BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3468—3471 (1970)

The Thermal Decomposition of $CuBr_2 \cdot 2NH_3$ and $CuBr_2$

Nobuyuki TANAKA and Masahiro KAGAWA*

Department of Chemistry, Faculty of Science, Tohoku University, Katahira, Sendai

(Received July 8, 1970)

The thermal decomposition of $CuBr_2 \cdot 2NH_3$ has been examined at the constant temperature, about 220°C. Copper(II) was reduced to copper(I), when bromine gas was found as one of the decomposition products, indicating that bromide anion may be the reducing agent for copper(II). The decomposition reaction of $CuBr_2$ has been investigated by measuring the weight loss under the condition of the constant temperature. In a closed system, the reaction,

$$CuBr_2(s) \leftrightarrows \gamma\text{-}CuBr(s) + \frac{1}{2}Br_2(g)$$

attained to equilibrium, and ΔG° for this reaction was determined in the range from 160°C to 220°C to be given by the equation,

$$\Delta G^\circ(\text{cal.}) = 1.10 \times 10^4 - 19.3\ T\ (160°\text{C—}220°\text{C}).$$

While the pressure of bromine gas was kept zero, $CuBr_2$ decomposed following a first-order rate law in the beginning of the decomposition, and the activation energy was found to be 25.4 kcal/mol.

When hexammine-[1-3] or aquopentammine-copper(II)[4] halides are heated, they lose ammonia or ammonia and water to form diammine complexes, $CuX_2 \cdot 2NH_3$ (X=Cl, Br and I). At higher temperatures, diammine complexes decompose with an electron transfer reaction and produce copper(I) halides, ammonia and other decomposition products. Smith and Wendlandt[3] showed that the primary reducing agent for copper(II) was ammonia in the case of the bromide and the chloride. There is, however, still left the possibility that halide anion may take part in reducing copper(II). In this investigation, therefore, the electron transfer reaction of $CuBr_2 \cdot 2NH_3$ was reexamined carefully. In addition, the thermal decomposition of $CuBr_2$ was studied as a simpler case of the electron transfer reaction of copper(II) complexes.

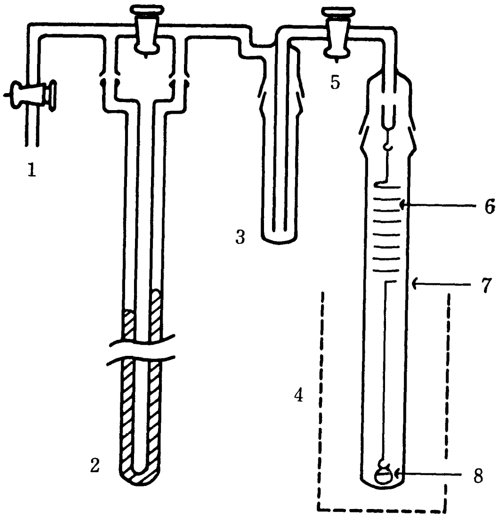

Fig. 1. Apparatus used for the manometric measurement of decomposition reactions.
(1) Outlet to vacuum pump, (2) mercury manometer, (3) trap, (4) electric furnace, (5) cock A, (6) spring balance, (7) reaction tube and (8) crucible.

Experimental

The Thermal Decomposition of $CuBr_2 \cdot 2NH_3$. Figure 1 shows the apparatus used in this experiment. $CuBr_2$ was put into a crucible, and ammonia gas (about 1 atm.) was introduced into the reaction tube with checking a manometer. $[Cu(NH_3)_6]Br_2$ was formed one or two days later. The reaction tube was heated at about 220°C by an electric furnace. In heating, the pressure of ammonia was kept 1 atm., because ammonia was evolved from $[Cu(NH_3)_6]Br_2$. Then, $CuBr_2 \cdot 2NH_3$ was formed. A trap was cooled with the freezing mixture, alcohol-dry ice. Ammonia gas was rapidly removed from the reaction tube by operating a vacuum pump and opening the cock A. The pyrolysis products were condensed in a cooled trap.

