# *The Stability Constants of Some Platinous Halide Complexes.**

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The equilibria $C_2H_4PtCl_3^- + L \rightleftharpoons$ *trans*-$C_2H_4,LPtCl_2 + Cl^-$ ($L = H_2O$, $Br^-$, $I^-$, and $NH_3$) are established within 2 min. in aqueous 0·2N-perchloric acid at 25°. Concentration equilibrium constants, $K$, were determined (see Table 1), and the affinities of the halides and thiocyanate ion for platinum shown to lie in the order $F \ll Cl < Br < I < SCN$. For most metals the order of halide stability is $F \gg Cl > Br > I$ and the possible significance of the reversal of order in the case of platinum(II) is discussed. Ammonia relative to water has a very high affinity for platinum(II).

IT has been known since 1936 that ethylene in its platinous complexes labilises the group in the *trans*-position to itself (Chernyaev and Hel'man, *Compt. rend. Acad. Sci., U.R.S.S.*, 1936, **4**, 181). Thus on the careful addition of ammonia to a solution of potassium ethylenetrichloroplatinite (Zeise's salt) there is immediate precipitation of *trans*-$C_2H_4,NH_3PtCl_2$, and on subsequent addition of dilute hydrochloric acid the precipitate immediately redissolves in the form of $NH_4^+ \; C_2H_4PtCl_3^-$. These substitution reactions are so rapid that they give every appearance of being ionic in type, in marked contrast to most substitution reactions in the platinous series of complexes.

It was of interest therefore to determine whether the ethylenetrichloroplatinite ion undergoes appreciable ionic dissociation in aqueous solution, and how rapidly equilibrium is established. By using silver–silver chloride electrodes to determine the chloride-ion concentration we find that in aqueous 0·2N-perchloric acid the equilibrium

$$C_2H_4PtCl_3^- + H_2O \rightleftharpoons \textit{trans-}C_2H_4,H_2OPtCl_2 + Cl^-$$

is established in the 2 minutes necessary to prepare the solution. Dissociation of the one chloride ion is practically complete in a $10^{-3}$M-solution of $C_2H_4PtCl_3^-$. Thus $C_2H_4PtCl_3^-$ behaves as a labile complex so far as one chlorine atom, presumably that in the *trans*-position to the ethylene molecule, is concerned. This lability has enabled us to determine the relative tendency of the halide and thiocyanate ions to complex formation with platinum(II), by using silver–silver halide or silver–silver thiocyanate electrodes. The use of a compound such as $K^+ \; C_2H_4PtCl_3^-$, which has essentially the same structure as other

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* Throughout this paper square brackets normally used to enclose Werner complexes have been omitted to avoid confusion with square brackets used as a symbol for concentration.

platinous complexes (Chatt and Duncanson, *J.*, 1953, 2939) yet contains a labile chlorine atom, allows the measurement of stability constants to be extended to metals in that region of the Periodic Table where co-ordination compounds are characteristically inert. This is important because the quantitative information on complex stability which is now available relates only to metals whose characteristic complexes are labile.

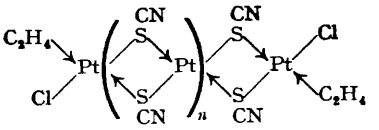
Potassium ethylenetrichloroplatinite undergoes auto-reduction to the metal in neutral or alkaline aqueous solutions but is stable indefinitely in dilute hydrochloric acid solution. These facts, and the knowledge that the *trans*-chlorine atom is labile, indicate that the unstable species in the aqueous solution is probably *trans*-$C_2H_4PtCl_2,OH^-$ formed by the acid dissociation of *trans*-$C_2H_4,H_2OPtCl_2$.

From the acidity of an aqueous solution of $K^+ \; C_2H_4PtCl_3^-$ we estimated the acid dissociation constant of the aqua-complex to be of the order $10^{-5}$. Since we could not make our equilibrium measurements in presence of a large excess of chloride ion we used 0·2N-perchloric acid to stabilise the ethylene complex and maintain the ionic strength of the reaction medium at about 0·2. In this medium the concentration of hydroxy-complex would be about 0·005% of that of the aqua-complex, and no detectable decomposition of the ethylene complex occurs within a week of preparing the solutions.

