Photometric Study on the Change of Basic Rhodochromium Ion to Basic Erythrochromium Ion in Aqueous Solution*

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The so-called rhodochromium salt has attracted the attention of some investigators in coordination chemistry because of the peculiar reaction of its aqueous solution toward aqueous alkalis. This reaction may be represented by the scheme in Table I.

When Jörgensen discovered these salts, he thought that I and IV were isomers, while II was isomeric to III. Wilmarth, Graff and Gustin1) investigated this problem using various methods. By careful analyses they denied this isomerism and found the correct formulae of the basic erythro salt and the erythro salt to be as given in Table I.

The reaction II → III may, therefore, be considered as a kind of replacement reaction of the coordinated ammonia molecule. Wilmarth and others called attention to the ease with which this reaction occurs and attributed it to the peculiar structure of the basic rhodo salt with a possible π-bonding as demonstrated by their magnetic measurements. They also found by visual observation that the reaction velocity is not affected by the hydroxide ion concentration ranging from 10^{-4} to 6.0 N in alkali.

It seemed to the present authors that the quantitative study of the kinetics of this reaction II → III would be of value in knowing the energy relation and the

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1) W. K. Wilmarth, H. Graff and S. T. Gustin, *J. Am. Chem. Soc.*, **78**, 2683 (1956).

TABLE I

THE RELATION BETWEEN THE RHODOCHROMIUM SALT AND ITS DERIVATIVES

$$\begin{tikzcd}
\begin{matrix}\text{Rhodochromium Salt}\\ [Cr(NH_3)_5OHCr(NH_3)_5]X_5\\ \text{(I)}\\ \text{red}\end{matrix} \arrow[d, shift right, "\text{Alkali}"'] & \begin{matrix}\text{Erythrochromium Salt}\\ [Cr(NH_3)_5OHCr(NH_3)_4OH_2]X_5\\ \text{(IV)}\\ \text{red}\end{matrix} \arrow[d, shift right, "\text{Alkali}"'] \\
\begin{matrix}\text{Basic}\\ \text{Rhodochromium Salt}\\ [Cr(NH_3)_5OCr(NH_3)_5]X_4\\ \text{(II)}\\ \text{blue}\end{matrix} \arrow[u, shift right, "\text{Acid}"'] \arrow[r, "\text{Time}"'] & \begin{matrix}\text{Basic}\\ \text{Erythrochromium Salt}\\ [Cr(NH_3)_5OHCr(NH_3)_4OH]X_4\\ \text{(III)}\\ \text{red}\end{matrix} \arrow[u, shift right, "\text{Acid}"']
\end{tikzcd}$$

TABLE II

THE RESULT OF ANALYSIS OF DECAMMINE-μ-OL-DICHROMIUM(III) CHLORIDE PERCHLORATE

$[Cr(NH_3)_5OHCr(NH_3)_5]_2Cl_3(ClO_4)_7\cdot xH_2O$

	Cr	N	Cl	Cl in ClO_4	H_2O
Calcd. $x=0$	15.02	20.22	7.68	17.91	0
Calcd. $x=2$	14.64	19.71	7.49	17.46	2.54
Found in Sample I	15.10	19.56	7.40	16.45	1.74
Found in Sample II	15.22	18.78	7.18	16.78	2.8, 3.4
Found in Sample III	15.07	19.60	6.90	17.15	2.58
Found in Sample IV	15.27	19.82	7.53	17.02	1.57

The poor agreement of the analytical data with the calculated values in some samples is possibly due to the incomplete removal of perchloric acid owing to the fineness of crystals. Special attention has been paid in sample IV to avoid this. It seemed difficult to determine the content of water molecules on account of the slow decomposition of the complex at 100°C.

structure of the related compounds. These salts have characteristic absorption spectra in the visible and ultraviolet region and, therefore, the reaction velocities can be readily pursued by the aid of a spectrophotometer.

Experimental

Materials.—Decammine-μ-ol-dichromium(III) chloride perchlorate, $[Cr(NH_3)_5OHCr(NH_3)_5]_2Cl_3(ClO_4)_7\cdot xH_2O$ has been used in most of the present research. The chloride prepared as described by Jörgensen was converted into this salt by dissolution in water and addition of perchloric acid. Even recrystallization with perchloric acid did not alter the composition. The preparation of the perchlorate was the first aim, but it was found fairly difficult owing to the high solubility and ready decomposition of the salt. The results of analyses of some chloride perchlorate preparations are given in Table II.

