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Chemistry

Academician A. A. GRINBERG and Yu. N. KUKUSHKIN

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Abstract

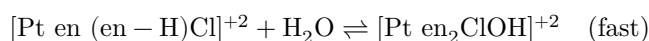
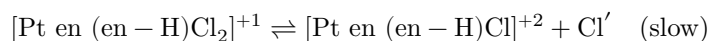
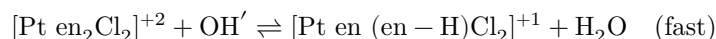
Full Text

Chemistry

Academician A. A. GRINBERG and Yu. N. KUKUSHKIN

ON THE KINETICS OF HYDROLYSIS OF CERTAIN COMPLEX COMPOUNDS OF Pt(IV)

Kinetic studies of substitution reactions in complex compounds of Pt(IV) were begun by Zvyagintsev and Karandasheva in 1956 ⁽¹⁾. Among the earlier works, one should note the qualitative study of the kinetics of hydrolysis of chloro- and bromoplatinate ⁽²⁻⁴⁾. Comparatively recently, brief reports appeared by Basolo and Pearson with coworkers on kinetic studies of the hydrolysis of trans-[Pt en₂Cl₂]⁺² ^(5,6). In these works it was reported that the hydrolysis of the dichlorodiethylenediamine ion proceeds by a zero-order reaction with respect to the alkali concentration. Variations in the concentration of the complex were not carried out. The rate of hydrolysis was judged from the increase in the concentration of chloride ions in solution. On this basis, for the hydrolysis of trans-[Pt en₂Cl₂]⁺² an S_N1CB mechanism was proposed, which may be schematically represented as follows:



In studying chlorine isotope exchange in the same compound, trans-[Pt en₂Cl₂]⁺², Basolo and Pearson established the catalytic influence of traces of divalent platinum on the rate of exchange and the absence of any influence of added Pt(II) on the rate of hydrolysis.

The aim of the present work was to study the kinetics of hydrolysis of complexes constituting the Werner-Miolati transition series: Na₂[PtCl₆], *k*[PtNH₃Cl₅], [Pt(NH₃)₂Cl₄], [Pt(NH₃)₃Cl₃]Cl (Cleve's salt), trans-[Pt(NH₃)₄Cl₂](NO₃)₂, [Pt(NH₃)₅Cl]Cl₃, and the pyridine complex *k*[PtPy^{**}Cl₅]. Because of their low solubility, the isomeric diammines from this series have as yet remained unstudied. Experiments on the kinetics of hydrolysis were carried out in vessels coated with red lacquer, under darkened conditions. The rate of hydrolysis was followed by the entry of alkali into the reaction, by visual titration.

Phenolphthalein was used as the indicator in all cases, with the exception of chloropentammine, where methyl orange was employed.

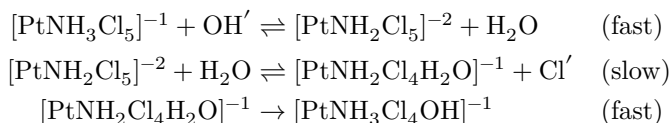
For complex compounds of Pt(IV), along with greater stability with respect to substitution reactions, one could have expected a more complicated picture of hydrolysis than that which the authors observed for Pt(II) compounds (7). The complication of the hydrolysis of Pt(IV) complexes should be caused by an increase in the number of coordinated groups capable of substitution, by the presence of pronounced acidic properties, and by the possibility of redox processes. The latter may play a major role in some reactions of isomerization and substitution (8,9). Experimental studies indeed showed a great variety in the kinetics of hydrolysis of individual members of the series under study.

* en —ethylenediamine.

** Py —pyridine.

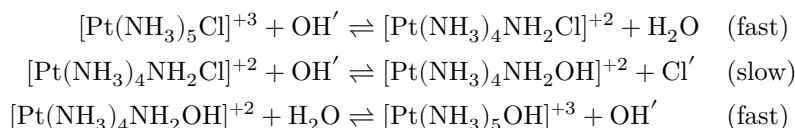
The dependence of the hydrolysis rate on alkali concentration is expressed by first order for $k[\text{PtNH}_3\text{Cl}_5]$, $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2](\text{NO}_3)_2$, and, with some approximation, for $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$. For $k[\text{PtPyCl}_5]$ and $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$, the rate of hydrolysis does not depend on the alkali concentration. These results already indicate that for Pt(IV) compounds there is not the uniformity in the hydrolysis mechanism that was observed for Pt(II) compounds (7). A dependence of the hydrolysis rate on the complex concentration equal to unity is observed for $k[\text{PtPyCl}_5]$ and $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$, whereas for $k[\text{PtNH}_3\text{Cl}_5]$, $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$, and $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2](\text{NO}_3)_2$ it proved to be equal to 1.75. Along with the unusually high order of the hydrolysis rate of mono-, tri-, and tetrammine with respect to the complex concentration, in the course of hydrolysis these compounds are partially reduced to Pt(II) compounds. By the end of the reaction at 25°, reduction of from 1 to 5% of the initial complex is observed. Raising the temperature increases the reduction. It should be noted that, in a qualitative comparison of the hydrolysis rates of the complexes studied, $k[\text{PtNH}_3\text{Cl}_5]$, $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$, and $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2](\text{NO}_3)_2$ have the highest rates.