The equilibria examined in the perchloric acid solutions were all of the type :

$$C_2H_4PtCl_3^- + L \rightleftharpoons \textit{trans}\text{-}C_2H_4,LPtCl_2 + Cl^- \quad . \; . \; . \; . \quad (1)$$

The equilibrium constants, concentration constants valid at ionic strength 0·2 ($HClO_4$) and 25°, were obtained by determining the concentrations of free L or $Cl^-$ electrometrically. The accuracy of the determinations is limited by slight interference of the platinum salt with the functioning of the electrodes and also, when L is $Br^-$ and $I^-$, by the occurrence of comparatively slow reactions following the instantaneously established equilibria. These side reactions are probably the replacement of the remaining chlorine atoms or of the ethylene by L. When $L = Br^-$ the interfering reactions are very slow; when $L = I^-$ they are faster but a reasonable constant could still be obtained. When $L = SCN^-$ no constant could be obtained, but only the information that the thiocyanate is taken from the solution into the complex much more avidly than either $Br^-$ or $I^-$. The side reactions led to the ultimate separation of indefinite decomposition products in the equilibria with bromide and iodide ions, but the thiocyanate ion caused the slow separation of a yellow precipitate of composition close to $(C_2H_4)_2Cl_2(SCN)_{10}Pt_6$. This could have the structure



(I)

(I) ($n = 4$) but is more probably a mixture of substances of that general type or else a mixture of the simplest member ($n = 0$) with $Pt(SCN)_2$. The constants, $K$, which were determined are :

$$K_{aq.} = [\textit{trans}\text{-}C_2H_4,H_2OPtCl_2][Cl^-][C_2H_4PtCl_3^-]^{-1}$$
$$K_{Br} = [\textit{trans}\text{-}C_2H_4PtBr,Cl_2^-][Cl^-][Br^-]^{-1}[C_2H_4PtCl_3^-]^{-1}$$

and similarly $K_I$, $K_{NH_3}$, and $K_F$.

These are listed in Table 1, together with the equilibrium constants, $K_s$, referring to the following reaction of formation of the complexes from the aqua-ion in aqueous 0·2N-perchloric acid solution at 25° :

$$\textit{trans}\text{-}C_2H_4,H_2OPtCl_2 + L \rightleftharpoons \textit{trans}\text{-}C_2H_4,LPtCl_2 + aq. \quad . \; . \; . \quad (2)$$

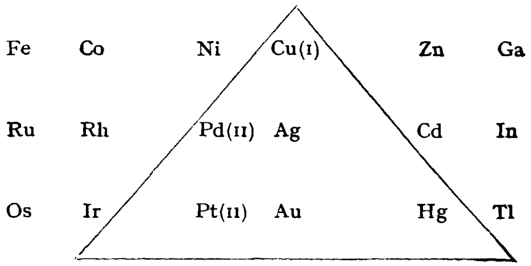
The latter are the fourth formation or stability constants which would be obtained if *trans*-$C_2H_4,LPtCl_2$ could be formed stepwise from the aquated $Pt^{++}$ ion, and the ligand L were the last to enter the complex. They are listed together with log $K_s$ for comparison with stability-constant data which are already available in the chemical literature for other metals (*e.g.*, J. Bjerrum, *Chem. Rev.*, 1950, **46**, 381).

TABLE 1. *Constants $K$ and $K_s$ referring to equilibria* (1) *and* (2) *respectively in aqueous* 0·2N-HClO$_4$ *at* 25°.

| L | $K$ | $K_s$ | log $K_s$ | L | $K$ | $K_s$ | log $K$ |
|---|---|---|---|---|---|---|---|
| $H_2O$ …… | $(3·0 \pm 0·5) \times 10^{-3}$ | (1) | 0 | $I^-$ …………… | $120 \pm 20$ | $4·0 \times 10^4$ | 4·60 |
| $F^-$ …… | $<0·03$ | $<10$ | $<1$ | $NH_3$ ………… | $\sim 10^5$ | $-3 \times 10^7$ | $\sim 7·5$ |
| $Cl^-$ …… | (1) | $3·3 \times 10^2$ | 2·52 | $SCN^-$ ……… | $>120$ | $>4 \times 10^4$ | $>4·6$ |
| $Br^-$ …… | $3·4 \pm 0·3$ | $1·1 \times 10^3$ | 3·04 | | | | |

On making this comparison, it will be noted that as fourth stability constants they are exceptionally high. However, in comparison with average stability constants, they are high but not exceptional; those of Hg(II) ($N = 2$) are all greater. (The average stability constant is the $N$th root of the product of the consecutive stability constants up to the last strongly bound ligand, which is the $N$th ligand attached to the metal.)

