Chemistry

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1961

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Abstract

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Chemistry

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ON THE STUDY OF THE KINETICS OF SUBSTITUTION REACTIONS IN THE INNER SPHERE OF COMPLEX MOLECULES

(Presented by Academician V. I. Spitsyn, 17 III 1961)

In recent years a number of investigations have been carried out on the quantitative aspect of the trans effect in complex compounds [1–9]. These works, performed by various methods, have shown that, apparently, the most promising approach is the study of the kinetics of reactions in the inner sphere of complex molecules.

With regard to the kinetics of reactions in complex compounds of platinum, quantitative data have been obtained in works [8–11], but the values of the rate constants of the reactions given in [8,9] refer only to one concentration of the reacting substances (0.03 M). It seemed to us that if the study were carried out at different concentrations of the reacting substances, more interesting data could be obtained, shedding some light on the mechanism of inner-sphere substitution reactions.

In the present brief communication we set forth the main results of our investigation. We used the procedure described in [8]; the objects of our investigation were the same reactions: the interaction of triacidomonoammineplatinates of divalent platinum $K[\mathrm{PtNH_3Cl_3}]$, $K[\mathrm{PtNH_3ClBrCl}]$, and $K[\mathrm{PtNH_3ClNO_2Cl}]$ with pyridine in aqueous solutions.

The determinations were carried out at concentrations of the reacting substances of 0.01, 0.03, 0.06, and 0.09 M and at a temperature of 25°. The ratio of triacidomonoammineplatinate to pyridine was 1 : 1. Pyridine was added to the solutions 2-3 min after their preparation. On the basis of the experimental data, the rate constants of the reactions were calculated. The calculation was performed using the equation for second-order reactions. Table 1 gives the mean values of the reaction rate constants ($K \cdot 10^4$) at different concentrations of the reacting substances.

Table 1

Mean values of the reaction rate constants at different concentrations of the reacting substances
(freshly prepared solutions)

Reaction	0.01 M	0.03 M	0.06 M	0.09 M
$K[\mathrm{PtNH_3Cl_3}] + \mathrm{Py}$	82.8	52.5	37.4	34.2
$K[\mathrm{PtNH_3Cl_2Br}] + \mathrm{Py}$	134	120	85	76
$K[\mathrm{PtNH_3Cl_2NO_2}] + \mathrm{Py}$	613	576	582	474

As is seen from Table 1, the reaction rate constants do not remain constant. For all three reactions we found a certain increase in the reaction rate constants with decreasing initial concentrations of the reacting substances, which, apparently, is due to aquation processes.

As early as 1940, A. A. Grinberg [14] put forward the supposition that exchange in complex molecules proceeds through intermediately formed aquo ions. Subsequently this supposition found experimental confirmation [10,11,13,15].

The fact that in dilute solutions the reaction rate constants have higher values is yet another confirmation that,

that the formation of aquo complexes plays a decisive role in substitution reactions occurring in aqueous solutions.

In the inner sphere of a complex molecule in an aqueous medium, the following transformations take place:

$$\begin{bmatrix} \mathrm{NH_3} & & \mathrm{Cl} \\ & \mathrm{Pt} & \\ \mathrm{X} & & \mathrm{Cl} \end{bmatrix} + \mathrm{H_2O} \rightleftharpoons \begin{bmatrix} \mathrm{NH_3} & & \mathrm{H_2O} \\ & \mathrm{Pt} & \\ \mathrm{X} & & \mathrm{Cl} \end{bmatrix} + \mathrm{Cl}'$$

$$\begin{bmatrix} \mathrm{NH_3} & & \mathrm{H_2O} \\ & \mathrm{Pt} & \\ \mathrm{X} & & \mathrm{Cl} \end{bmatrix} \rightleftharpoons \begin{bmatrix} \mathrm{NH_3} & & \mathrm{OH} \\ & \mathrm{Pt} & \\ \mathrm{X} & & \mathrm{Cl} \end{bmatrix} + \mathrm{H}'$$

After this, interaction with component Y (for example, pyridine) proceeds:

$$\begin{bmatrix} \mathrm{NH_3} & & \mathrm{OH} \\ & \mathrm{Pt} & \\ \mathrm{X} & & \mathrm{Cl} \end{bmatrix} + \mathrm{Y} \rightleftharpoons \begin{bmatrix} \mathrm{NH_3} & & \mathrm{Y} \\ & \mathrm{Pt} & \\ \mathrm{X} & & \mathrm{Cl} \end{bmatrix} + \mathrm{OH}'$$

Such a mechanism for exchange reactions in tetrachloroplatinate molecules is considered in work ($^\frown$4) to be the most probable. Apparently, reactions for triacidomonoammineplatinates proceed in the same way, which is confirmed by the change in the pH of solutions over time. Measurement of the pH of solutions of the initial salts at certain time intervals showed that the concentration of hydrogen ions increases, and the equilibrium state is reached comparatively quickly (Table 2).