---

* Present address: The Research Institute for Iron, Steel and Other Metals, Tohoku University, Katahira, Sendai.

1) W. Biltz, H. Bröhan and W. Wein, *Z. Anorg. Allg. Chem.*, **148**, 207 (1925).

2) F. Ephraim, *Ber.*, **52**, 940 (1919).

3) J. P. Smith and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, **26**, 1157 (1964).

4) G. G. Urazov, A. K. Kirakosyan and V. D. Galustyan, *Zh. Neorg. Khim.*, **2**, 1094, 1104 (1957).

The Thermal Decomposition of $CuBr_2$. The same apparatus as shown in Fig. 1 was used. The manometer was detached when $CuBr_2$ was treated, because mercury reacts with bromine gas evolved from $CuBr_2$. $CuBr_2$ was put into a quartz crucible (121 mg), which was hung on a quartz spring balance (4.10 mg/mm in sensitivity). The contraction due to the weight loss of the sample was measured with a cathetometer (0.05 mm in accuracy). The reaction tube of Pyrex glass was kept at a constant temperature in the range of ±1°C with the electric furnace. As bromine gas reacts with mercury even at room temperature, the pressure of bromine gas cannot be directly measured with a mercury manometer. It, however, could be calculated from the equation, $PV=n\boldsymbol{R}T$, P being the pressure of bromine gas, V, the volume of the reaction tube (0.162 l), n, moles of bromine gas calculated from the observed weight loss, T, absolute temperature, and $\boldsymbol{R}$, gas constant. As the upper part of the reaction tube, however, was left at room temperature, the correction due to this difference in temperature must be considered in calculating the pressure. The values for this correction were obtained experimentally as follows. The trap was removed and the manometer was directly connected to the reaction tube so that the volume between the reaction tube and the manometer could be made as small as possible. From the weight loss at t°C, the pressure of bromine gas, P_{25} was calculated when the whole part of the reaction tube was supposed to be at room temperature, 25°C. Nitrogen gas, the pressure of which was P_{25} was introduced at the room temperature into the reaction tube with checking the manometer. When the reaction tube was heated under the same experimental condition as in the treatment of $CuBr_2$, the pressure of nitrogen gas increased to P_t. From P_t and P_{25}, the correction coefficient, γ_t, characteristic to only this apparatus was obtained as,

$$\gamma_t = P_t/P_{25} \text{ (1.12 at 160°C, 1.14 at 215°C).}$$

Assuming that γ_t was applicable to the case of bromine gas, P_{Br_2} which means the pressure of bromine gas at t°C is given by

$$P_{Br_2} = \gamma_t \times P_{25}$$

In this correction, the volume change of the reaction tube due to heating and the quantity of adsorbed bromine on the wall of the reaction tube were neglected.

After the reaction,

$$CuBr_2(s) \rightleftarrows CuBr(s) + \frac{1}{2}Br_2(g),$$

had reached to the equilibrium completely, a vacuum pump was operated and the cock A was opened. The reaction proceeded to the right side. The time when the cock A was opened was defined as time zero, and the weight loss was followed. The weight loss was converted to the degree of decomposition, α (α equals 0 when the sample was $CuBr_2$, and 1 when the reaction finished and $CuBr_2$ was changed completely to CuBr), and, then, α *vs.* t(time) curves were obtained. Though α at time zero was different according to the temperature, the largest value of α in this experiment was 0.05, which was found in the measurement at 134°C. The sample taken for the measurement ranged from 15 to 25 mg. $CuBr_2$ used in the kinetic investigation had been pulverized as small as possible using an agate mortar in the room where relative humidity was kept under 40%, because $CuBr_2$ was very deliquescent.