As a rule, the order of thermodynamic stability of the halide complexes of metals which form labile complexes is F $\gg$ Cl $>$ Br $>$ I in aqueous solution, but it has been noted by a number of workers (Carleson and Irving, *J.*, 1954, 4390; Leden, Diss., Lund, 1943, p. 27; J. Bjerrum, *loc. cit.*; Ahrland and Larsson, *Acta Chem. Scand.*, 1954, **8**, 354) that a very small group of elements, copper(I), silver(I), cadmium(II), and mercury(II) have the opposite sequence of stabilities, *viz.*, F $\ll$ Cl $<$ Br $<$ I. It is obvious that platinum(II) belongs to this latter group. In this group of metals the great stability of the chloro-complexes relative to the fluoro-complexes has its analogy in the qualitatively observed much greater stability of thio-ether complexes relative to ether complexes, and trialkylphosphine complexes relative to trialkylamine complexes. It is to be noted that all the metals of this group have low valencies yet tend to form strongly covalent complexes with donor atoms of low electronegativity. The increase in stability of the halides as the difference in electronegativity between the metal and halogen falls is evidence of the essentially covalent character of the metal-to-halogen bond. The metals in this group also have filled $d$-orbitals immediately under their valency shells. Chlorine, bromine, and iodine but not fluorine have vacant $d$-orbitals in their valency shells and so dative $\pi$-bonding might occur with all except fluorine. These facts may account for the abnormal sequence of stabilities of the halide complexes of the above metals in a way similar to that suggested to explain the greater stability of the phosphine relative to the amine complexes of platinum(II) (Chatt and Wilkins, *J.*, 1952, 4300). If that explanation be true, then the reversal in the normal sequence of thermodynamic stabilities of the common halide complexes in water should be most marked in the triangle of elements (II) in the Periodic Table which form olefin complexes in their usual valency states, and change over to the normal sequence in the elements bordering on this triangle. This is certainly true of the series of ions Ag$^+$, Cd$^{++}$, and In$^{+++}$ (see Carleson and Irving, *loc. cit.*).



(II)

It is interesting to speculate on what would be the effect on the platinous halide equilibria of replacing the olefin in the complex ion by ammonia. It is known that the chlorine atom in the *trans*-position to ammonia is not labile, but work at present in progress indicates indirectly that the effect on the position of equilibrium, if equilibrium could be established, should be slight. The replacement of ethylene by ammonia will not alter the sequence of halide stabilities; rather, we expect that the " abnormal " order may be slightly more pronounced.

## EXPERIMENTAL

Microanalyses are by Messrs. W. Brown and A. G. Olney of these laboratories.

*Materials.*—The acids ($HClO_4$, HCl, HBr, and HI) were of " AnalaR " grade diluted to provide 0·2N-stock solutions, and standardised against 0·1N-potassium hydroxide. Zeise's salt, $K^+C_2H_4PtCl_3^-,H_2O$ was prepared according to Chatt and Duncanson (*J.*, 1953, 2939), and recrystallised from 0·2N-hydrochloric acid to remove potassium chloride and then from ethanol. The crystals were finally dried *in vacuo* over concentrated sulphuric acid and potassium hydroxide pellets. The infrared spectrum of the solid showed that the material was not anhydrous, but the remaining crystal water was negligible (Found : C, 6·5; H, 1·3; Cl, 28·6; Pt, 52·2. Calc. for $C_2H_4Cl_3KPt$ : C, 6·5; H, 1·1; Cl, 28·8; Pt, 52·9%). The quinhydrone (QH) was of " AnalaR " grade. Ammonium perchlorate was dried at 120° and made up to a 0·2M-solution which had pH 4·96. Sodium thiocyanate dihydrate was also used in 0·2M-solution whose concentration was determined by silver nitrate titration with fluorescein indicator.

*Symbols.*—The following symbols are used in the Tables and mathematical equations :

$Z = C_2H_4PtCl_3^-$

$Z_{Br} =$ *trans*-$C_2H_4PtBr,Cl_2^-$

$Z_{aq.} =$ *trans*-$C_2H_4,H_2OPtCl_2$

$Z_I$, $Z_F$, $Z_{SCN}$, and $Z_{NH_3}$ similarly

$C_Z$, $C_{HCl}$, etc. = initial molar concentration of ethylene complex, hydrochloric acid, etc.

$e$ = the e.m.f. of an electrolytic cell (in mv)

$E$ = the change in the e.m.f. of a cell (in mv) on addition of $C_2H_4PtCl_3^-$.

All concentrations are in molarities (M) or normalities (N) at 25°.

