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Abstract

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ON THE QUESTION OF THE OXIDATION OF TETRAAMMINEPLATINOCHLORIDE BY IODINE

A considerable number of works have been devoted to the study of the oxidation-reduction interaction of Pt^II complexes with halogens, which is of theoretical and applied importance, whereas experimental data confirming one or another reaction mechanism have not yet appeared in the literature. Thus, in considering the question of possible mechanisms for the oxidation of Pt^II complexes, A. A. Grinberg suggested the interaction of an oxidizing agent with a complex having a planar configuration owing to the absence of substituents in the 3-coordinate position (^1). The same idea was also expressed in an earlier work by A. A. Grinberg and B. V. Ptitsyn (^1), as well as in works (^3, ^4). Unfortunately, these considerations, though rather interesting, are hypothetical in character and require direct confirmation.

In the present work an attempt has been made, on the basis of the potentiometric method, to establish experimentally the mechanism of oxidation of tetraammineplatinochloride by iodine; the thermodynamics of this reaction was studied in work (^5).

A platinum electrode was placed in an iodine solution with a concentration of $2.652 \cdot 10^{-5}$ mol/l, which was prepared by dissolving iodine without addition of KJ in $0.1M\ H_2SO_4$ in order to suppress hydrolysis. Under these conditions the concentration of hydrolyzed iodine is 10^{-10} mol/l, the amount of which may be neglected. The equilibrium concentration of iodide was calculated from the initial potential by the Nernst equation and proved to be $5.0 \cdot 10^{-7}$ mol/l. Thus, the formation of the J_3^- complex may be disregarded; since ammonia has a small trans influence, its replacement by iodide in our experiments may be neglected. Thus, in the iodine solution a potential is established on the platinum electrode, the magnitude of which, E_{τ_0}, expressed in millivolts at 25°, may be written by the Nernst equation as

$$E_{\tau_0} = E_0 + 29.5 \lg \frac{[J_2]}{[J^-]^2}. \qquad (1)$$

Taking into account that the iodide concentration is small and does not change during the experiment, expression (1) may be written in the following form:

$$E_{\tau_0} = E_0' + 29.5\,\lg[J_2], \tag{2}$$

i.e., the platinum electrode operates as an iodine electrode of the first kind. After the potential on the platinum electrode had been established, a freshly prepared solution of tetraammineplatinochloride of various concentrations in 0.1 N H_2SO_4 was added, and the change of potential with time was recorded with an EPPV-51M electronic potentiometer with an accuracy of ±0.5 mV.

In all experiments, addition of $[\mathrm{Pt(NH_3)_4^{2+}}]$ causes a rapid fall of potential owing to a decrease in the equilibrium concentration of iodine. The Nernst equation at time τ is written as follows:

$$E_\tau = E_0' + 29.5\,\lg[J_2 - x]. \tag{3}$$

Subtracting equation (3) from equation (2), from the change in potential ΔE we find the remaining equilibrium concentration of iodine according to the equation

$$\Delta E = 29.5\,\lg\frac{[\mathrm{J_2}]}{[\mathrm{J_2} - x]}. \tag{4}$$

The change in potential with time, taking into account the dilution correction for several experiments, as a function of the concentration of the added complex, is shown in Fig. 1.

In all experiments there is a rapid drop in potential, over approximately 2 sec. This drop in potential as a function of the amount of $[\mathrm{Pt(NH_3)_4}]^{2+}$ added is given in Table 1.

The rapid drop in potential may occur as the result of two processes: 1) rapid oxidation of the complex by iodine and 2) addition of iodine along the third coordinate with formation of the complex $[\mathrm{Pt}^{II}(\mathrm{NH_3})_4(\mathrm{J_2})_2]^{2+}$ and with subsequent self-oxidation to $[\mathrm{Pt}^{IV}(\mathrm{NH_3})_4\mathrm{J_2}]^{2+}$. In both cases a drop in potential should be observed. But if the process proceeded by the first path, no changes in potential, apart from its drop, should have occurred. In fact, as can be seen from Fig. 1, after the instantaneous drop in potential the electrode behaves in a somewhat peculiar way. Three cases are observed:

Fig. 1. Change in potential with time as a function of the concentration of added tetrammineplatochloride.
I –$0.72 \cdot 10^{-5}$ mol/l,
II –$1.43 \cdot 10^{-5}$,
III –$2.51 \cdot 10^{-5}$,
IV –$3.94 \cdot 10^{-5}$,
V –$5.37 \cdot 10^{-5}$ mol/l

1. In experiments where the ratio of the concentration of J_2 to $[Pt(NH_3)_4]^{2+}$ was greater than 1, the potential increased with time, i.e., the equilibrium concentration of iodine again increased. Such a change in potential can occur only if, to the square-planar complex, $[Pt(NH_3)_4]^{2+}$, two molecules of J_2 add at the third coordinate, and $[Pt^{II}(NH_3)_4(J_2)_2]^{2+}$ is formed. Then oxidation of Pt^{II} to Pt^{IV} takes place; the complex $[Pt^{IV}(NH_3)_4J_2]^{2+}$ and two iodine radicals are formed, which, recombining, give an iodine molecule, whence the increase in potential. Since the rate constant of recombination is very large, $K = 1.7 \cdot 10^{12}$ $mol^{-2} \cdot cm^{-1}$ (6), the slow stage of the entire oxidation-reduction reaction will be the self-oxidation process of the complex $[Pt^{II}(NH_3)_4(J_2)_2]^{2+}$, i.e., the time-unstable complex will be in equilibrium with the initial reactants.

