Chemistry

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Abstract

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ON THE INTERACTION OF ALKALI WITH trans-$(\text{Pten}_2^*\text{Cl}_2)\text{Cl}_2$

It was reported earlier (^{1}) that, in studying the rates of hydrolysis of complex compounds of tetravalent platinum, attention was drawn to the different character of the hydrolysis kinetics of trans-$[\text{Pt(NH}_3)_4\text{Cl}_2]^{2+}$ and trans-$[\text{Pten}_2\text{Cl}_2]^{2+}$. Whereas the dependence we established for the hydrolysis rate of the ammine tetramine is first order with respect to the concentration of hydroxyl ions, according to the data of Basolo and Pearson (^{2}), the hydrolysis rate of the ethylenediamine tetramine does not depend on the concentration of alkali. The hydrolysis rate of trans-$[\text{Pten}_2\text{Cl}_2]^{2+}$ was studied by them only from the increase in the concentration of chlorine ions in solution. On the basis of their experiments Basolo and Pearson consider that the interaction of trans-$[\text{Pten}_2\text{Cl}_2]^{2+}$ with alkali proceeds by an $S_\text{N}1\text{CB}$ mechanism, which may be represented schematically as follows:

$$[\text{Pten}_2\text{Cl}_2]^{2+} + \text{OH}' \rightleftharpoons [\text{Pten(en}-\text{H)Cl}_2]^{1+} + \text{H}_2\text{O} \quad \text{(rapid)}$$

$$[\text{Pten(en}-\text{H)Cl}_2]^{1+} \rightleftharpoons [\text{Pten(en}-\text{H)Cl}]^{2+} + \text{Cl}' \quad \text{(slow)}$$

$$[\text{Pten(en}-\text{H)Cl}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Pten}_2\text{ClOH}]^{2+} \quad \text{(rapid).}$$

The kinetic investigations of Basolo and Pearson were carried out with a 0.005 M solution of the complex while varying the alkali concentration from 0.20 mole/l to 0.55 mole/l. The rate constant for the interaction of the ethylenediamine analogue of Gros' salt, according to these authors' data, is $5.3 \cdot 10^{-5}$ sec^{-1} at 25°.

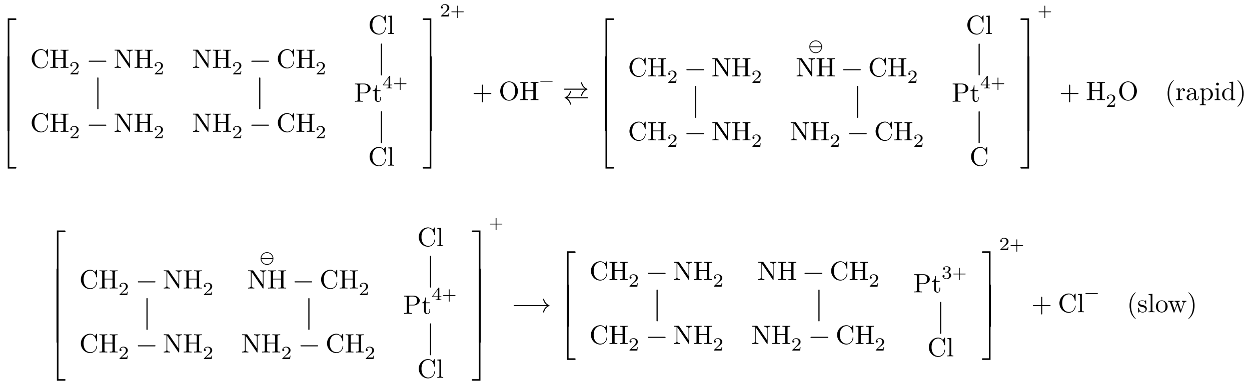
In order to elucidate the reasons for the different behavior of Gros' salt and of its ethylenediamine analogue toward alkali, we repeated the study of the hydrolysis kinetics of trans-$[\text{Pten}_2\text{Cl}_2]\text{Cl}_2$.

The **procedure of the investigation** was as follows. A weighed portion of the complex was dissolved in a volumetric flask; to the resulting solution the appropriate amount of KOH solution was added, and the total volume was brought to the mark. The reaction was carried out in a thermostat at 25°

under conditions excluding the influence of light. The consumption of alkali was monitored from the results of titration of samples with hydrochloric acid in the presence of phenolphthalein. The concentration of free chloride ions was determined by titration with $Hg(NO_3)_2$ solution in the presence of sodium nitroprusside, and the amount of reduced platinum was judged from the titration of samples with potassium permanganate solution.

For the interaction of a 0.005 M solution of trans-$[Pten_2Cl_2]Cl_2$ with alkali, our data are in exact agreement with the data of Basolo and Pearson; namely, the rate of increase in the concentration of free chloride ions in the solution is almost independent of the alkali concentration, and the rate constant of this process may be taken as $5.7 \cdot 10^{-5}$ sec^{-1}. However, we were able to establish that, along with the increase in the concentration of chloride ions in solution and the corresponding consumption of hydroxyl ions, reduction of the complex to a compound of divalent platinum proceeds at the very same rate. By the time the reaction is complete, $[Pten_2][PtCl_4]$ can be isolated from the solution by the action of potassium chloroplatinite. Thus, the interaction of trans-$[Pten_2Cl_2]Cl_2$ with alkali should be regarded not as its hydrolysis, but as reduction. The increase in the concentration of free chlorine ions in the solution is a consequence of such reduction.

