[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

The Thermal Decomposition of Copper(II) Fluoride Dihydrate[1]

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RECEIVED JULY 24, 1953

The thermal decomposition of copper(II) fluoride dihydrate has been studied by differential thermal analysis, X-ray diffraction and chemical analysis. It undergoes a two-stage decomposition, forming $CuOHF \cdot CuF_2$ at 132°, followed by decomposition to the oxide and fluoride at 420°. The related basic fluoride, CuOHF, also undergoes a two-stage decomposition, first forming $CuOHF \cdot CuF_2$ at 345°.

Introduction

An indication of the unusual behavior of copper(II) fluoride dihydrate on heating was first given by Berzelius,[2] who reported the formation of a basic salt when an aqueous suspension of the hydrate was boiled. Balbiano[3] prepared this basic salt, CuOHF, and reported the formation of the oxide on heating it in air. A similar observation was made on the hydrate by Kurtenacker, Finger and Hey.[4]

This is in sharp contrast to the behavior of copper(II) chloride dihydrate, which loses its water of hydration above 130°, forming the anhydrous chloride. The fluoride hydrate loses water and hydrogen fluoride, and the anhydrous fluoride cannot be prepared by this method. A study of the action of fluorine on copper compounds has shown the fluorination of anhydrous copper(II) sulfate or of the sulfides to be an effective method of preparation.

Because of these peculiarities this study of the thermal decomposition of copper(II) fluoride dihydrate was undertaken as part of a general investigation of decompositions of complex fluorides and hydrates.

Experimental

Copper(II) Fluoride Dihydrate.—The dihydrate was prepared by adding basic copper(II) carbonate, $Cu(OH)_2 \cdot CuCO_3$, with stirring, to a twofold excess of 40% hydrofluoric acid.[4,5] Polyethylene apparatus was used to prevent formation of fluosilicate. After standing several hours with occasional stirring the precipitated hydrate was filtered, washed with ethanol, air dried briefly and stored in platinum. It was found advisable to use freshly prepared material since the hydrate slowly reacts on standing, presumably forming the basic fluoride.

Anal. Calcd. for $CuF_2 \cdot 2H_2O$: Cu, 46.20; F, 27.62. Found: Cu, 45.78, 45.82, 45.86; F, 27.16, 27.16, 27.20.

The X-ray powder pattern of the material was in agreement with that of a sample made by hydrating anhydrous copper(II) fluoride by the method suggested by Walton.[6] The weight gain of the anhydrous fluoride was within 1% of the theoretical value for dihydrate formation.

Basic Copper(II) Fluoride.—The basic fluoride, CuOHF, was prepared by boiling an aqueous suspension of the dihydrate.[7] Boiling over an extended period of time seemed to have no effect on the composition. The filtered fluoride was washed with alcohol and ether, and air-dried.

Anal. Calcd. for CuOHF: Cu, 63.84; F, 19.08. Found: Cu, 62.88, 62.99, 63.14; F, 18.57, 18.81, 18.95.

General.—The procedure for the thermal decomposition has been reported previously.[8] All runs were made at atmospheric pressure.

The X-ray powder diffraction photographs were made with copper radiation, filtered by nickel, using a 114.59-mm. Phillips camera. Samples were mounted on Pyrex fibers, in the dry-box if necessary, using Formvar "T" in ethylene chloride and were then coated with Formvar for protection against atmospheric moisture. Intensities were estimated visually by comparison with a film of known intensity.

Copper was determined electrolytically,[9] and fluorine was determined by the volumetric lead bromofluoride method.[10]

Results and Discussions

Differential heating curves (Fig. 1) obtained during the thermal decomposition of the hydrate, at atmospheric pressure and without free access to air, show two maxima, corresponding to the reactions

$$2[CuF_2 \cdot 2H_2O] \xrightarrow{132°} CuOHF \cdot CuF_2 + HF + 3H_2O \quad (1)$$

$$CuOHF \cdot CuF_2 \xrightarrow{420°} CuO + CuF_2 + HF + H_2O \quad (2)$$

A weighed sample of the hydrate, heated in a stream of dry nitrogen to 150°, came to constant weight with a weight loss corresponding to that expected for equation 1.

Anal. Calcd. for $CuOHF \cdot CuF_2$: Cu, 63.21; F, 28.34. Found: Cu, 63.00, 62.87, 62.72; F, 28.30, 28.50, 28.63.

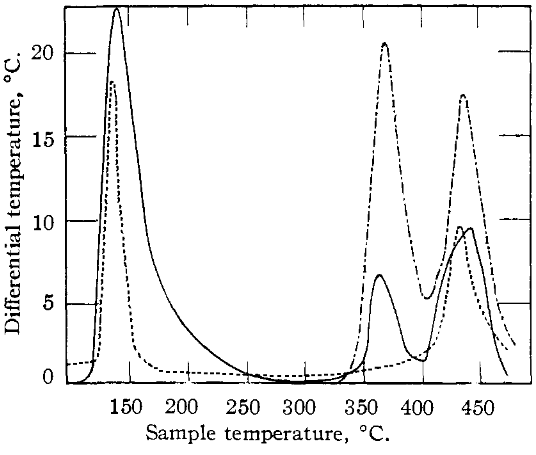

Fig. 1.—Thermal decomposition of $CuF_2 \cdot 2H_2O$, - - -; CuOHF, —·—; CuOHF + $CuF_2 \cdot 2H_2O$, —.

