

Kinetics of Silver Catalyzed Aquation of Chloropenta-Aminocobalt (III) Perchlorate at 50°C

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Summary: The silver ion induced aquation of $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ has been carried out at 50°C and constant ionic strength (0.80 M). The rate of reaction is expressed empirically as $k_{\text{obs}} C = k_0 C + \frac{C[\text{Ag}]_0}{a + [\text{Ag}]_0}$ where a and b take the values of 50 and 6.3 respectively. Suitable mechanism has been proposed to explain the kinetic data and the significance of the empirical constants a and b are discussed.

Introduction

Many studies on metal ion induced aquation of halogenopenta-amminecobalt (III) and chromium (III) complexes have been reported [1-7]. However, very few studies have been reported in the case of Ag(I). Lalor and Rusted studied the kinetics of Ag(I)-catalyzed aquation of iodopenta-amminecobalt (III) [8] and of chromium analogue [9] where the reaction was found to proceed via homogeneous and heterogeneous pathways.

The present investigation is concerned with a study of the Ag(I) catalyzed aquation of the chloropenta-amminecobalt (III) ion, which has not been studied before, from the mechanistic view point.

Experimental

AnalaR grade chemicals were used. Chloropenta-amminecobalt (III) nitrate

was prepared as recommended [10] and converted to perchlorate from warm acidified solution of concentrated LiClO_4 by cooling in ice-water. The product was washed until free from acid using alcohol and ether and then dried at 60°C. Anal. calcd. for cobalt and perchlorate, are 15.57 and 52.57 %; found, 15.43 and 52.36% respectively. The molar extinction coefficient was found to be 50 at 530 nm which is in good agreement with that reported in literature [11]. Silver perchlorate was prepared from silver oxide and perchloric acid. Its slightly acidified stock solution was standardised and stored away from light.

The kinetic measurements were made at 50°C. A well-stoppered pyrex flask is used as a reaction vessel. The reaction is initiated by the addition of a weigh quantity of the chloro-complex to a silver perchlorate solution con-

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Table-1: Typical kinetic run for Ag(I) catalyzed aquation of $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ complex.

$$[\text{AgClO}_4] = 0.050 \text{ M} \quad \mu = 0.80 \text{ M} \quad A_\infty = 0.0080$$

$$[\text{Complex}] = 0.0015 \text{ M} \quad T = 50^\circ\text{C}$$

| Time in min | A_t | $A_t - A_\infty$ | $Y = \log(A_t - A_\infty) + 1$ | ΔY | Δt |
|-------------|-------|------------------|--------------------------------|------------|------------|
| 10 | 0.563 | 0.555 | 0.744 | 0.000 | 0 |
| 20 | 0.523 | 0.515 | 0.712 | 0.032 | 10 |
| 30 | 0.454 | 0.446 | 0.649 | 0.095 | 20 |
| 40 | 0.434 | 0.426 | 0.629 | 0.115 | 30 |
| 62 | 0.388 | 0.380 | 0.580 | 0.164 | 52 |
| 87 | 0.350 | 0.342 | 0.534 | 0.210 | 77 |
| 120 | 0.255 | 0.247 | 0.393 | 0.351 | 110 |
| 145 | 0.220 | 0.212 | 0.326 | 0.418 | 135 |
| 155 | 0.202 | 0.194 | 0.288 | 0.456 | 145 |
| 177 | 0.186 | 0.178 | 0.250 | 0.449 | 160 |

taining 0.0010 M HClO_4 after the latter was equilibrated in a thermostat. Aliquots (10 ml) are removed at fixed intervals using a rapid delivery pipette, cooled to 0°C and filtered through a fine fritted-glass filter and the optical densities are measured in 1-cm cells at 280 nm.

Results and Discussion

(a) Spectral studies

In order to detect the possible formation of reaction intermediate, spectrophotometric studies were carried out in the visible region in a thermostated cell-holder at 10°C to retard the aquation reactions.

The concentration of the chloro-complex (slightly acidified with HClO_4) was kept constant at $7.9 \times 10^{-3} \text{ M}$ while that of the AgClO_4 was varied between 1.0×10^{-4} and $1.2 \times 10^{-3} \text{ M}$.

However, there is nothing in the shape of the curves, but a relatively small increase in O.D. at 530 nm is observed indicating the existence of an intermediate.

This reaction intermediate is probably a silver adduct, whose concentration is very small as indicated by the relatively small increase in O.D. at 530 nm. Such behaviour was previously

found in the iodo-complex reaction analogue [8].

(b) Kinetic studies

A series of kinetic runs are carried out in which AgClO_4 varies from 0.050 to 0.300 M at fixed ionic strength of 0.8 M using LiClO_4 . The kinetic data of a typical run is shown in table 1. The linear first order plot is represented by the equation

$$-\Delta [\log (A_t - A_\infty)] = k_{\text{obs}} \Delta t \dots (1)$$

where A_t and A_∞ are the optical densities (measured at 280 nm) at time t and infinity time respectively. The first order plots are presented in Fig.1. A linear least square computer program is used to fit the kinetic data to equation (1). The computed k_{obs} values for each AgClO_4 are tabulated in table 2. A linear plot of $1/(k_{\text{obs}} - k_0)$ versus $1/[\text{Ag}^+]_0$ with a positive slope and a positive intercept is obtained (Fig.2), where k_0 and $[\text{Ag}^+]_0$ are the spontaneous first order rate constant and the stoichiometric concentration of AgClO_4 respectively; the correlation coefficient being 1.000. The empirical rate equation for the Ag(I)-catalyzed aquation can be represented by:

$$\frac{1}{(k_{\text{obs}} - k_0)} = a + \frac{b}{[\text{Ag}^+]_0} \dots (2)$$

a and b takes the values of 50 and 6.3 respectively

The proposed reaction mechanism

Equation (2) can take another form as,

$$k_{\text{obs}} = k_0 + \frac{[\text{Ag}^+]_0}{b + a [\text{Ag}^+]_0} \dots (3)$$