*Aquation of* $C_2H_4PtCl_3^-$ : $C_2H_4PtCl_3^- + H_2O \rightleftharpoons$ *trans*-$C_2H_4H_2OPtCl_2 + Cl^-$.—The equilibrium constant ($K_{aq.}$) for this reaction was determined by measuring the e.m.f of the following cell at 25° :

| | | | |
|---|---|---|---|
| + Au,QH | 0·2N-$HClO_4$ | $K^+$ $C_2H_4PtCl_3^-$ ($C_Z$)<br>HCl ($C_{HCl}$)<br>$HClO_4$ (0·2 − $C_{HCl}$) | Ag,AgCl − |

*Silver–silver chloride electrodes.* These (2·5 cm. long) were prepared as recommended by Brown (*J. Amer. Chem. Soc.*, 1934, **56**, 646) on 1·4-mm. diameter platinum wire. The cell was checked without any Zeise's salt but with various amounts of hydrochloric acid to show that the e.m.f. obeyed Nernst's law at 25°, $e = e_0 + 59{\cdot}16 \log [Cl^-]$. The constant $e_0$ was determined (421·5), and the stock perchloric acid shown to be 3 × $10^{-5}$M in hydrochloric acid, which was allowed for in the experiments. When the cell contained Zeise's salt its potential was not constant, but drifted slowly (usually less than 1 mv per min.). This was probably due to the reduction of the platinous salt by the silver of the electrode. The drift was minimised by using rather large, well-coated electrodes. In the absence of platinous salts the electrodes reached equilibrium, to within 1 mv, with the solutions within 30 sec., usually within 15 sec. The e.m.f. of the cell was therefore measured every minute, for 5 min. from the immersion of the electrode, and extrapolated to zero time. Typical examples are (time in min.; e.m.f. in mv) : (*a*) (1; 256·7) (2; 256·5) (3; 256·2) (4; 256·0) (5; 255·8) extrapolated to $e$ = 257; (*b*) (1; 280·5) (2; 279·9) (3; 279·1) (4; 278·3) (5; 277·7) extrapolated to $e$ = 281. The most rapid shift in all the experiments recorded in this paper was (1; 300·7) (2; 297·5) (3; 294·5) (4; 292·3) extrapolated to $e$ = 304. The drift in the e.m.f. of the cell was not very reproducible with different electrodes, but in general it was greater the higher the concentration of Zeise's salt. After the 5-min. period of immersion in presence of platinous salt, the silver–silver chloride electrode was noticeably more sluggish in response to a change in chloride-ion concentration, even in a fresh solution containing no platinum, and so a new electrode was used for every determination. This procedure was checked by confirming that the electrode potential in a solution containing $C_2H_4PtCl_3^-$, and sufficient hydrochloric acid to suppress its dissociation entirely, obeyed Nernst's law on dilution with 0·2N-perchloric acid. We consider that the extrapolation procedure gave us the true " chloride " potential of the cell to within ±2 mv.

*Stability of Zeise's Salt in* 0·2N-*Perchloric Acid.*—Although the e.m.f. of the cell was normally measured as soon as the Zeise's salt solutions had been prepared, some solutions were examined at intervals and the e.m.f. was found to be constant, to within experimental error, over a period of two days. As a typical example we kept a solution of $10^{-2}$M-K+ $C_2H_4PtCl_3^-$ in 0·2N-perchloric acid at 25° for 8 days, then measured the e.m.f. of the cell containing it. The e.m.f. was 283 mv, as compared with 281 and 279 mv for two freshly prepared, but otherwise identical, solutions. Most of the solutions were kept, and after 14 days traces of platinum or other decomposition products were obvious. After 6 weeks some of the solutions had decomposed completely and all showed signs of considerable decomposition.

*Determination of the Equilibrium Constant,* $K_{aq.}$.—The solutions were prepared by adding known (pipetted) volumes of the acids to a weighed amount of $K^+ C_2H_4PtCl_3^-$ at 25° in the appropriate cell compartment. When dissolution and mixing were complete (2 min.) the electrodes were introduced and the potential of the cell determined as described above. The most dilute solutions were obtained by diluting the more concentrated ones with 0·2N-perchloric acid. The results are given in Table 2: $K_{aq.} = ([Cl^-] - C_{HCl})[Cl^-](C_Z + C_{HCl} - [Cl^-])^{-1}$. Obviously a maximum of one chlorine atom of Zeise's salt dissociates reversibly from the complex ion in solution.

*Approximate Determination of the Acid Strength of* trans-$C_2H_4,H_2OPtCl_2$.—A solution of Zeise's salt in water is slightly acid and a 0·04M-solution has a pH of about 3·5 (universal indicator paper). Since about 25% of the salt would be in the form of the aqua-complex it follows that the latter has an acid dissociation constant of about $10^{-5}$.