Results and Discussion

The Thermal Decomposition of $CuBr_2 \cdot 2NH_3$. $CuBr_2 \cdot 2NH_3$ did not decompose in a closed system as long as ammonia coexisted. It, however, decomposed when the pressure of ammonia was suddenly reduced, and bromine was found to condense on the wall of the cooled trap. These results indicate that the equilibrium has established between ammonia gas and solid $CuBr_2 \cdot 2NH_3$ before the electron transfer reaction occurs, and that bromide anion takes part in reducing copper(II). The latter result is inconsistent with that of Smith and Wendlandt.[3] They reported that, as the temperature was raised, higher ammine complexes such as $[Cu(NH_3)_6]Cl_2$, $[Cu(NH_3)_6]Br_2$ and $[Cu(NH_3)_4]I_2$ reversibly dissociated ammonia, and diammine complexes, $CuX_2 \cdot 2NH_3$ (X=Cl, Br and I) were formed. Upon further heating, the irreversible reduction of copper(II) to copper(I) took place, of which stoichiometries were

$$6CuX_2 \cdot 2NH_3 \rightarrow 6CuX + 6NH_4X + N_2 + 4NH_3 \quad (X=Cl,\ Br)$$

$$2CuI_2 \cdot 2NH_3 \rightarrow 2CuI + I_2 + 4NH_3$$

These equations indicate that iodide anion reduces copper(II) in the case of the iodide whereas ammonia does in the case of the chloride and the bromide.

Some questions, however, arose about their discussion on the electron transfer reactions, and a new explanation will be given to their results.

(1) The above stoichiometries may be explained from the standpoint that halide anions reduce copper(II). After the halide anion donates an electron to copper(II), it reaches to the active state of atom or forms halogen gas, which in turn reacts with ammonia. Consequently, nitrogen and ammonium halide are formed by the following reaction.

$$8NH_3 + 3X_2 \text{ (or } X^*) \rightarrow 6NH_4X + N_2$$
$$X=Cl,\ Br;\ X^*=\text{active atom}$$

Really this reaction proceeds very fast at room temperature.

(2) The temperature at which the reduction of copper(II) took place was found to increase in the following order:

the iodide < the bromide < the chloride

As this order is consistent with that of the depolarizability, halide anions are suggested to be the reducing agent for copper(II).

(3) If ammonia reduces copper(II), the electron transfer reaction is expected to take place easily at the state of hexammine complexes where copper(II) is coordinated with six ammonia molecules. It, however, took place after $CuX_2 \cdot 2NH_3$

was formed in which halide anions were coordinated with copper(II).

(4) Gažo⁵⁾ has already discussed the effect of coordinated ammonia on the reduction of copper (II). CuI_2 does not exist at room temperature whereas $CuI_2 \cdot 2NH_3$ is stable even when it is heated at 100°C in ammonia atmosphere. Usually the reduction temperature of $CuX_2 \cdot 2NH_3$ (X=Cl, Br) is higher than that of CuX_2. These facts suggest that coordinated ammonia can not promote the reduction of copper(II), but can hinder the electron transfer from halide anion to copper(II).

These explanations suggest that the coordinated halide anion can have more chance to reduce copper(II) than the coordinated ammonia. Although the results obtained in this investigation cannot completely deny that ammonia is reducing agent, its possibility might be considered less. Therefore, the following reactions may be the main paths of the decomposition.

$$CuBr_2 \cdot 2NH_3 \rightleftarrows CuBr_2 \cdot NH_3 + NH_3 \tag{1}$$

$$CuBr_2 \cdot NH_3 \rightleftarrows CuBr_2 + NH_3 \tag{2}$$

$$CuBr_2 \rightarrow CuBr + \frac{1}{2}Br_2 \tag{3}$$

$$CuBr_2 \cdot NH_3 \rightarrow CuBr \cdot NH_3 + \frac{1}{2}Br_2 \tag{4}$$

$$CuBr \cdot NH_3 \rightarrow CuBr + NH_3 \tag{5}$$

$$8NH_3 + 3Br_2 \rightarrow 6NH_4Br + N_2 \tag{6}$$

The equilibrium reactions (1) and (2) well explain the fact shown by Smith and Wendlandt³⁾ that the reduction temperatures observed with mass spectrometry were lower than those obtained by thermomagnetic analysis; the former was carried out in vacuum while the latter was in ammonia atmosphere.

