Reports of the Academy of Sciences of the USSR

Academician A. A. GRINBERG and M. A. KUZMINA

1962

SovietRxiv

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1962. Volume 144, No. 4

CHEMISTRY

Academician A. A. GRINBERG and M. A. KUZMINA

ON THE ISOTOPIC EXCHANGE OF CHLORINE IN ZEISE' S SALT

In recent years systematic investigations have been carried out in our laboratory on the kinetics of isotopic exchange of anionic ligands in salts of the Koss type, of the general formula $K[PtAX_3]$, where $A = NH_3$ or Py, and X = Cl or Br.

Fig. 1. Dependence of $\ln(1 - F)$ on time at different concentrations of the complex salt (10^{-2} mol/l): 1—0.83; 2—1.66; 3—3.32

Fig. 2. Dependence of $\ln(1-F)$ on time at different concentrations of the ligand (10^{-2} mol/l): 1—4.98; 2—14.94

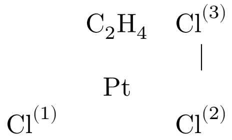
The salt of composition $K[PtNH_3Cl_3]$ was also studied in this respect by American investigators. Elleman, Reishas, and Martin (1) came to the conclusion that, with respect to the rate of isotopic exchange, all three chlorine atoms in the ion $[PtNH_3Cl_3]^-$ behave practically identically. However, one of us, together with G. A. Shagisultanova (2), as early as 1959 obtained data indicating kinetic nonequivalence of the bromine atoms in the ion $[PtNH_3Br_3]^-$. Analogous data were obtained in studying the kinetics of isotopic exchange of chlorine in the ion $[PtPyCl_3]^-$ and of bromine in the ion $[PtPyBr_3]^-$. The kinetic nonequivalence of the halogen ions in the complexes mentioned is consistent with the idea of a higher exchange rate on the coordinate X—Pt—X as compared with the exchange rate on the coordinate A—Pt—X, where $A = NH_3$ or Py. Taking into account the considerable magnitude of the trans influence of ethylene, established by I. I. Chernyaev and A. D. Gelman (3) as early as 1937, it seemed to us of interest to investigate the kinetics of isotopic exchange of chlorine in Zeise' s salt $K[PtC_2H_4Cl_3]$.

From all that is known about the reactivity of Zeise' s salt (3, 4, 6), it could be expected that chlorine situated in the trans position to ethylene would ex-

Fig. 3. Dependence of the logarithm of the exchange rate on the logarithm of the concentration of the complex salt

Figure 2: Fig. 3. Dependence of the logarithm of the exchange rate on the logarithm of the concentration of the complex salt

change much faster than the other two chlorine atoms standing on the coordinate Cl—Pt—Cl.



$$\begin{array}{ccc} & C_2H_4 & Cl^{(3)} \\ & & | \\ & Pt & \\ Cl^{(1)} & & Cl^{(2)} \end{array}$$

On the other hand, in this system one could expect a negative cis effect, i.e., a slowing of exchange on the coordinate Cl—Pt—Cl as a result of the very great tendency of the ethylene molecule to form a dative bond with the ion of divalent platinum. The experiment fully confirmed the assumptions made.

Experimental Part

Potassium Zeise's salt, $K[PtC_2H_4Cl_3]$, was synthesized by the method of (4), and its composition was checked by analyses. The procedure for the exchange experiments consisted in mixing solutions of the complex salt and potassium chloride labeled with Cl^{36} in the reaction vessel and keeping them in a thermostat for a specified time. At definite time intervals, aliquot samples of the solution under study were withdrawn. To separate the exchanging forms, tetrapyridineplatochloride $[PtPy_4]Cl_2$ was used. Zeise' s salt was precipitated with a twofold excess of precipitant under strong cooling with ice. The precipitate of the salt $[PtPy_4][PtC_2H_4Cl_3]_2$ was filtered off, washed with cooled water, alcohol, and ether, and dried in air. The separation proceeded fairly completely. The yield of the precipitate $[PtPy_4][PtC_2H_4Cl_3]_2$ was 95-97% of the theoretically possible value. From the well-ground powder $[PtPy_4][PtC_2H_4Cl_3]_2$, an ether suspension was prepared, which was then applied to weighed Plexiglas targets. After drying in air, the target with the uniformly deposited precipitate was weighed and measured on an end-window counter.