*Equilibrium between* $C_2H_4PtCl_3^-$ *and Bromide Ions.*—When $K^+ C_2H_4PtCl_3^-$ is added to a solution containing bromide ions, the bromide-ion concentration is immediately reduced owing to the formation of *trans*-$C_2H_4PtBr,Cl_2^-$. The equilibrium:

$$C_2H_4PtCl_3^- + Br^- \rightleftharpoons trans\text{-}C_2H_4PtBr,Cl_2^- + Cl^- \quad . \quad . \quad . \quad . \quad (3)$$

was therefore examined at 25°, by using the cell:

$$+\ \mathrm{Au,QH}\ \left|\ 0{\cdot}2\text{N-}HClO_4\ \right|\ \begin{matrix} K^+\ C_2H_4PtCl_3^-\ (C_Z) \\ HCl\ (C_{HCl}) \\ HBr\ (C_{HBr}) \\ HClO_4\ (0{\cdot}2 - C_{HCl} - C_{HBr}) \end{matrix}\ \left|\ \mathrm{Ag,AgBr}\ -\right.$$

The silver–silver bromide electrodes were prepared in the same way as the silver–silver chloride electrodes. They also underwent slow poisoning by the platinous salt, and the extrapolation procedure was used, as previously.

The potential of the cell at 25° was first determined without Zeise's salt. A known quantity of the bromide solution (usually 2 c.c.) was then pipetted into a small tube containing a weighed quantity of Zeise's salt. When dissolution and mixing were complete (2 min.) the electrode and bridge from the quinhydrone half-cell were quickly transferred from the first cell into the small tube, and the potential noted. The difference ($E$) between the two potentials gives the bromide concentration directly: $E = 59{\cdot}16\ (\log C_{HBr} - \log\ [Br^-])$. This technique has the advantage that the effect of any interference of chloride ion with the silver–silver bromide electrode is minimised. It is necessary to measure the potential as soon as possible after the addition of Zeise's salt because, in addition to the immediate decrease in bromide-ion concentration on adding Zeise's salt to the solution, there is a further slow removal of bromide ion

TABLE 2. *Equilibrium constant* ($K_{aq.}$) *for the aquation of* $C_2H_4PtCl_3^-$ *at* 25° *and ionic strength* 0·2.

| $10^3C_Z$ | $10^3C_{HCl}$ | $e$ | $10^3[Cl^-]$ | $10^3K_{aq.}$ | $10^3C_Z$ | $10^3C_{HCl}$ | $e$ | $10^3[Cl^-]$ | $10^3K_{aq.}$ |
|---|---|---|---|---|---|---|---|---|---|
| 10 | 10 | 310 | 13·1 | (6) | 2 | 0·03 | 251 | 1·3 | 2·4 |
| 40 | 0·03 | 304 | 10·4 | 3·6 | 2 | 0·03 | 253 | 1·4 | 3·3 |
| 20 | 0·03 | 292 | 6·5 | 3·1 | 1 | 1·03 | 257 | $1{\cdot}6_7$ | 3·0 |
| 10 | 0·03 | 279 | 3·9 | 2·5 | 1 | 0·03 | 240 | $0{\cdot}8_6$ | (4) |
| 10 | 0·03 | 281 | 4·2 | 3·0 | 0·5 | 0·03 | 227 | $0{\cdot}5_1$ | — |
| 5 | 0·03 | 270 | 2·7 | 3·2 | 0·1 | 0·13 | 206 | $0{\cdot}2_3$ | — |

TABLE 3. *The constant,* $K_{Br}$, *for equilibrium* (3) *at* 25° *and ionic strength* 0·2.

| Solution | $10^3C_Z$ | $10^3C_{HCl}$ | $10^3C_{HBr}$ | $E$ | $10^3[Br^-]$ | $10^3[Z_{Br}]$ | $10^3[Cl^-]$ | $10^3[Z]$ | $K_{Br}$ |
|---|---|---|---|---|---|---|---|---|---|
| B1 | 20 | 0 | 10 | 36·7 | 2·4 | 7·6 | 10·4 | 9·6 | 3·4 |
| B2 | 20 | 0 | 1 | 58 | 0·11 | 0·89 | 6·8 | 13·2 | 4·1 |
| B3 | 20 | 0 | 40 | 12·5 | 24 | 16 | 16·6 | 3·4 | 3·2 |
| B4 | 10 | 10 | 5 | 22·4 | 2·1 | 2·9 | 14 | 6 | 3·2 |
| B5 | 5 | 10 | 5 | 12·5 | 3·1 | 1·9 | 12·5 | 2·5 | 3·1 |