Table 2

Change in the pH of solutions over time

Salt	Conc., M	pH of fresh solution	after 5 min	after 10 min	after 15 min	after 20 min	after 25 min	after 30 min
$K[PtNH_3Cl_3]$	0.01	5.2	4.9	4.8	4.6	4.55	4.5	4.5
$K[PtNH_3Cl_3]$	0.03	4.4	4.3	4.2	4.1	4.05	4.0	4.0
$K[PtNH_3Cl_3]$	0.06	4.2	4.0	4.0	3.95	3.9	3.8	3.8
$K[PtNH_3Cl_2Br]$	0.01	5.15	4.9	4.7	4.5	4.45	4.4	4.4
$K[PtNH_3Cl_2Br]$	0.03	4.7	4.3	4.2	4.15	4.1	4.0	4.0
$K[PtNH_3Cl_2Br]$	0.06	4.1	3.9	3.85	3.8	3.75	3.7	3.7
$K[PtNH_3Cl_2NO_2]$	0.01	4.5	4.2	4.0	3.9	3.8	3.7	3.7
$K[PtNH_3Cl_2NO_2]$	0.03	4.2	4.0	3.8	3.6	3.5	3.45	3.4
$K[PtNH_3Cl_2NO_2]$	0.06	4.0	3.6	3.5	3.35	3.3	3.35	3.3

Thus, in speaking of the interaction of salts $K[PtNH_3ClXCl]$ with pyridine in aqueous solutions, it should be borne in mind that substitution in fact occurs not at the coordinates X–Pt–Cl (where X = Cl, Br, NO_2), but at the coordinates X–Pt–OH.

Our experiments also showed that the interaction with pyridine of solutions of potassium triacidomonoammineplatinates that had been kept at room temperature for some time proceeds considerably faster than the interaction of freshly prepared solutions.

To establish the dependence of the rate of the substitution reaction on the aging time of the solutions, a series of experiments was carried out with solutions of the salts $K[PtNH_3Cl_3]$ and $K[PtNH_3Cl_2Br]$. We treated fresh

freshly prepared solutions of these salts, as well as solutions aged at 25° for 1, 2, and 3 hours. The results obtained are presented in Fig. 1. As can be seen from Fig. 1, the difference in the values of the reaction-rate constants for solutions aged for 1, 2, and 3 hours in most cases becomes insignificant, and it is possible that after a longer time the values of the constants for solutions with concentrations of 0.03–0.09 M will become very close.

As was to be expected, the aquation process proceeds most rapidly in dilute solutions.

Unfortunately, we were unable to determine the reaction-rate constants of $K[PtNH_3Cl_2NO_2]$ + Py in aged solutions. In these cases the reaction proceeds so rapidly that the procedure we used did not make it possible to titrate pyridine without the risk of introducing a large error.

If the data obtained are considered from the standpoint of the trans-influence rule, they are in full agreement with this regularity for divalent platinum compounds. The ratio of the reaction-rate constants of freshly prepared solutions of the salts studied with pyridine varies as a function of concentration, but at any concentration the reaction-rate constant with pyridine for potassium dichloronitromonoammineplatinate is greater than for potassium dichlorobromomonoammineplatinate, and for the latter, in turn, greater than for potassium trichloromonoammineplatinate (Table 3).

Table 3

Ratio of the reaction-rate constants of K[$PtNH_3Cl_3$], K[$PtNH_3Cl_2Br$], K[$PtNH_3Cl_2NO_2$] with pyridine at various concentrations of the reacting substances (freshly prepared solutions)

Ratio of constants	0.01 M	0.03 M	0.06 M	0.09 M
K_{Br}/K_{Cl}	1.6	2.3	2.3	2.2
K_{NO_2}/K_{Br}	4.6	4.8	6.8	6.2
K_{NO_2}/K_{Cl}	7.4	10.9	15.5	13.9

In paper (8) the ratios of the reaction-rate constants of K[$PtNH_3Cl_3$], K[$PtNH_3Cl_2Br$], and K[$PtNH_3Cl_2NO_2$] with pyridine are given at a concentration of the reacting substances of 0.03 M.

For comparison, we give the ratios of the reaction-rate constants of K[$PtNH_3Cl_2Br$] and K[$PtNH_3Cl_3$], occurring in solutions aged at 25° for 3 hours.

Concentration of reacting substances	0.01 M	0.03 M	0.06 M	0.09 M
K_{Br}/K_{Cl}	2.4	1.8	1.5	1.4

Fig. 1. Dependence of reaction-rate constants on the aging time of solutions. a –K[$PtNH_3Cl_3$], b –K[$PtNH_3Cl_2Br$]

The interaction of triacidomonoammineplatinates with pyridine is a complex process, and calculation of the rate constants of these reactions by a second-order equation is conditional.

Since substitution takes place at the coordinates Cl–Pt–OH, Br–Pt–OH, NO_2 –Pt–OH, and not at the coordinates Cl–Pt–Cl, Br–Pt–Cl, NO_2–Pt–Cl, until an equation has been found for calculating the rate constants of reactions with allowance for hydrolysis, for a quantitative assessment of the trans effect of different addends it is more correct to compare with one another the values of the rate constants of reactions occurring in aged solutions.

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Received
30 XII 1960

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