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THE SOLID-STATE POLYMERIZATION OF CYANOTETRAMMINECOBALT(III)-μ-CYANOAQUOTETRAMMINE-COBALT(III) PERCHLORATE: EFFECT OF WATER VAPOR PRESSURE

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ABSTRACT

The effect of the water vapor pressure on the solid-state polymerization reaction of cyanotetramminecobalt(III)-μ-cyanoaquotetramminecobalt(III) perchlorate was investigated. The reaction temperature increased with increasing water vapor pressure. At a constant water vapor pressure, the reaction temperature increased as the heating rate increased. A reaction mechanism for these phenomena is postulated.

INTRODUCTION

The kinetic and thermodynamic parameters associated with the solid-state polymerization of the compound, $[Co(NH_3)_4(H_2O)\text{-}CN\text{-}Co(NH_3)_4(CN)](ClO_4)_4$, have recently been determined[1]. The reaction[2], which is similar to others previously described[3-5], involves the evolution of coordinated water and the formation of cyanide bridges between the cobalt(III) ions, according to the equation:

$$n[Co(NH_3)_4(H_2O)\text{-}CN\text{-}Co(NH_3)_4(CN)](ClO_4)_4 \rightarrow [\sim Co(NH_3)_4\text{-}CN\text{-}Co(NH_3)_4\text{-}CN\sim]_n(ClO_4)_{4n} \qquad (1)$$

A change in crystal structure apparently accompanies the polymerization reaction[1]. The reaction temperatures were found to be dependent not only on the heating rate but also on the presence or absence of water vapor in the furnace temperature. This fact suggested that a more quantitative study of the effects of the water vapor pressure on the reaction temperature may shed some light on the nature of the reaction mechanism. In this investigation, the reaction temperatures for various water partial pressure values in the furnace chamber were determined for different heating rates.

EXPERIMENTAL

Compound

The compound, $[Co(NH_3)_4(H_2O)\text{-}CN\text{-}Co(NH_3)_4(CN)](ClO_4)_4$, was obtained from the Sandia Corporation, Albuquerque, New Mexico.

TG studies

The reaction temperatures were determined by the use of a DuPont Model 950 thermogravimetric analyzer. The water vapor partial pressure in the furnace chamber was controlled by bubbling nitrogen gas through various aqueous solutions with known vapor pressures and then through the furnace chamber. The solutions used, along with their water vapor pressures, are listed[6] in Table I. Sample sizes from 2 to 5 mg were studied at heating rates of 5, 10, and 15°C/min.

TABLE I

VAPOR PRESSURES OF VARIOUS AQUEOUS SOLUTIONS[6] AT 25°C

Solution	*Relative humidity*	*Vapor pressure (mm Hg)*
Distilled water	1.00	24
Saturated $(NH_4)_2SO_4$	0.81	19
Saturated $Ca(NO_3)_2$	0.51	12
Saturated $CaCl_2$	0.31	7

RESULTS AND DISCUSSION

The TG curves for reaction (1) are given in Fig. 1. As can be seen, the temperature at which reaction occurs increases with increasing water vapor pressure, if the heating rate is constant. Similar effects have been noted under self-generated atmospheres[7]. With constant water vapor pressure, the temperature at which reaction occurs increases with increasing heating rate.

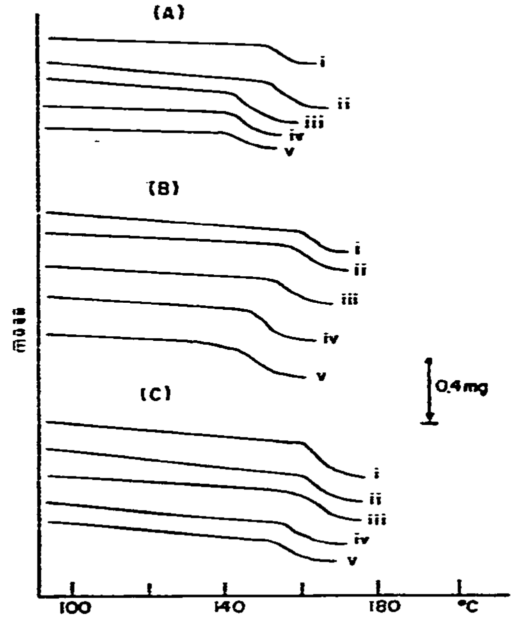

Fig. 1. TG curves for reaction (1). Heating rate: A, 5°C/min; B, 10°C/min; C, 15°C/min. Vapor pressure in mm Hg: i, 24; ii, 19; iii, 12; iv, 7; v, 0.

The reaction temperatures were determined as illustrated on the idealized TG curve in Fig. 2. The temperature, T_r, at the intersection of the extrapolated lines was taken as the reaction temperature. Values of T_r obtained in this manner are listed in Table II.

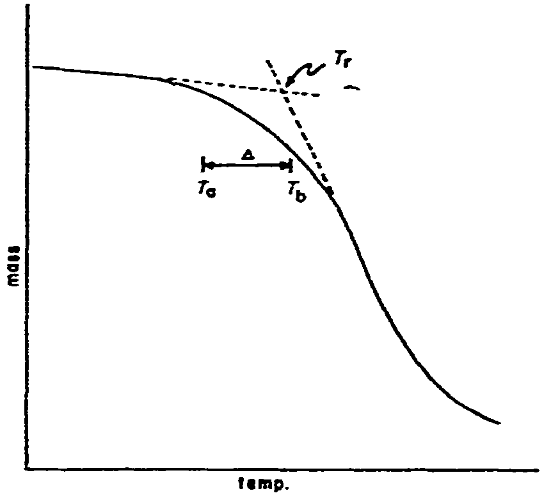

Fig. 2. Idealized TG curve. T_r, reaction temperature; T_A, temperature below which equilibrium (3) predominates; T_B, temperature above which reaction (4) predominates; Δ, $T_B - T_A$, temperature interval in which reactions (3) and (4) compete.