Absorption Measurements.—The absorption mearsurement was carried out with a Beckman DU spectrophotometer. In the kinetic study a solution of rhodo salt (about 0.004 g. ion/l. in 0.1 N perchloric acid) and an equal volume of aqueous ammonia (about 4 N) were first mixed. At the moment of mixing ($t=0$) the whole complex salt should be of the form of basic rhodo salt (II), which will be changed to basic erythro salt (III) as the reaction proceeds. Then at proper intervals the absorbance (A_t) at 392 mμ and the time (t) of the measurement were recorded. Finally the absorbance was measured after the lapse of sufficient time, when the reaction was virtually complete. This absorbance A_∞ should correspond to that of the basic erythro salt (III). It is readily seen that A_t-A_∞ is proportional to the amount of the rhodo salt remaining at time t.

Results and Discussion

When $\log(A_t-A_\infty)$ is plotted against time, the resulting curves are nearly straight lines as shown in Figs. 1a~1d. The slight bending of the curve at the end of each experiment is possibly due to further decomposition of the basic erythro salt produced. A very slow change of absorbance is actually observed in a solution of purified basic erythro salt. However, its velosity is quite low compared with that of the main reaction and its effect seems negligible in the present discussion.

The reaction is, therefore, of the first order and represented by the equation:

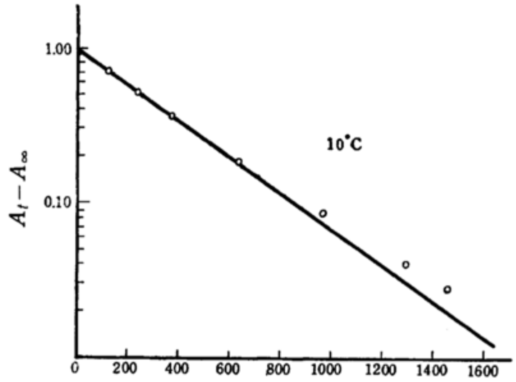

Fig. 1a.

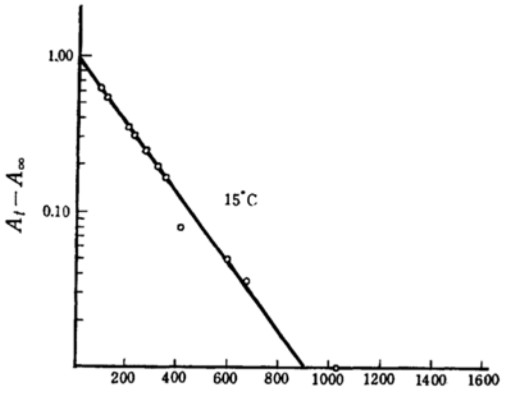

Fig. 1b.

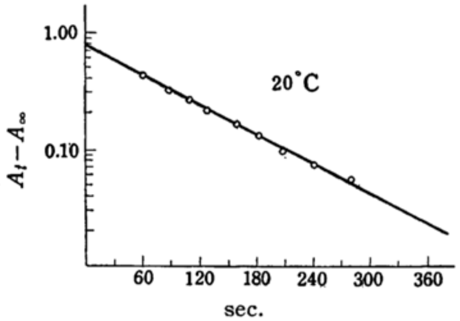

Fig. 1c.

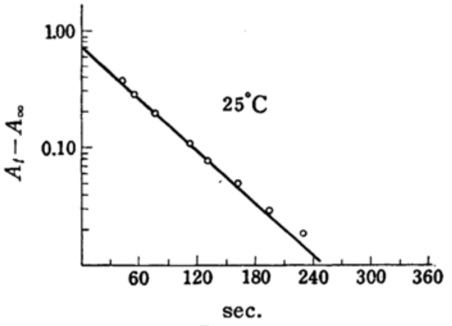

Fig. 1d.

Fig. 1. Change of A_t-A_∞ with time (in a semilog scale).

$$kt=\ln(A_0-A_\infty)-\ln(A_t-A_\infty)$$

where k is the velocity constant and A_0 is absorbance at $t=0$ and corresponds to the absorbance of the basic rhodo salt initially present. These values are readily estimated from the plot in Fig. 1. In Table III are given the velocity constant k and the half-value period $\tau=0.693/k$ obtained in this way.