The Thermal Decomposition of $CuBr_2$. When $CuBr_2$ was heated in vacuum after the cock A was closed, bromine gas was evolved and the weight loss was observed. The weight loss reached to a constant value within one or two hours, which did not change even after twenty four hours. When the evolved bromine was evacuated from the system, the weight loss began again and arrived at a new constant value. When $CuBr_2$ was heated in vacuum, the weight loss reached to a value which would be obtained when all of $CuBr_2$ was assumed to change completely to CuBr. This suggests that there must be the equilibrium reaction

$$CuBr_2(s) \rightleftarrows CuBr(s) + \frac{1}{2}Br_2(g)$$

The weight loss in equilibrium was measured under the following conditions: (1) The quantity and the grain size of $CuBr_2$ were changed, (2) inert gas, N_2, was introduced into the system, (3) the equilibrium was made to establish from the side of $CuBr_2$ or from that of $CuBr+1/2\ Br_2$. As the result, the weight loss was found to be independent of these conditions, but dependent only on temperature. This means that the pressure of bromine gas is constant provided that the temperature is given, *i.e.*, the equilibrium of the electron transfer of $CuBr_2$ is dependent on the pressure of bromine gas or temperature.

The weight loss was measured at various temperatures and it was converted to the pressure by following the procedure described in the experimental section. The linearity was obtained between $\log P_{Br_2}$ and $1/T$ as shown in Fig. 2, which is represented by

$$\log P_{Br_2} = 8.43 - \frac{4.79\times10^3}{T}$$

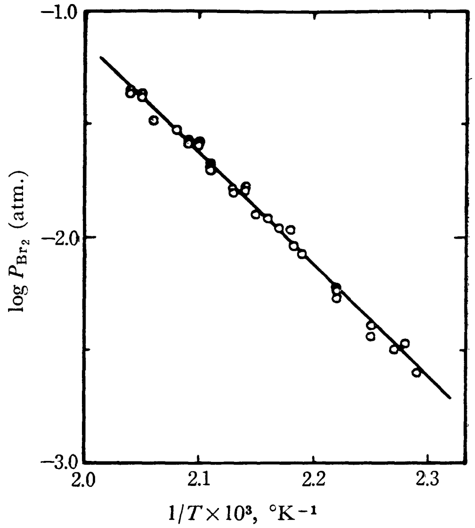

Fig. 2. Temperature dependence of the equilibrium pressure of bromine gas.

As the standard free energy change, $\Delta G°$, is expressed by

$$\Delta G° = -\boldsymbol{R}T\ln K_p = -\boldsymbol{R}T\ln P_{Br_2}^{1/2}$$

where K_p is the equilibrium constant, $\Delta G°$ for the reaction is given by

$$\Delta G°\ (\text{cal.}) = 1.10\times10^4 - 19.3\ T$$

in the range from 160°C to 220°C.

The structural investigations of $CuBr_2$⁶⁾ and CuBr⁷⁾ have been reported. $CuBr_2$ has the polymeric chain structure in which a bromine atom bridges two copper(II) atoms and a copper(II) atom is coordinated with four bromine atoms. The bond Cu–Br largely bears covalency. CuBr has three modifications of α-, β- and γ-forms, and transition temperatures are 385°C for γ to

---

5) J. Gažo, *Chem. Zvesti*, **15**, 20 (1961).

6) L. Helmholz, *J. Amer. Chem. Soc.*, **69**, 886 (1947).

7) S. Hoshino, *J. Phys. Soc. Jap.*, **7**, 560 (1952).

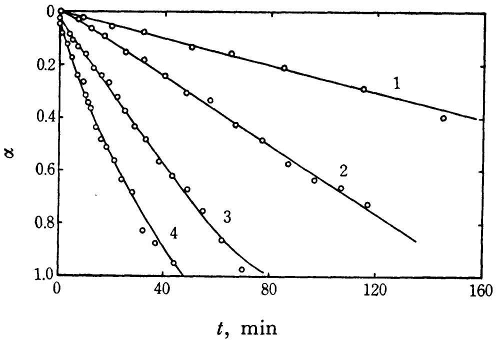

Fig. 3. Typical decomposition curves of $CuBr_2$ *in vacuo* obtained at (1) 105°, (2) 115°, (3) 125° and (4) 134°C.

