentration, under conditions where $[PtBr_3(H_2O)]^-$ would be expected to participate. Furthermore, Martin *et al.*[20] have shown that hydroxocomplexes of the type $[Pt(NH_3)_2Cl(OH)]^-$ are unreactive towards ammonia.

Gray and Olcott[21] measured the kinetics of anation, by a variety of ligands, Y, of $[Pt(dien)(H_2O)]^{2+}$ in order to establish that the reaction of this species with Y is faster than the substitution of X in [Pt(dien)X] by Y, as required by the overall mechanism. In these reactions, only one mechanistic route is to be expected, since the reactant is of the form of the intermediate of the solvent path. However, Gray and Olcott found that a rate equation of the form (1) was obeyed. The nature of Gray and Olcott's k_1 path is not clear and appears not to have been investigated further. The existence of two mechanistic paths for the substitution reactions of $[Pt(dien)(H_2O)]^{2+}$, together with the anomalous behaviour noted above, suggests that the generally accepted mechanism (2) is an oversimplification. The conditions that determine the non-reactivity of the solvospecies have yet to be determined, but it would appear that in these instances of "anomalous" behaviour, the intermediate is not adequately described as the solvospecies $[PtA_3(H_2O)]$. It is hoped that work currently in progress in this laboratory will shed some light on the problem.

Results of a limited number of experiments with $[PtCl_3(H_2O)]^-$ indicate that the aquocomplex is anated by chloride with a half-time in reasonable agreement with the value predicted by Elding's rate constant[15]. Thiosulphate, thiourea, iodide and bromide also anate the complex, the last at a rate that appears to be slower than expected on the basis of its n_{Pt}^0 value. Basic ligands and nitrite, because of its biphilicity in acid solutions, were not investigated.

The values of $\Delta S^{\ddagger}$ in Table V are noteworthy in that they are very large and negative. Activation entropies for substitution reactions of square-planar complexes are generally negative[1,2], and those measured here are among the highest negative values reported. Apart from[4] the exchange of labelled chloride with $[PtCl_4]^{2-}$, few activation parameters have been reported for reactions between square planar complexes with a double negative charge and an anion. The transition state will carry a triple negative charge and can be expected to be significantly more solvated than the ground state. This probably accounts in large measure for the observed values. The reason for the large difference between the values observed here and the unexpectedly small value of -34 J $mol^{-1}K^{-1}$ for the exchange reaction is not clear. It has been pointed out[22] that stringent steric requirements in the transition state are often accompanied by highly negative $\Delta S^{\ddagger}$ values, and this has been discussed in the case of thiocyanate[23] as the entering group. It would be of interest to compare activation parameters for chemically similar systems that do not show anomalous behaviour.

TABLE IV. Temperature Dependence for the Reaction of $[PtCl_4]^{2-}$ with SCN^- : a = fast reaction, b = slow reaction.

T/(C)	$10^3\ k_{obs,a}/(sec)^{-1}$	$10^4\ k_{obs,b}/(sec)^{-1}$
25.0	3.48	3.28
29.9	5.13	4.02
36.7	7.40	6.18

$[PtCl_4^{2-}] = 2 \times 10^{-4}M$; $[SCN^-] = 0.25M$; pH = 4.62; Values quoted are means of runs at various chloride concentrations.

TABLE V. Activation Parameters for the Reaction of $[PtCl_4]^{2-}$ with SCN^-.

	$\Delta H^{\ddagger}/(kJ\ mol^{-1})$	$\Delta S^{\ddagger}/$ $(J\ K^{-1}\ mol^{-1})$
Fast reaction	48.7 ± 5	−128 ± 8
Slow reaction	40.0 ± 4	−177 ± 8

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