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Abstract

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ON THE EXISTENCE OF EXCHANGE BETWEEN IRRADIATED METALLIC PLATINUM AND COMPLEX IONS OF DIVALENT PLATINUM IN AQUEOUS SOLUTIONS

As was shown by two of us (^{1}), when the potentials of a platinum electrode were measured in solutions of complex compounds of divalent platinum, the platinum electrode behaved not as an indifferent electrode, but as an electrode responding to the concentration of Pt^{2+} ions. The detailed mechanism of the corresponding interaction has not been established, but the suggestion was made that an exchange of platinum takes place between the electrode and the complex ions (^{2}).

To test this assumption, the experiments described below were carried out. Irradiated platinum containing the isotope Pt^{197} was in the form of two pieces of foil, each weighing about 0.3 g; the total activity of each sample was about 2.5 mCi. After washing with water, the corresponding portions of the irradiated metal were immersed in 50 ml of a 1 M KCl solution (a) and in 50 ml of a 1 M KCl solution containing 0.45 g of chloroplatinite $K_2[PtCl_4]$ (b). The solutions with platinum were shaken for 2 hours. After shaking was completed, 20-ml samples of the solutions were taken and measured in special vessels on an AS-1 type β-counter.

In the case of the KCl solution, 190 imp/min passed into the solution, and in the case of the solution containing $K_2[PtCl_4]$, 565 imp/min above background. These solutions were used to estimate the half-life values of the metal that had passed into solution. For solution (a) this value was close to 25 hours,* and for solution (b), to 20 hours. According to the literature data, the half-life of Pt^{197} is 18 hours. The shaking of the platinum foil in the same solutions was then continued. Shaking in solution (a) continued for another 3 hours, and in solution (b) for 2 hours. In the KCl solution, 290 imp/min was found, and in the solution containing platinit , 726 imp/min. All figures are given with respect to the time at which the experiment began.

After completion of the repeated shaking, the solution with $K_2[PtCl_4]$ was precipitated with an excess amount of the chloride of Reiset' s base $[Pt(NH_3)_4]Cl_2$. The precipitated green Magnus salt was filtered off, washed with alcohol and ether, and dissolved on heating in a KOH solution. The activity of the Magnus salt solution, as well as that of its filtrate together with the wash liquids, was measured as indicated above. The following data were obtained: in the Magnus salt solution, 545 imp/min, and in the filtrate, 262 imp/min. The sum of the measured activities, within the limits of measurement error, agrees satisfactorily with the activity value of the original solution.

For the solution of Magnus salt in alkali, a determination of the half-life was carried out; it proved to be practically coincident with the literature data (18 hours).

This experiment shows that approximately 2/3 of all the platinum that passed into solution was present in a form precipitated by the ion $[Pt(NH_3)_4]^{2+}$. The fact that part of the platinum did not precipitate in the form of Magnus salt may be explained by the fact that, in the course of the interaction of the platinum foil with our solution, there forms— not only the ions $[PtCl_4]^{2-}$, but also certain other forms not precipitated by tetrammine, for example $[PtCl_2(H_2O)_2]$.

Special experiments with $K_2[PtCl_4]$ labeled with platinum showed that, in the process of formation and decomposition of Magnus' green salt, exchange of the central atoms does not occur. From a solution containing 0.14 g of $K_2[PtCl_4]$, active with respect to platinum (Pt^{197}), Magnus' salt was precipitated. A 0.2 g portion of the latter was thoroughly ground in a mortar, after which it was left in the dark for a long time. After 18 hours had elapsed, Magnus' salt was decomposed with a solution of 0.113 g of $AgNO_3$. The precipitate $Ag_2[Pt^{197}Cl_4]$ was filtered off and thoroughly washed with water. The filtrate and wash waters were measured on a β-counter. The measurements showed that the entire initial amount of active platinum was concentrated in the ion $[PtCl_4]^{2-}$, i.e., exchange of central atoms between $[Pt(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$ does not occur.

After completion of repeated shaking of the platinum foil with the KCl solution, the platinum foil was thoroughly washed with distilled water and immersed in 50 ml of 0.05 M ammonia solution containing 0.2 g of tetrammineplatochloride $[Pt(NH_3)_4]Cl_2$ and 3.8 g of $NaNO_3$ (solution B). Shaking was continued for 2 hours. 153 imp/min passed into the solution. After repeated shaking for 3.5 hours, the activity reached 336 imp/min. The solution was then separated from the platinum and precipitated with an excess of $K_2[PtCl_4]$. The Magnus salt obtained, as in the previous case, was dissolved in a hot KOH solution. The activity of the alkaline solution of Magnus' salt proved to be 159 imp/min, and the activity of the filtrate 121 imp/min. Taking into account the small activity values, the balance in this case too should be considered satisfactory. It

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* The somewhat high value of the half-life of platinum found in the KCl solution is possibly explained by traces of the radioactive isotope of gold, Au^{199}, present as an impurity.

follows from this experiment that about half of all the platinum that passed into solution was present in the form of $[Pt(NH_3)_4]^{2+}$ ions. Thus it was established that ions of the indicated composition are indeed formed from metallic platinum. An approximate calculation shows that the amount of platinum that passed into solution in our experiments was of the order of 10^{-8} g. The fact that the process of formation of the ions $[PtCl_4]^{2-}$ and $[Pt(NH_3)_4]^{2+}$ under the conditions described did not proceed to completion seems natural, since not only Cl^- ions and NH_3 molecules, but also solvent molecules, can add to the Pt^{2+} ion on the surface of the foil. It is possible that if hydrochloric acid had been used instead of KCl, or if the ammonia concentration had been higher, the degree of formation of the ions $[PtCl_4]^{2-}$ and, correspondingly, $[Pt(NH_3)_4]^{2+}$ would have been still greater. The solutions that we used in these experiments corresponded to the solutions used in measurements of the potentials of platinum electrodes ([1,2]).

The results of our experiments, together with the data of the cited works, indicate that, under the conditions described, exchange between platinum foil and the ions $[PtCl_4]^{2-}$ and $[Pt(NH_3)_4]^{2+}$ actually took place. As for the mechanism of this exchange, one of its possible pathways is a process of the type that we described in the preceding work ([2]). In the case of platinite systems it may also be imagined that exchange proceeds owing to interaction with metallic platinum of the platinite formed in solution in the process of disproportionation of platinite. We recognize that, during irradiation of metallic platinum, the nature of the surface layer could have changed and, in particular, surface oxides could have formed. However, measurement of potentials in the solutions mentioned was also carried out with a platinized electrode, i.e., under conditions in which an active surface was present.

In the future we propose to carry out experiments to determine whether exchange occurs with irradiated platinum that has first been subjected to reduction.

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CITED LITERATURE

1. A. A. Grinberg, M. I. Gel’ fman, DAN, **133**, No. 5 (1960).
2. A. A. Grinberg, M. I. Gel’ fman, DAN, **137**, No. 1 (1961).

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