ON THE MECHANISM OF THE SUBSTITUTION REACTION OF TRANS-DICHLORO-DIETHYLENEDIAMINE COBALTIC CHLORIDE IN ITS AQUEOUS SOLUTION.

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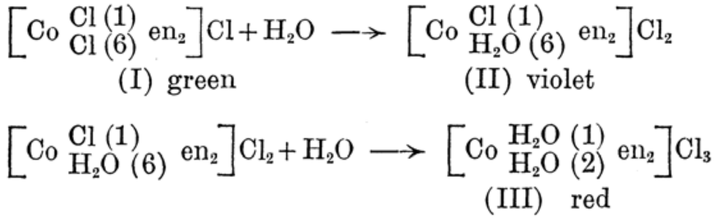
Introduction. In the previous paper⁽¹⁾ it has been shown that the chemical changes in aqueous solutions of some cobaltammines could be followed by utilising the valency effect on the coagulation of arsenious sulphide sol. The present investigation was undertaken by the same method, to study the kinetics of the change of trans-dichloro-diethylenediamine cobaltic chloride, $\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\ (1)\\ \mathrm{Cl}\ (6)\end{matrix}\ \mathrm{en}_2\right]\mathrm{Cl}$, in its aqueous solution. It is well known that the aqueous solution of this salt changes its colour gradually from green to violet and finally to red. This colour change is generally considered to be due to the following reactions which take place in the solution,⁽²⁾



$$\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\ (1)\\ \mathrm{Cl}\ (6)\end{matrix}\ \mathrm{en}_2\right]\mathrm{Cl}+\mathrm{H_2O}\longrightarrow\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\ (1)\\ \mathrm{H_2O}\ (6)\end{matrix}\ \mathrm{en}_2\right]\mathrm{Cl_2}$$

(I) green (II) violet

$$\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\ (1)\\ \mathrm{H_2O}\ (6)\end{matrix}\ \mathrm{en}_2\right]\mathrm{Cl_2}+\mathrm{H_2O}\longrightarrow\left[\mathrm{Co}\begin{matrix}\mathrm{H_2O}\ (1)\\ \mathrm{H_2O}\ (2)\end{matrix}\ \mathrm{en}_2\right]\mathrm{Cl_3}$$

(III) red

As seen in the above formulae, the substitution of chlorine atoms by water molecules in the complex radicals causes not only the colour change but also the increase of the valency of the complex ions of the salts thus produced. The substitution reactions above mentioned may, therefore, be easily followed by observing the colour change as well as the electrolytic conductivity of the solution,⁽³⁾ and also by means of the coagulation of arsenious sulphide sol.

The last method consists in measuring from time to time the limiting concentrations of the solution which just failed to produce any perceptible

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(1) K. Matsuno, *J. Coll. Sci. Imp. Univ. Tokyo*, Vol. 41, Art. 11 (1921).

(2) Werner, *Ann. Chem.*, 386 (1912), 54.
Y. Shibata, *J. Coll. Sci. Imp. Univ. Tokyo*, Vol, 37, Art. 2 (1915), 25.
K. Matsuno, ibid., Vol. 41, Art. 10 (1921), 19.

(3) Compare Werner and Herty, *Z. physik. Chem.*, 38 (1901), 341; Lamb and Marden, *J. Am. Chem. Soc.*, 33 (1911), 1787.

coagulation of arsenious sulphide sol within five minutes. The present experiments were carried on with the same sample of arsenious sulphide sol as in the former experiment, so that the empirical formula previously deduced could be used in the following calculations without any transformation. It will be seen that the limiting concentrations thus measured are related to the actual concentrations of the complex salts in the solution and from the sequel the velocity constants of the substitution reactions can be calculated.

Theoretical. As regards to the concentrations of each salt in the solution of $\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\,(1)\\ \mathrm{Cl}\,(6)\end{matrix}\mathrm{en}_2\right]\mathrm{Cl}$, which were very difficult to estimate, they could be connected with the limiting concentrations by the following consideration.