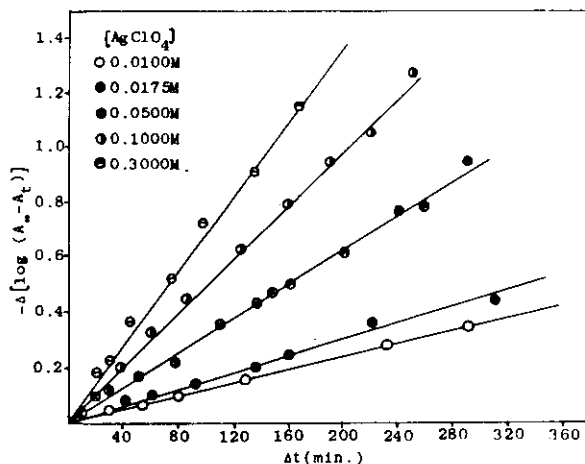


Fig.1: First order plots of the Ag(I)-catalyzed equation of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$.

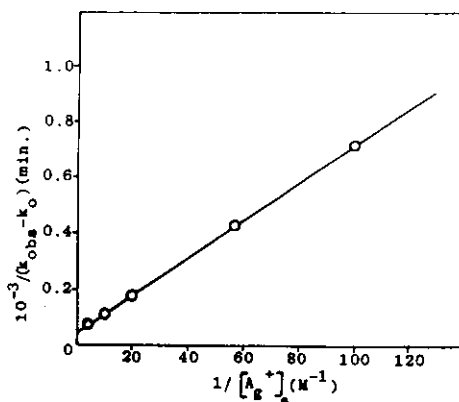


Fig.2: Plot of $1/(k_{\text{obs}} - k_0)$ versus $1/[\text{Ag}^+]_0$

In order to discuss the empirical rate equation (3) and to give significance to the empirical constants a and b , a proposed reaction mechanism is considered as,

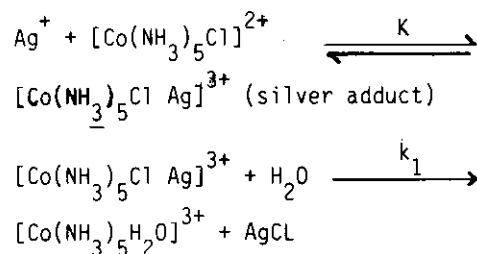


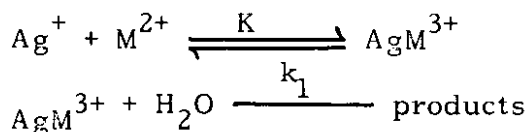
Table-2: Values of k_{obs} at different $[\text{AgClO}_4]$

$$\mu = 0.8 \text{ M} \quad T = 50^\circ\text{C}$$

$$k_o = 1.350 \times 10^{-3} \text{ min}^{-1}$$

| $10^2 [\text{AgClO}_4]$ | $10^3 (k_{\text{obs}} + S)$ (min^{-1}) | $10^{-3} / (k_{\text{obs}} - k_o)$ (min.) | $1 / [\text{Ag}^+]_o (\text{M}^{-1})$ |
|-------------------------|--|--|---------------------------------------|
| 1.00 | 2.76 ± 0.10 | 0.710 | 100.00 |
| 1.75 | 3.68 ± 0.21 | 0.430 | 57.14 |
| 5.00 | 7.14 ± 0.14 | 0.173 | 20.00 |
| 10.00 | 11.28 ± 0.09 | 0.101 | 10.00 |
| 30.00 | 15.66 ± 0.28 | 0.070 | 3.33 |

The above mechanism can be simply represented as,



where $\text{M}^{2+} = [\text{Co}(\text{NH}_3)_3\text{Cl}]^{2+}$

omitting charges, thus,

$$K = \frac{[\text{AgM}]}{[\text{Ag}]_o (\text{C} - [\text{AgM}])} \quad (4)$$

Where $\text{C} \ll [\text{Ag}]_o$ is the stoichiometric concentration of complex salt.

The overall reaction rate is expressed by:

$$\text{rate} = k_{\text{obs}} \text{C} = k_o \text{C} + k_1 [\text{AgM}] \dots \quad (5)$$

Substituting from (4) in (5) we obtain,

$$K_{\text{obs}} = K_o + \frac{[\text{Ag}]_o}{\frac{1}{k_1 k} + \frac{[\text{Ag}]_o}{k_1}} \dots \dots (6)$$

Equation (6) explains the empirical rate equation (3) where $a = 1/k_1 K$ and $b = 1/k_1$. Using the values of a and b one can determine the values of k_1 and K as 3.33×10^{-4} and 7.94 M^{-1} respectively.

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