Chloroplatinate, pyridine monoammine, and pentammine are not reduced by alkali under the concentration conditions studied, even on heating. The high order of the hydrolysis rate of $k[\text{PtNH}_3\text{Cl}_5]$, $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$, and $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2](\text{NO}_3)_2$ can be explained by the presence of redox processes in the system and, in particular, by the formation of molecular compounds of the type $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl} \cdot [\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$. One way or another, it may be thought that some "active" complexes participate in these reactions. Since this aspect of the question has not yet been fully clarified, in interpreting the reaction mechanisms of the compounds under consideration we shall conditionally assume that the initial complex participates in the reaction. In view of the foregoing, the following mechanism of the hydrolysis reaction may be represented for $k[\text{PtNH}_3\text{Cl}_5]$:



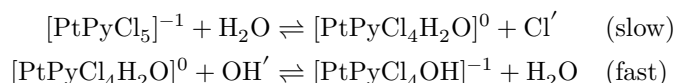
An analogous hydrolysis mechanism may also be proposed for $[\text{Pt} \cdot (\text{NH}_3)_3\text{Cl}_3]^{+1}$. The difference in the dependences of the hydrolysis rates on alkali concentration in $k[\text{PtNH}_3\text{Cl}_5]$ and $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$ can be explained by the fact that the acidic properties of the triammine must be expressed more strongly than the acidic properties of the monoammine and, consequently, the acid-base equilibrium (the first stage) must be shifted more strongly to the right.

The mechanism of hydrolysis of $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{+2}$ may already include direct replacement of chlorine in $[\text{Pt}(\text{NH}_3)_3\text{NH}_2\text{Cl}_2]^{+1}$ by hydroxyl. Coulomb attraction of oppositely charged ions should favor such replacement. The hydrolysis mechanism of $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$ (a second-order reaction) does not require the adoption of the condition that was applied to the preceding complexes. The most probable mechanism should be considered the following:



According to this mechanism, for the reaction to proceed an excess amount of alkali is required over and above one equivalent consumed in the formation of the amide. This proposition is in agreement with the experimental data.

The hydrolysis of $k[\text{PtPyCl}_5]$ probably proceeds as follows:



According to work ⁽²⁾, the rate of hydrolysis of chloroplatinate is so low that, over the measured time, the amount of alkali entering into the reaction was at the limit of experimental error. However, a qualitative comparison of the hydrolysis rates of $\text{Na}_2[\text{PtCl}_6]$, $k[\text{PtPyCl}_5]$, and $k[\text{PtNH}_3\text{Cl}_5]$ (under identical concentration conditions) shows that in this series the reaction rate increases from chloroplatinate to the pyridine monoamine and further to the ammonia monoamine.

At the beginning of the article, the study by Basolo and Pearson on the kinetics of hydrolysis of $\text{trans-}[\text{Pt en}_2\text{Cl}_2]^{+2}$ was already considered. In comparing the kinetic results for the hydrolysis of $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{+2}$ with the results of Basolo and Pearson for the hydrolysis of $\text{trans-}[\text{Pt en}_2\text{Cl}_2]^{+2}$, the authors were puzzled by the difference in the dependences of the hydrolysis rates of these

compounds on the alkali concentration. It therefore became necessary to carry out a comparative study of the hydrolysis rates of $\text{trans-[Pt(NH}_3)_4\text{Cl}_2]^{+2}$ and $\text{trans-[Pt en}_2\text{Cl}_2]^{+2}$. In these investigations it was found that, in the course of hydrolysis of $\text{trans-[Pt en}_2\text{Cl}_2]^{+2}$, along with an increase in the concentration of chloride ions, appreciable amounts of $[\text{Pt en}_2]^{+2}$ appear in solution, which is the reduction product of the initial complex. Further studies of the kinetics of the interaction of $\text{trans-[Pt en}_2\text{Cl}_2]^{+2}$ with alkali were carried out by the parallel investigation, as a function of time, of alkali consumption, the increase in chloride ion concentration, and the accumulation in solution of divalent platinum. Our investigations showed that all these three processes proceed at approximately the same rates.

Thus, the S_N1CB mechanism for the hydrolysis of $\text{trans-[Pt en}_2\text{Cl}_2]^{+2}$ does not reflect the processes occurring in solution. The mechanism of the interaction of $\text{trans-[Pt en}_2\text{Cl}_2]^{+2}$ with alkali is much more complex. These investigations are now being completed, and their results will soon be submitted for publication.

Radium Institute named after V. G. Khlopin
Academy of Sciences of the USSR

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