TABLE III

THE VELOCITY CONSTANT AND HALF-VALUE PERIOD OF THE REACTION

T°C	10	15	20	25
$k\times10^3$	2.64	5.08	9.66	17.3
τ	258	136	72	40

The k values at different temperatures give us the energy of activation E, the frequency factor A and the entropy of activation $\Delta S^{\ddagger}$ according to the relations:

$$\ln k=\ln A-E/\boldsymbol{R}T$$

$$\ln A=\ln(\boldsymbol{k}T/\boldsymbol{h})+\Delta S^{\ddagger}/\boldsymbol{R}-1$$

The numerical data thus obtained are as follows: $E=21$ kcal/mole, $A=4.5\times10^{13}$ l./mole sec., $\Delta S^{\ddagger}=2$ kcal/deg. mole.

The effect of the hydroxide ion concentration on the reaction velocity was examined by the use of different species and concentration of alkalis. The result, given in Table IV, shows that the increase in the hydroxide ion concentration caused the decrease in the observed velocity constant. This decrease in the reaction velocity may be due to the increase in the viscosity of the solution; but there is also a possibility that some side reactions or slow deposition of hydrous chromium oxide increased the apparent absorption, and consequently decreased the calculated velocity constant. However, the fact that the reaction is not accelerated by the hydroxide ion excludes the possibility of the $S_{N}2$ mechanism involving a direct attack of the complex by the hydroxide ion.

TABLE IV

THE EFFECT OF THE HYDROXIDE ION CONCENTRATION ON THE VELOCITY CONSTANT AT 10°C

Concentration of the complex (In the reacting system)	Concentration of the alkali (In the reacting system)	k
0.00215 g. ion/l.	2.25 N in NH_3	0.00264
0.00107 〃 〃	3.37 N in NH_3	0.00259
0.00107 〃 〃	0.0735 N in NaOH	0.00237
0.00215 〃 〃	0.490 N in NaOH	0.00223
0.00107 〃 〃	0.735 N in NaOH	0.00214

The addition of sodium perchlorate to the reacting system at 20°C showed that the ionic strength over 0.08 to 1.32 has little effect on the velocity constant. When the concentration of sodium perchlorate exceeded 2.5F, the reaction velocity seemed to decrease, but the fluctuation of the data was significant. This fluctuation may be due to the formation of a fine precipitate of basic rhodo perchlorate even though not visually perceptible.

As seen from the preceeding argument, the aqueous solution of basic rhodo salt is unstable, so that it is difficult to obtain its absorption spectrum directly. When the kinetic data are available, however, the absorbance of the basic rhodo salt (A_0) can be derived from A_t and A_∞ by calculation or on the graph. The curve of the absorption spectrum drawn in this way is shown in Fig. 2. The very characteristic feature of the absorption spectrum probably demonstrates the different electronic structures of the basic rhodo salt from those of other chromium ammines, but the assignment of any electronic transition to each observed absorption band possibly requires a further investigation.

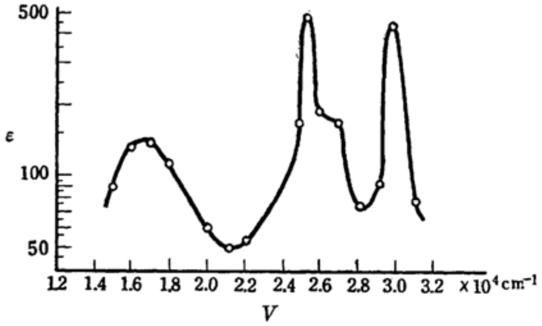

Fig. 2. Absorption spectrum of basic rhodo salt obtained from kinetic data.

Summary

The conversion reaction of the basic rhodo ion to the basic erythro ion in an alkaline solution was found to be of the first order. The velocity constants at 10°, 15°, 20° and 25°C were measured, and the energy of activation, the frequency factor and the entropy of activation calculated. The reaction velocity appeared to be somewhat diminished by higher concentration of sodium hydroxide. The absorption spectrum of unstable basic rhodo salt was derived from the kinetic data.

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