from the solution. If we assume that the immediate removal of bromide ion is caused by the establishment of the above equilibrium, then $K_{\mathrm{Br}} = [\mathrm{Z_{Br}}][\mathrm{Cl^-}][\mathrm{Z}]^{-1}[\mathrm{Br^-}]^{-1}$ should be constant when the concentrations refer to the metastable equilibrium obtained immediately after mixing. If $K_{\mathrm{aq.}}$ is known, the quantities in the above equation can be determined from the equations :

$$[\mathrm{Z_{aq.}}] = K_{\mathrm{aq.}}[\mathrm{Z}][\mathrm{Cl^-}]^{-1} \qquad C_{\mathrm{HCl}} = [\mathrm{Z}] + [\mathrm{Cl^-}] - C_{\mathrm{Z}}$$
$$C_{\mathrm{Z}} = [\mathrm{Z}] + [\mathrm{Z_{Br}}] + [\mathrm{Z_{aq.}}] \qquad C_{\mathrm{HBr}} = [\mathrm{Z_{Br}}] + [\mathrm{Br^-}]$$

$C_{\mathrm{Z}}$, $C_{\mathrm{HCl}}$, and $C_{\mathrm{HBr}}$ are all known from the composition of the solution and $[\mathrm{Br^-}]$ from the values of $E$. Solving these equations for $[\mathrm{Cl^-}]$ we find

$$2[\mathrm{Cl^-}] = C_{\mathrm{HCl}} + C_{\mathrm{HBr}} - [\mathrm{Br^-}] - K_{\mathrm{aq.}} + \{(C_{\mathrm{HCl}} + C_{\mathrm{HBr}} - [\mathrm{Br^-}] - K_{\mathrm{aq.}})^2 + 4K_{\mathrm{aq.}}(C_{\mathrm{HCl}} + C_{\mathrm{Z}})\}^{\frac{1}{2}}$$

and hence $K_{\mathrm{Br}}$. The values of $K_{\mathrm{Br}}$ are listed in Table 3. Although $[\mathrm{Br^-}]$ and $[\mathrm{Z_{Br}}]$ vary widely, $K_{\mathrm{Br}}$ is constant to within experimental error, confirming that the instantaneous removal of bromide ion from solution is due to reversible exchange of a chlorine atom in the complex ion for a bromide ion in the solution. The further slow removal of bromide ion from solution is probably due to slow replacement of the ethylene or a *cis*-chlorine atom by bromine. This reaction was followed for a period of up to 27 hr. in the above solutions, as recorded in Table 4; but it is accompanied by decomposition and was not further investigated.

*Equilibrium between* $C_2H_4PtCl_3^-$ *and Iodide Ions.*—This equilibrium was studied with silver-silver iodide electrodes in analogous manner to the corresponding bromide equilibrium. The solutions were kept in a nitrogen atmosphere to prevent oxidation with liberation of iodine. The first instantaneous reaction was followed by a more rapid slow reaction than in the case of the bromide solutions, leading to a fairly rapid decomposition of the complex. Table 5 lists the results.

Decomposition of the solutions I1 to I5 was as follows : (I1) obvious decomposition after 5 min. (I2) no visible decomposition after 20 min.; colloidal suspension after 1 hr.; $E = 76$ mv after 77 min.; a precipitate collected at the bottom of the container after 3 hr. (I3) completely decomposed in 16 hr. (I4) $E = 26$ mv after 88 min.; 31 mv after 169 min.; no Tyndall effect in 2 hr.; completely decomposed in 20 hr. (I5) decomposed after 2 hr.

TABLE 4. *The change, with time, of the e.m.f.'s of cells containing bromide ion and Zeise's salt at* 25°.

| B1 | | B2 | | B3 | | B4 | | B5 | |
|---|---|---|---|---|---|---|---|---|---|
| Time | $E$ | Time | $E$ | Time | $E$ | Time | $E$ | Time | $E$ |
| 2 min. | 36·4 | 3 min. | 58 | 5 min. | 12·5 | 6 min. | 22·4 | 5 min. | 12·5 |
| 7·0 hr. | 73 | 27·3 hr. | 77 | 1·0 hr. | 14 | 51 min. | 22·7 | 1·8 hr. | 14 |
| 27·0 hr.* | 76 | | | 19·7 hr. | 35 | 7·0 hr. | 39 | 3·8 hr. | 15 |
| | | | | 27·5 hr. | 36 † | 16·8 hr. | 47 | 22·0 hr. | 30 |
| | | | | | | 23·7 hr. | 50 | | |

* Decomposition had started.