After determining the activity of the filtrate, it was possible to judge the activity balance, which in all experiments was satisfactory; the difference between the activity of the initial solution and the sum of the activities of the precipitate and filtrate did not exceed 6%. The exchange experiments were carried out in a dark vessel (to avoid the possible effect of light) at a temperature of 25°. The experimental data obtained are compared in Tables 1, 2, 3, and also in Figs. 1-3.

Fig. 3. Dependence of the logarithm of the exchange rate on the logarithm of the concentration of the complex salt

The exchange rate was studied as a function of the concentration of the complex ion (at constant ligand concentration), of the ligand concentration (at constant concentration of the complex ion), and also of temperature. Figure 1 shows the dependence of isotopic exchange in the system $K[PtC_2H_4Cl_3] + 3KCl^* \rightarrow$ on the concentration of the complex ion at constant ligand concentration and constant temperature. Along the abscissa is plotted the time from the start of the experiment (in hours), and along the ordinate $\ln(1 - F)$, where F is the degree of exchange. It can be seen that, at all three studied concentrations of the complex ion, we are dealing with a rectilinear dependence characteristic of so-called simple exchange in the presence of functional equivalence of the exchanging groups. In this respect, the nature of the dependence differs strongly from the curves characteristic of the corresponding systems $K[PtNH_3Br_3] + 3KBr^*$, $K[PtPyBr_3] + 3KBr^*$, and $K[PtPyCl_3] + 3KCl^*$. The presence of a rectilinear dependence in Zeise' s salt becomes entirely understandable if one takes into account that in this case there is a very large zero exchange, amounting on average to about 35% of the total possible exchange. This "zero" exchange takes place within 30 sec from the start of the experiment. Taking into account the data given in ([5],[6]), there can be no doubt that this apparent zero exchange is in fact a practically instantaneous exchange of chlorine located in the trans-position to ethylene. As for the time dependence of exchange shown in Figs. 1 and 2, it refers practically only to the exchange of functionally equivalent chlorine atoms on the coordinate Cl—Pt—Cl. From the data of Fig. 1, the half-exchange periods were determined graphically.

for the three concentrations of the complex ion studied. The corresponding values are given in Table 1. Further, using the known formula

$$R = \frac{AB}{A + B} \cdot \frac{0.693}{\tau_{1/2}},$$

where A is the concentration of chlorine exchanging at a measurable rate, in g-at. Cl per 1 l in the composition of the complex salt; B is the concentration of external chlorine, in g-at. Cl per 1 l; R is the exchange rate, in g-at. Cl per 1 l per min.; $\tau_{1/2}$ is the half-exchange period in minutes, the values of the exchange rate are calculated for the concentrations of the complex ion studied. Plotting $\lg C$ on the abscissa and $\lg R$ on the ordinate, one can find graphically the order of the reaction with respect to the complex salt. This value is close to unity (1.23) (Fig. 3).

Table 1

Concentr. $K[PtC_2H_4Cl_3]$ (mol/l (g-at. Cl per 1 l))	Concentr. $KCl \cdot 10^2$	Concentr. $Cl_{(1-3)}$ in the complex salt $\cdot 10^2$	$\tau_{1/2}$ (min.)	$R_1 \cdot 10^6$ (g-at. Cl per 1 l per min.)	$K_1 \cdot 10^3$ (min^{-1})
0.83 (2.49)	4.98	1.66	$33.5 \cdot 60$	4.3	0.259
1.66 (4.98)	4.98	3.32	$27.4 \cdot 60$	8.4	0.253
3.32 (9.96)	4.98	6.64	$13.3 \cdot 60$	24.7	0.370

From Fig. 2 it is seen that the exchange rate is practically independent of the concentration of the ligand (chloride ion). In this connection it proved possible to calculate the rate constant of isotopic exchange by the formula $R = KC$, where R is the exchange rate, C is the concentration of ions $Cl_{(1-3)}$ in the complex salt, and K is the rate constant (see Table 1).