TABLE II

REACTION TEMPERATURES

Heating rate (°C/min)	*Water vapor pressure (mm Hg)*	*Reaction temperature (°C)*
5	24	151
5	19	149
5	12	144
5	7	140
5	0	137
10	24	159
10	19	156
10	12	151
10	7	149
10	0	145
15	24	161
15	19	160
15	12	158
15	7	152
15	0	148

Plots of the water vapor pressure *vs.* T_r for each heating rate employed are illustrated in Fig. 3. A straight line was obtained, the slopes of which were, within experimental error, independent of the heating rate, although the intercepts decreased with increasing heating rates. The values of the slopes and intercepts of the curves

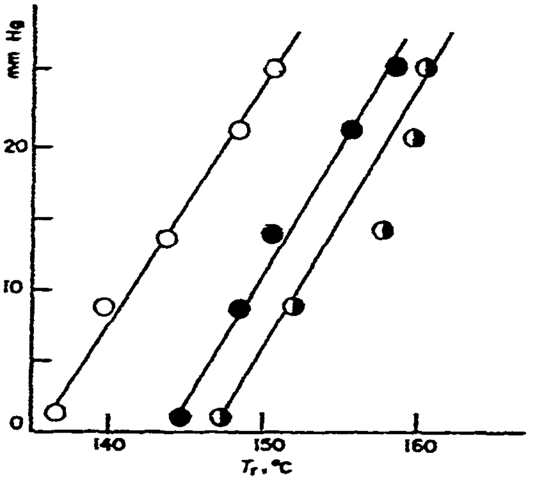

Fig. 3. Plots of water vapor pressure *vs.* reaction temperature. ○, 5°C/min; ●, 10°C/min; ◑, 15°C/min.

are listed in Table III. The water vapor pressure dependence of the reaction temperature of reaction (1) described by the equation:

$$p_{H_2O} = ST_r + I(\beta) \quad (2)$$

where p_{H_2O} is the water vapor pressure, S the slope, and $I(\beta)$ the intercept, which is a function of the heating rate, β.

TABLE III

VALUES OF THE SLOPES AND INTERCEPTS OF THE PLOTS OF WATER VAPOR PRESSURE *vs.* REACTION TEMPERATURE

Heating rate (°C/min)	*Slope (mmHg/°C)*	*Intercept (mm Hg)*
5	1.65	−136.3
10	1.74	−144.5
15	1.73	−147.4
Average	1.71 ±0.05[a]	

[a] Standard deviation.

Since the reaction depends upon the water vapor pressure, an equilibrium must exist in the reaction mechanism. However, the reaction is irreversible, even if stopped after only a small amount of water has evolved. Thus, there must be an irreversible step in the reaction which is apparently not connected with the crystalline rearrangement. These facts suggest the following reaction mechanism:

$$M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M^* + H_2O \quad (3)$$

$$M^* \xrightarrow{k_2} P \quad (4)$$

where M is the reactant, M^* the intermediate perhaps involving a 5-coordinated cobalt(III) ion and P the polymer product. Reaction (3) is the equilibrium step responsible for the dependence on the water vapor pressure while reaction (4) is the irreversible step.

For an isothermal reaction, the rate equation could easily be obtained from the above mechanism. In the case of a nonisothermal reaction, however, the steady-state approximation may not be valid; hence the rate equation is not easily obtained. However, the qualitative behavior of the reaction may be ascertained from Fig. 2. Assuming the mechanism given in Eqns. (3) and (4), it is apparent that at temperatures below T_A, the equilibrium [Eqn. (3)] predominates; little or no weight is lost and $k_{-1}\, p_{H_2O} > k_2$. At temperatures above T_B, however, the irreversible reaction [Eqn. (4)] predominates since weight is rapidly lost; therefore $k_2 > k_{-1}\, p_{H_2O}$. It follows that at some temperature not greatly different from T_r in the rather small interval Δ, the following relationship must exist:

$$k_1\, p_{H_2O} = k_2 \tag{5}$$

Eqn. (5) predicts the dependence of the reaction temperature on the water vapor pressure, the temperature being included in the rate constant in the usual Arrhenius manner. Therefore, the mechanism given by Eqns. (3) and (4) explains both the water vapor dependence of the reaction temperature and the fact that the reaction is irreversible.

It should be pointed out that although the postulated mechanism does explain the fact that the reaction is dependent on the water vapor pressure, it does not explain the *linear* relationship between T_r and p_{H_2O}. The several complicated factors which are involved are: First, because of the equilibrium step [Eqn. (3)] the sample generates a water vapor pressure in its immediate vicinity above that in the nitrogen gas in the reaction chamber. Since the equilibrium is temperature dependent, the water vapor pressure in the immediate vicinity of the sample is temperature dependent. Secondly, the water molecules in the immediate vicinity of the sample, which are the result of the equilibrium, may diffuse away from the sample due to the vapor pressure gradient. The rate of diffusion is also temperature dependent. Because of these complicated factors the simple linear relationship between T_r and p_{H_2O} is surprising and cannot at present be explained.

Finally it is apparent that the dependence of the reaction temperature on the heating rate is readily explained when the diffusion of water away from the immediate vicinity of the sample is considered. For a low heating rate, the water vapor pressure in the immediate vicinity of the sample is less than at a high heating rate because there is more time available for the diffusion of water away from the sample. Because of the smaller water vapor pressure, the reaction temperature is lower for a lower heating rate than for a higher one.

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