Let the concentrations of (I), (II) and (III) at the time t be C_A, C_M and C_B respectively, the velocities of decreasing of the first salt and increasing of the last salt will be :

$$\frac{-dC_A}{dt}=k_1C_A \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

$$\frac{dC_B}{dt}=k_2C_M \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

The velocity of the formation of the intermediate salt is :

$$\frac{dC_M}{dt}=-\frac{dC_A}{dt}-\frac{dC_B}{dt} \quad \cdots\cdots\cdots\cdots\cdots\cdots (3)$$

By integration, C_A, C_M and C_B can be obtained as follows :

$$\left.\begin{aligned}
C_A&=C_{0A}e^{-k_1t}\\
C_M&=C_{0A}\frac{k_1}{k_2-k_1}\left(e^{-k_1t}-e^{-k_2t}\right)\\
C_B&=C_{0A}\frac{k_1\,k_2}{k_2-k_1}\left(\frac{1}{k_2}e^{-k_2t}-\frac{1}{k_1}e^{-k_1t}\right)
\end{aligned}\right\}\cdots\cdots\cdots (4)$$

where C_{0A} denotes the initial concentration and is equal to the sum of C_A, C_M and C_B.

In the substitution reaction in question, the limiting concentration is denoted by S which was assumed to be related to each other as below :

$$S_1\times\frac{C_A}{C_{0A}}+S_2\times\frac{C_M}{C_{0A}}+S_3\times\frac{C_B}{C_{0A}}=S \quad \cdots\cdots\cdots (5)$$

S_1, S_2 and S_3 represent the values corresponding to the monovalent, divalent and trivalent cations respectively.

This assumption implies the fact that the coagulation of the sol by the electrolytes is purely an adsorption phenomenon.

In the previous paper (loc. cit.), it was shown that the relation between the valency of the complex radicals of the cobaltammines and their coagulating power on arsenious sulphide sol may be expressed by the following equation :

$$S_n = S_1 \times \frac{1}{N^4} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (6)$$

where S_n is the limiting concentration (eq. mol) of an N-valent complex ion. Combining (5) with (6), we obtain

$$C_A + \frac{1}{2^4} C_M + \frac{1}{3^4} C_B = \frac{C_{0A}}{S_1} S \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (7)$$

Eliminating the term of the concentrations by the substitution of (4) in (7), we get the following equation :

$$\frac{S-S_3}{S} = 1 - \frac{1}{k_1-k_2}\left(\frac{k_1}{2^4} - \frac{k_2}{3^4}\right)e^{-k_1t} + \left(\frac{1}{2^4} - \frac{1}{3^4}\right)\frac{k_1}{k_1-k_2} e^{-k_2t} \cdots\cdots (8)$$

Since S_1 and S_3 were known in the previous experiment, the equation (8) may be solved, if we could determine k_1 and k_2.

In order to determine these velocity constants, the initial and the last state of the reaction were considered. In the beginning of the reaction, we can assume $C_A + C_M = C_{0A}$ neglecting C_B which will be very small compared with C_A and C_M.

The velocity of decaying of the starting substance is

$$-\frac{dC_A}{dt} = k_1 C_A.$$

Now combining the following two equations

$$C_A + C_M = C_{0A}$$

$$S_1 C_A + S_2 C_M = C_{0A} S$$

we get

$$(S_1 - S_2) C_A = C_{0A}(S - S_2)$$

or

$$C_A = \frac{C_{0A}}{S_1 - S_2}(S - S_2).$$

Then, by the integration of the above mentioned velocity equation, we get

$$C_A = C_{0A} e^{-k_1 t}$$

and by the substitution,

$$\frac{S - S_2}{S_1 - S_2} = e^{-k_1 t}.$$

Using the common logarithm,

$$k_1 = \frac{2.303}{t} \log \frac{S-S_2}{S_1-S_2} \cdots\cdots\cdots\cdots\cdots\cdots \quad (9)$$

By the equation (9), k_1 was now calculated as below, taking $S_1=56$ and $S_2=20$.