† This solution had initially a high concentration of bromide ion and on an average the complex ion had absorbed 1·5 bromide ions after 27·5 hr.

TABLE 5. *The constant,* $K_{\mathrm{I}}$, *at* 25° *and ionic strength* 0·2 *for the equilibrium,*
$C_2H_4PtCl_3^- + I^- \rightleftharpoons$ *trans*-$C_2H_4PtCl_2,I^- + Cl^-$.

| Solution | $10^3C_{\mathrm{Z}}$ | $10^3C_{\mathrm{HCl}}$ | $10^3C_{\mathrm{HI}}$ | $E$ | $10^3[\mathrm{I^-}]$ | $10^3[\mathrm{Z_I}]$ | $10^3[\mathrm{Cl^-}]$ | $10^3[\mathrm{Z}]$ | $K_{\mathrm{I}}$ |
|---|---|---|---|---|---|---|---|---|---|
| I1 | 20 | 0 | 10 | 133 | 0·056 | 10 | 12 | 8 | (270) |
| I2 | 10 | 100 | 5 | 48·5 | 0·75 | 4·25 | 104 | 5·5 | 110 |
| I3 | 6 | 180 | 4 | 30 | 1·2 | 2·8 | 183 | 3·2 | 130 |
| I4 | 2 | 184 | 3·2 | 12 | 2·0 | 1·2 | 185 | 0·8 | 140 |
| I5 | 7·5 | 195 | 1 | 40 | 0·21 | 0·79 | 196 | 6·6 | 110 |
| I6 | 2 | 40 | 1·6 | 28 | 0·54 | 1·06 | 41 | 0·84 | 100 |

TABLE 6. *Reaction of* $C_2H_4PtCl_3^-$ *with thiocyanate ion at* 25° *and ionic strength* 0·2.

| Solution | $10^3C_{\mathrm{Z}}$ | $10^3C_{\mathrm{SCN^-}}$ | $10^3C_{\mathrm{HCl}}$ | $E$ | $10^3[\mathrm{SCN^-}]$ | Solution | $10^3C_{\mathrm{Z}}$ | $10^3C_{\mathrm{SCN^-}}$ | $10^3C_{\mathrm{HCl}}$ | $E$ | $10^3[\mathrm{SCN^-}]$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| T1 | 20 | 20 | 9 | 100 | 0·41 | T3 | 6 | 4 | 196 | 49 | 0·6 |
| T2 | 10 | 5 | 152 | 61 | 0·46 | T4 | 3 | 4 | 196 | 30 | 1·2 |

*Equilibrium between* $C_2H_4PtCl_3^-$ *and Fluoride Ions.*—This equilibrium was examined by using the same electrolytic cell as was used in the aquation experiments, but the reaction vessel was made of Polythene, and glass tubes supporting the electrodes were covered with paraffin wax. The e.m.f. of the cell containing $C_Z = 0{\cdot}4$, $C_{HCl} = 0$, and $C_{HClO_4} = 0{\cdot}2$M was determined (303 mv) and then 40% hydrofluoric acid was added to make the solution about 2N in this acid. The potential of the cell (with a fresh silver chloride electrode) was now 304 mv, which is unchanged to within experimental error. If the reaction :

$$\mathrm{C_2H_4PtCl_3^- + F^- \longrightarrow C_2H_4PtCl_2,F^- + Cl^-}$$

occurs it must change the chloride-ion concentration by less than 10% which would correspond to 2·5 mv change in e.m.f. and be outside experimental error. Since the dissociation constant of hydrofluoric acid is about $10^{-3}$, the above solution must be about 0·01M in fluoride ion. Hence it follows that the equilibrium constant, $K_F = [Z_F][\mathrm{Cl^-}][Z]^{-1}[\mathrm{F^-}]^{-1}$, must be less than 0·03.