It may be assumed that the reduction of tetravalent platinum proceeds through complete transfer of an electron from the imido group to the central atom. The reactions leading to reduction of the complex may be represented as follows:



$$\left[\begin{array}{cccc} & & & Cl \\ CH_2-NH_2 & & NH_2-CH_2 & | \\ | & & | & Pt^{4+} \\ CH_2-NH_2 & & NH_2-CH_2 & | \\ & & & Cl \end{array}\right]^{2+} + OH^- \rightleftarrows \left[\begin{array}{cccc} & & & Cl \\ CH_2-NH_2 & & \overset{\ominus}{N}H-CH_2 & | \\ | & & | & Pt^{4+} \\ CH_2-NH_2 & & NH_2-CH_2 & | \\ & & & C \end{array}\right]^{+} + H_2O \quad \text{(rapid)}$$

$$\left[\begin{array}{cccc} & & & Cl \\ CH_2-NH_2 & & \overset{\ominus}{N}H-CH_2 & | \\ | & & | & Pt^{4+} \\ CH_2-NH_2 & & NH_2-CH_2 & | \\ & & & Cl \end{array}\right]^{+} \longrightarrow \left[\begin{array}{cccc} CH_2-NH_2 & & NH-CH_2 & Pt^{3+} \\ | & & | & | \\ CH_2-NH_2 & & NH_2-CH_2 & Cl \end{array}\right]^{2+} + Cl^- \quad \text{(slow)}$$

Repetition of this process, which may include the disproportionation reaction of the trivalent platinum compound, must lead

Fig. 1. Kinetic curves of the interaction of a 0.025 M solution of trans-$[Pten_2Cl_2]Cl_2$ with a 0.1 M KOH solution:

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* en —ethylenediamine.

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Figure 1: Fig. 1. Kinetic curves of the interaction of a 0.025 M solution of trans-$[Pten_2Cl_2]Cl_2$ with a 0.1 M KOH solution: 1—consumption of alkali, 2—accumulation in solution of divalent platinum, 3—increase of chlorine ions in solution

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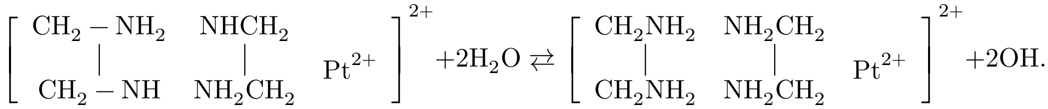
to the formation of a divalent platinum compound. Such a complex ion should contain the radical $NHCH_2CH_2NH_2$. It is not excluded that these radicals interact with water according to the following scheme:



$$\left[\begin{array}{ccc} CH_2-NH_2 & NHCH_2 & \\ | & | & Pt^{2+} \\ CH_2-NH & NH_2CH_2 & \end{array}\right]^{2+} + 2H_2O \rightleftarrows \left[\begin{array}{ccc} CH_2NH_2 & NH_2CH_2 & \\ | & | & Pt^{2+} \\ CH_2NH_2 & NH_2CH_2 & \end{array}\right]^{2+} + 2OH.$$

In the presence of an amino group in the radical $NHCH_2CH_2NH_2$, its detachment from the complex should be hindered. The fact that the ion $[Pten_2]^{2+}$ is isolated at the end of the reaction from the solution in 70% yield indicates the predominant retention of ethylenediamine in the complex. If the presence in the complex of the biradical $NHCH_2CH_2NH$ is assumed, then the probability of its cleavage should increase.

The presence of free radicals was established by the acrylonitrile polymerization reaction. This reaction makes it possible to judge the presence of free radicals, but not their nature. The nature of the free radicals is being elucidated at the present time.

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At a complex concentration of 0.005 mol/l, the kinetic curve has the usual form —with consumption of the complex the reaction rate decreases. As the complex concentration is increased to values of 0.025 and 0.05 mol/l, the character of the kinetic curves clearly changes with time (see Fig. 1). In addition, at high concentrations of the complex the influence of the alkali concentration on the kinetics of the interaction becomes apparent, which may be associated with the presence of reactions occurring with the participation of free radicals. At low concentrations of the complex, the concentration of free radicals should likewise be low. In this case their influence on the reaction may not be manifested.

The interaction of propylenediamine tetramine trans-$[Ptpn_2Cl_2]Cl_2$ with alkali proceeds analogously to trans-$[Pten_2Cl_2]Cl_2$. At the same time, the interaction of cis-$[Ptpn_2Cl_2]Cl_2$, obtained by one of us together with L. V. Vrublevskaya ([3]), under the same conditions is practically not accompanied by reduction of platinum; however, hydrolysis of the cis isomer proceeds extremely rapidly.

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

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