Table 1

Change in the oxidation potential upon addition of $[Pt(NH_3)_4]^{2+}$ and calculation of the formation function $\bar{n}$

$C_{[Pt(NH_3)_4]^{2+}} \cdot 10^5$, mol/l	E_h, mV	ΔE, mV	$[J_2]$, mol/l	$C_{J2} \cdot 10^5$, mol/l	$\bar{n}$
0	798.0	0			
0.72	787.5	10.5	$1.169 \cdot 10^{-5}$	1.483	2.06
1.07	780.0	18.0	$0.65 \cdot 10^{-5}$	2.00	1.869
1.43	771.5	26.5	$0.337 \cdot 10^{-5}$	2.315	1.619
1.79	763.0	35.0	$0.172 \cdot 10^{-5}$	2.480	1.385
2.51	748.0	50.0	$5.4 \cdot 10^{-7}$	2.598	1.035
2.86	741.0	57.0	$3.3 \cdot 10^{-7}$	2.619	0.916
3.58	731.5	66.5	$1.50 \cdot 10^{-7}$	2.637	0.736
3.94	727	71.0	$1.0 \cdot 10^{-7}$	2.642	0.670
4.65	721.5	77.5	$0.60 \cdot 10^{-7}$	2.646	0.569
5.37	718.5	79.5	$0.5 \cdot 10^{-7}$	2.647	0.492

Note. $\bar{n}$ is the Bjerrum formation function, calculated by the formula

$$\bar{n} = \left[\frac{C_{J2}}{C_{[Pt(NH_3)_4]^{2+}}} \right],$$

C_{J2} is the concentration of iodine bound in the complex; $[J_2]$ is the equilibrium concentration of iodine; $C_{[Pt(NH_3)_4]^{2+}}$ is the total concentration of tetrammineplatochloride.

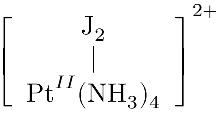
2. In experiments where the ratio of the concentration of J_2 to $[Pt(NH_3)_4]^{2+}$ is less than 1, a further decrease of the potential with time occurs. This can be explained by the fact that one molecule of J_2 is added, then oxidation

occurs and further binding of iodine proceeds, whence the decrease in potential.

3. In experiments where the ratio of the concentration of J_2 to $[Pt(NH_3)_4]^{2+}$ is approximately equal to 1, no further change in potential is observed. This is explained by compensation of both processes, and no change in the concentration of J_2 occurs.

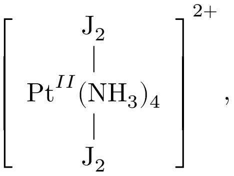
Calculating the equilibrium concentration of iodine by formula (4), one can, by Bjerrum' s method (^{7}), determine the composition and stability constants of these complexes. The results of calculations by this method are presented in Table 1.

The average coordination number $\bar{n}$ varies from 0.4 to 2.0, which indicates the formation of the complexes:



$$\left[\begin{array}{c} J_2 \\ | \\ Pt^{II}(NH_3)_4 \end{array}\right]^{2+}$$

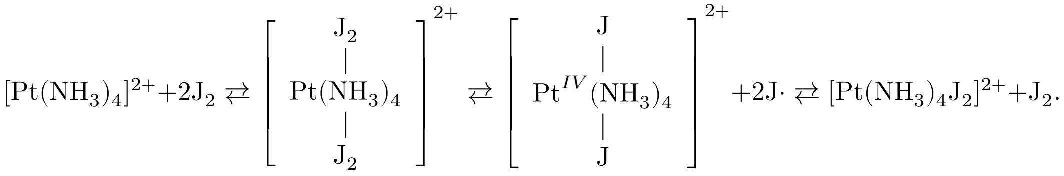
and



$$\left[\begin{array}{c} J_2 \\ | \\ Pt^{II}(NH_3)_4 \\ | \\ J_2 \end{array}\right]^{2+},$$

the partial stability constants determined by this method being, respectively, $1.7 \cdot 10^7$ and $4.1 \cdot 10^5$ at $\mu = 0.1$ and a temperature of 25°.

Thus, the mechanism of oxidation of tetrammineplatochloride by iodine is expressed by the following scheme:



$$[Pt(NH_3)_4]^{2+} + 2J_2 \rightleftarrows \left[\begin{array}{c} J_2 \\ | \\ Pt(NH_3)_4 \\ | \\ J_2 \end{array}\right]^{2+} \rightleftarrows \left[\begin{array}{c} J \\ | \\ Pt^{IV}(NH_3)_4 \\ | \\ J \end{array}\right]^{2+} + 2J\cdot \rightleftarrows [Pt(NH_3)_4J_2]^{2+} + J_2.$$

It appears very probable that this mechanism occurs in the oxidation of complexes with a planar configuration by various halogens.

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Note: Figure translations are in progress. See original paper for figures.