*Reaction between Zeise's Salt and Sodium Thiocyanate.*—Attempts to investigate an equilibrium corresponding to those with halide ions by using the silver–silver thiocyanate electrodes were not successful. The thiocyanate ion was avidly taken up by the platinum complex; hence measurements were attempted in presence of relatively large quantities of chloride ion with the results listed in Table 6. Calculation of $K_{SCN} = [Z_{SCN}][\mathrm{Cl^-}][Z]^{-1}[\mathrm{SCN^-}]^{-1}$ gave values ranging from 300 to 4000. The behaviour of solution T4 in which the thiocyanate ions were in greater molar concentration than $\mathrm{C_2H_4PtCl_3^-}$ seems to indicate that only one thiocyanate ion immediately enters the complex ion. It is also evident that the platinum has a much greater affinity for thiocyanate than for iodide ions. Lack of success in obtaining a constant may have been caused by all or any one of the following : (*a*) the slower response of the silver–silver thiocyanate electrode than of the silver–silver halide electrodes (on the other hand the drift in presence of platinous salt was less than with the halide electrodes) ; (*b*) interference with the electrode by the comparatively high chloride-ion as compared with the thiocyanate-ion concentrations in the solution; (*c*) more rapid subsequent reactions than in the halide system. In solution T1 a Tyndall effect developed within 5 min. and from all solutions a yellow precipitate had formed after 24 hr. This precipitate was stable in contact with the 0·2N-perchloric acid solution for several weeks, and estimation of the halide (Mohr's titration) in the supernatant solution indicated that the thiocyanate had been replaced by about twice its equivalent of halide ion.

The nature of the precipitate was examined by adding 2·20 mmoles of sodium thiocyanate (0·2M) to 2·00 mmoles of $\mathrm{K^+\,C_2H_4PtCl_3^-}$ in 0·2N-perchloric acid (100 c.c.). The yellow precipitate formed during two days was filtered off, washed with 0·2N-perchloric acid, and then with a little water, and dried; weight 0·403 g. (Found : C, 9·0; H, 0·7; N, 7·7; S, 16·8%). It dissolved in aqueous potassium cyanide with effervescence, indicating the probable presence of ethylene. The filtrate from the yellow precipitate contained no thiocyanate, 0·69 mmole of platinum, and 5·5 mmole of chlorine, indicating an approximate analysis of Pt, 63·5; Cl, 4·(4)%, and ratio SCN : Pt = 1·68 for the precipitate. The analysis is in very close agreement with structure (I) ($n = 4$), *i.e.*, $\mathrm{C_{14}H_8N_{10}Cl_2S_{10}Pt_6}$ which requires Cl, 3·8; S, 17·1; Pt, 62·3%; SCN : Pt = 1·67.

*Equilibrium between* $\mathrm{C_2H_4PtCl_3^-}$ *and Ammonia.*—When Zeise's salt is added to a solution of ammonium perchlorate or chloride, the solution becomes strongly acid :

$$\mathrm{NH_4^+ + C_2H_4PtCl_3^- \rightleftharpoons} \textit{trans}\text{-}\mathrm{C_2H_4,NH_3PtCl_2 + Cl^- + H^+} \quad . \quad . \quad . \quad (4)$$

By using indicator paper to determine pH, an approximate value of the equilibrium constant, $K_{NH_4}$, of reaction (4) was obtained (Table 7A). That chloride ion is also liberated on adding Zeise's salt to ammonium perchlorate was demonstrated by measuring the e.m.f. of the following cell :

| | | | |
|---|---|---|---|
| − Ag,AgCl | HCl (0·01N)<br>$\mathrm{NH_4ClO_4}$ (0·19M) | $\mathrm{K^+\,C_2H_4PtCl_3^-}$ ($C_Z$)<br>$\mathrm{NH_4ClO_4}$ (0·2M) | Ag,AgCl + |

From the chloride-ion concentration $K_{NH_4}$ was also calculated (Table 7B).

TABLE 7. *The constant,* $K_{NH_4}$, *for equilibrium* (4) *at* 25° *and ionic strength* 0·2.

| A | | | | B | | |
|---|---|---|---|---|---|---|
| $10^3C_Z$ | $\mathrm{NH_4^+}$ salt (0·2M) | pH | p$K_{NH_4}$ | *e* | $10^3[\mathrm{Cl^-}]$ | p$K_{NH_4}$ |
| 40 | $\mathrm{NH_4ClO_4}$ | 2·0 | 3·5 | + 9 | 14·4 | 3·5 |
| 10 | $\mathrm{NH_4ClO_4}$ | 2·4 | 4 | −11 | 6·5 | 3·6 |
| 40 | $\mathrm{NH_4Cl}$ | 2·7 | 4 | | | |

Since $pK_{NH_4}$ is approximately 4 and the acid dissociation of the ammonium ion about $10^{-9}$ (J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," Haase and Son, Copenhagen, 1941, p. 290), it follows that the equilibrium constant $K_{NH_3}$ for reaction (5) is about $10^5$.

$$C_2H_4PtCl_3^- + NH_3 \rightleftharpoons trans\text{-}NH_3,C_2H_4PtCl_2 + Cl^- \quad . \ . \ . \ . \quad (5)$$

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