β and 470°C for β to α. γ-CuBr is of a zinc-blend type, but it shows an anomalous change with temperature. In this investigation, as the temperature was lower than 220°C, CuBr belonged to γ-type. The reaction, therefore, must be expressed as,

$$CuBr_2(s) \rightleftarrows \gamma\text{-}CuBr(s) + \frac{1}{2}Br_2(g)$$

Figure 3 shows the plots of α, *vs.* t. The decomposition reaction was found to follow a first-order rate law expressed by

$$d\alpha/dt = k_1\,(1-\alpha)$$

at the beginning of the reaction, and a second-order rate law given by

$$d\alpha/dt = k_2\alpha\,(1-\alpha)$$

at the intermediate stage of the reaction. This result indicates that the reaction in the beginning may be controlled only by the process of the electron-transfer reaction, while the reaction at the intermediate period may be affected by the formation of decomposition product, CuBr.

This may be well understood by the consideration of the structure of $CuBr_2$. As $CuBr_2$ has polymeric chain structure and covalent bond, the structure change in the formation of Cu(I) might give a great effect to its neighboring chains successively. In view of this, the reaction in the beginning will be discussed so that some informations on the electron-transfer reaction can be obtained.

Since the integral form of the equation

$$d\alpha/dt = k_1\,(1-\alpha)$$

is expressed by

$$-\ln(1-\alpha) = k_1t + C$$

where C is constant, k_1 can be obtained from the slope of the plots of $-\log\,(1-\alpha)$ *vs.* t. Really, these plots gave straight lines in the beginning of the reaction as shown in Fig. 4. The value of k_1 was independent of the quantity and the grain size of $CuBr_2$ within the experimental error. Figure 5 shows the plots of $\log k_1$ *vs.* $1/T$, from which activation energy (E) and the frequency factor (A) were calculated to be 25.4 kcal/mol and $10^{10.4}$, respectively. Both of the values are almost the same as those of hexamminecobalt(III) complexes.[8] Though $CuBr_2$ had a polymer structure while hexamminecobalt(III) complexes had a monomer one, the difference could not be distinguished by the kinetic investigation.

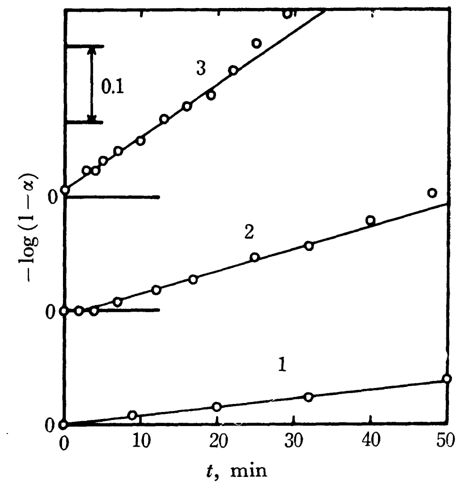

Fig. 4. Linear relationship between $-\log(1-\alpha)$ and time obtained at (1) 105°, (2) 115° and (3) 125°C.

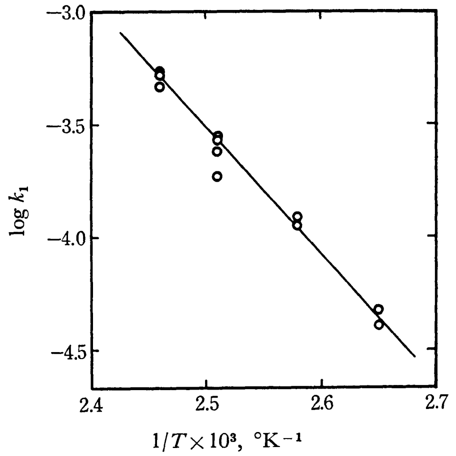

Fig. 5. Arrhenius plots of the first-order reaction rates for the decomposition reaction of $CuBr_2$ *in vacuo.*

The authors wish to thank the Ministry of Education for the financial support granted for this research.

---

[8] N. Tanaka and K. Nagase, This Bulletin, **41**, 1143 (1968).