TABLE 1.

Time (min.)	$S\times 60000$	k_1	mean
22.5	48	0.0111	0.011
56.0	40	0.0105	
92.0	30	0.0139	
120.5	20	0.172	

In the next calculation, the mean value of the first two of the third column in Table 1, namely $k_1=0.011$, was taken.

In the last stage of the substitution reactions, it is expected that there remains so small quantity of the trans-dichloro-diethylenediamine cobaltic chloride that it can be neglected as compared with those of the intermediate and the final salts. A quite similar method of computation can be applied to determine k_2, which is formulated as follows:

$$C_M + C_B = C_{0A}$$

$$S_2 C_M + S_3 C_B = C_{0A} S$$

$$(S_3 - S_2) C_B = C_{0A}(S - S_2)$$

$$C_B = \frac{C_{0A}}{S_3 - S_2}(S - S_2)$$

$$\frac{dC_B}{dt} = k_2 (C_M - C_B).$$

By integration

$$-\ln \frac{C_{0A}}{S_2 - S_3}(S - S_3) = k_2 t + \text{const.}$$

$$\ln \frac{S' - S}{S'' - S_3} = k_2 (t'' - t')$$

or

$$k_2 = \frac{2.303}{t'' - t'} \log \frac{S' - S_3}{S'' - S_3} \cdots\cdots\cdots\cdots\cdots\cdots \quad (10)$$

Table 2 shows the values of k_2, the mean of which, $k_2=0.0031$, was taken in the further calculation.

TABLE 2.

Time (min.)	$(S-S_3)\times 60000$	$t''-t'$	k_2
120.5	20	507	0.00317
154	16	473	0.00293
193	15	434	0.00304
259	13	368	0.00319
382	9	245	0.00330
507	6	120	0.00337
627	4	—	—

Now that $k_1=0.011$ and $k_2=0.0031$ had been determined, the equation (8) has been solved as below :

$$\frac{S-S_3}{S_1}=0.918\,e^{-0.011t}+0.0698\,e^{-0.0031t}\cdots\cdots(11)$$

Experimental. The method of determining the limiting concentration was entirely the same as in the previous case (loc. cit.) One c.c. of the sol was placed in each of ten carefully cleaned test-tubes of Jena glass which were kept in a thermostat regulated to be 25°C. A certain amount of the salt solution, kept in the same temperature, was taken out, from time to time and each set of the solutions of different dilutions were quickly prepared. Two c.c. of them were added to each of one c.c. of the sol. During addition, the tube were vigorously shaken to ensure thorough mixing. In this way two such concentrations were obtained that the lower did not show any perceptible coagulation whereas the higher did. This concentration was then more carefully examined if necessary and thus the limiting concentration was determined.

(1) (6) Dichloro-diethlenediamine cobaltic chloride, $\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\,(1)\\ \mathrm{Cl}\,(6)\end{matrix}\Big\}\,\mathrm{en}_2\right]\mathrm{Cl}$, which was used in this study was freshly prepared.(1) From the nature of this kind of experiments, an accuracy of high grade could not be expected. In Table 3, S (calc.) denotes the limiting concentration calculated by the equation (11), which could be compared with S (obs.). The theoretical values were fairly well concordant with the experimental. (See Table 3 and Fig. 1).

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(1) Joergensen, *J. prakt. Chem.*, (2) 39 (1889), 16.

TABLE 3.

Time (min.)	S (obs.)	S (calc.)
0	$56\times\frac{1}{60000}$	—
22.5	48 ,,	$51.8\times\frac{1}{60000}$
56	40 ,,	39.1 ,,
92	30 ,,	29.6 ,,
120.5	24 ,,	24.3 ,,
154	20 ,,	19.9 ,,
193	19 ,,	16.3 ,,
259	17 ,,	12.7 ,,
382	13 ,,	10.0 ,,
507	10 ,,	9.0 ,,
627	8 ,,	8.6 ,,

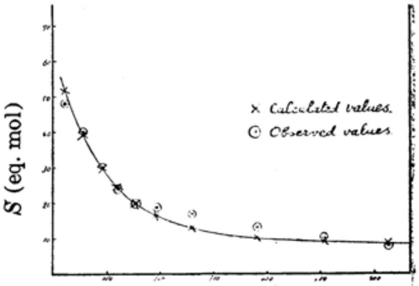

Fig. 1.