Table 2

Temp., °C	Concentr. $K[PtC_2H_4Cl_3]$, (mol/l (g-at. Cl per 1 l))	Concentr. $KCl \cdot 10^3$	Concentr. $Cl_{(1-3)}$ in the complex salt	$\tau_{1/2}$ (min.)	$R \cdot 10^6$ (g-at. Cl per 1 l per min.)
25	1.66 (4.98)	4.98	3.32	$27.4 \cdot 60$	8.4
18	1.66 (4.98)	4.98	3.32	$43 \cdot 60$	5.35
10	1.66 (4.98)	4.98	3.32	$81.4 \cdot 60$	2.83

Finally, Tables 2 and 3 give data on the dependence of the isotopic-exchange rate on temperature and approximate values of the activation energy.

Table 3

Temp., °C	$\frac{1}{T} \cdot 10^3$	$K_1 \cdot 10^5$	E (kcal/mol · deg), calculated	E (kcal/mol · deg), found graphically
25	3.36	25.3	11.1	12
18	3.44	16.1	12.9	
10	3.54	8.52	12.1	

The results obtained once again confirm that the ethylene molecule has a very large trans effect. With respect to the rate of isotopic exchange, the chlorine situated opposite ethylene behaves like ionic chlorine. On the other on the other hand, the rate of isotopic exchange of chlorine on the coordinate Cl—Pt—Cl is greatly reduced in comparison with the rate of isotopic exchange on the analogous coordinate in Koss salts, in which ammonia or pyridine is present instead of ethylene.

In a number of earlier studies we have already shown that, on passing from ions PtX_4^{2-} (where X = Cl or Br) to ions of the type $PtAX_3^-$ (where A = NH_3 or Py), an increase takes place in the rate of exchange or substitution reactions. The increase in the rate was explained by the cis effect of ammonia or pyridine molecules on the rate of exchange on the coordinate Cl—Pt—Cl. The cis effect was interpreted in the sense that ammonia or pyridine molecules cannot form dative bonds with platinum and thereby the probability of formation of such bonds by the coordinated chlorine ions, which thereby become more trans-active, is increased. The ethylene molecule, in contrast to ammonia or pyridine molecules, on the contrary, has a very great tendency to form a dative bond, and consequently the probability of formation of such bonds with chlorine atoms is sharply reduced; the consequence of this is the decrease in the trans-activity of chlorine. It should be noted that the observed phenomena, generally speaking, may find an explanation even without assuming the formation of dative bonds, from the standpoint of the view expressed by one of us as early as 1943, according to which the magnitude of the trans influence of a ligand is connected with its reducing properties.

As early as 1957, one of us, in a joint study with Yu. N. Kukushkin [7], pointed out that such a situation cannot be considered excluded, in which a group that labilizes the opposite substituent stabilizes an adjacent one, and vice versa. The data presented in this article are a vivid illustration of this situation.

It is very interesting that our kinetic data agree well with the crystallochemical data of G. B. Bokii and G. A. Kukina [8] concerning the influence of the trans effect on the magnitudes of interatomic distances in Zeise' s salt.

In conclusion it should be noted that the data presented once again emphasize that exchange proceeds by a dissociation mechanism with the probable intermediate formation of aquo ions.

Received
8 I 1962

CITED LITERATURE

1. T. S. Elleman, J. W. Reishus, D. S. Martin, *J. Am. Chem. Soc.*, **81**, No. 1, 10 (1959).

2. A. A. Grinberg, G. A. Shagisultanova, *Radiokhimiya*, **1**, No. 1, 91 (1959).

3. I. I. Chernyaev, A. D. Gel' man, *Izv. Sekt. platiny i drugikh blagorodnykh metallov*, issue 14, 77 (1937).

4. A. D. Gel' man, *Complex Compounds of Platinum with Unsaturated Molecules*, Publishing House of the Academy of Sciences of the USSR, 1945.

5. O. E. Zvyagintsev, E. F. Karpanashëva, *DAN*, **101**, No. 1, 93 (1955).

6. L. Leden, I. Chatt, *J. Am. Chem. Soc.*, 1955, 2936.

7. A. A. Grinberg, Yu. N. Kukushkin, *ZhNKh*, **2**, issue 1, 111 (1957).

8. G. B. Bokii, G. A. Kukina, *Kristallografiya*, **2**, issue 3, 400 (1957).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.