As regard the intermediate compound, $\left[\mathrm{Co}\,\begin{matrix}\mathrm{Cl}\ (1)\\ \mathrm{H_2O}\ (6)\end{matrix}\ \mathrm{en}_2\right]\mathrm{Cl}_2$, its concentration will become maximum, when

$$\frac{dC_M}{dt}=0$$

or

$$C_{0A}\times\frac{k_1}{k_2-k_1}\left(k_2\,e^{-k_2t}-k_1\,e^{-k_1t}\right)=0$$

Replacing $k_1=0.011$, $k_2=0.0031$ and equating $k_2e^{-k_2t}-k_1e^{-k_1t}=0$, we could easily find the time when the concentration of $\left[\mathrm{Co}\,\begin{matrix}\mathrm{Cl}\ (1)\\ \mathrm{H_2O}\ (6)\end{matrix}\ \mathrm{en}_2\right]\mathrm{Cl}_2$ was maximum. Namely,

$$t=\frac{2.303}{0.0079}(\log 0.011-\log 0.0031)=160.^{\mathrm{min.}}$$

The second differential of C_M, d^2C_M/dt^2, is equal to

$$C_{0A}\frac{k_1}{k_2-k_1}\left(k_1^2\,e^{-k_1t}-k_2^2\,e^{-k_2t}\right).$$

At the point where $d^2C_M/dt^2=0$, we find an inflexion point, the time of which could be calculated as below:

$$t=\frac{2.303\times 2\,(\log k_1-\log k_2)}{k_1-k_2}=320.^{\mathrm{min.}}$$

Similarly the inflexion point on the velocity curve of the final product of the substitution reactions could be computed thus:

$$\frac{d^2C_B}{dt^2}=\frac{C_{0A}k_1k_2^2}{k_2-k_1}e^{-k_2t}-\frac{C_{0A}k_1^2k_2}{k_2-k_1}e^{-k_1t}=0$$

or

$$k_2\,e^{-k_2t}=k_1\,e^{-k_1t}$$

Substituting $k_1=0.011$ and $k_2=0.0031$, we get $t=160^{\mathrm{min.}}$

The inflexion point of C_B curve coincide with the maximum point of C_M curve. (See Fig. 2).

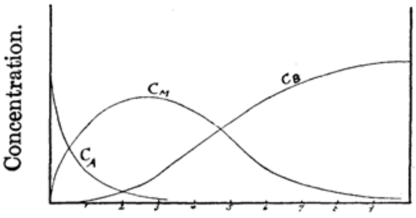

Fig. 2.

Summary.

1. By means of the coagulation of arsenious sulphide sol, the mechanism of the substitution reactions,

$$\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\,(1)\\ \mathrm{Cl}\,(6)\end{matrix}\,\mathrm{en}_2\right]\mathrm{Cl}\xrightarrow[\mathrm{aq}]{}\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\,(1)\\ \mathrm{H_2O}\,(6)\end{matrix}\,\mathrm{en}_2\right]\mathrm{Cl}_2\xrightarrow[\mathrm{aq}]{}\left[\mathrm{Co}\begin{matrix}\mathrm{H_2O}(1)\\ \mathrm{H_2O}(2)\end{matrix}\,\mathrm{en}_2\right]\mathrm{Cl}_3$$

has been studied, and it has been proved that this change is a monomolecular successive reaction.

2. The velocity constants of the first and second reaction of the substitution above mentioned has been calculated as $k_1=0.011$ and $k_2=0.0031$.

3. The time when the intermediate compound would be in its maximum concentration could be computed.

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