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[1] This work is from a program of research on inorganic fluorides supported in part by the Research Corporation and the Atomic Energy Commission.

[2] J. J. Berzelius, *Pogg. Ann.*, **1**, 28 (1824); *Ann. chim. phys.*, [2] **24**, 61 (1823); J. W. Mellor, "A Comprehensive Treatise on Inorganic and Physical Chemistry," Vol. III, Longmans, Green and Co., London, 1923, p. 155.

[3] L. Balbiano, *Gazz. chim. ital.*, **14**, 74 (1884); *Chem. Centr.*, **56**, 931 (1885).

[4] H. Kurtenacker, W. Finger and F. Hey, *Z. anorg. Chem.*, **211**, 83 (1933).

[5] F. H. Edmister and H. C. Cooper, THIS JOURNAL, **42**, 2419 (1920).

[6] H. F. Walton, "Inorganic Preparations," Prentice-Hall, Inc., New York, N. Y., 1948, p. 24.

[7] H. Martin, R. L. Wain and E. H. Wilkinson, *Ann. Applied Biol.*, **29**, 412 (1942).

[8] H. M. Haendler, C. M. Wheeler, Jr., and D. W. Robinson, THIS JOURNAL, **74**, 2353 (1952).

[9] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1952, p. 407.

[10] P. Ehrlich and G. Pietzka, *Z. anal. Chem.*, **133**, 84 (1951).

The X-ray powder pattern was unique, as shown in Fig. 2, which also shows the comparison of the second-stage decomposition products with copper(II) oxide and fluoride.

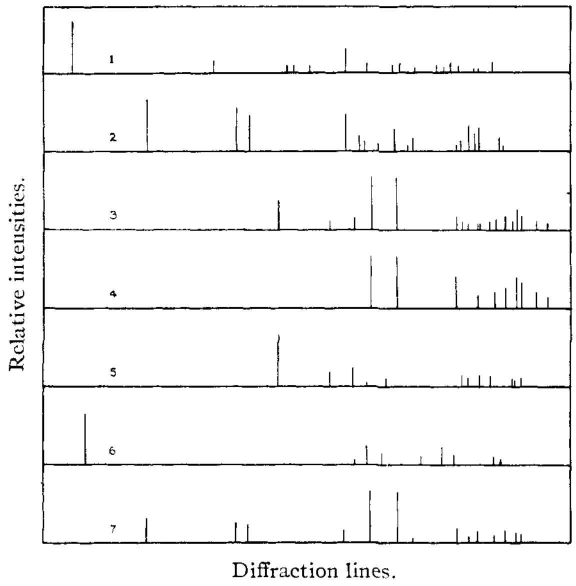

Fig. 2.—Diffraction diagrams: 1, $CuF_2 \cdot 2H_2O$; 2, $CuF_2 \cdot 2H_2O$ heated at 132° ($CuOHF \cdot CuF_2$); 3, $CuOHF \cdot CuF_2$ heated at 420° ($CuO + CuF_2$); 4, CuO; 5, CuF_2; 6, CuOHF; 7, CuOHF heated at 345° ($CuOHF \cdot CuF_2 + CuO$).

The related basic fluoride also undergoes a two-step decomposition, as shown by the differential data and the X-ray patterns, with the reaction

$$4CuOHF \xrightarrow{345°} CuOHF \cdot CuF_2 + 2CuO + HF + H_2O \quad (3)$$

being following by decomposition of the $CuOHF \cdot CuF_2$ at 410–420°, as in equation 2.

The first decomposition product of the dihydrate, white $CuOHF \cdot CuF_2$, reacts with atmospheric moisture to form an equimolar mixture of CuOHF and $CuF_2 \cdot 2H_2O$, as shown by X-ray patterns taken during the reaction. A sample of $CuOHF \cdot CuF_2$ was exposed to water vapor until the weight gained indicated absorption of two moles of water per mole of starting material. The mixture was placed in a desiccator over anhydrous $CuOHF \cdot CuF_2$ and allowed to reach constant weight. Hydrogen fluoride evolves slowly on standing, presumably because of decomposition of the dihydrate to the basic fluoride.

Anal. Calcd. for [$CuOHF + CuF_2 \cdot 2H_2O$]: Cu, 53.61; F, 24.03. Found: Cu, 53.67, 53.33, 53.59; F, 23.47, 23.33, 23.93.

Differential heating curves of the "hydrate" mixture show three maxima: the first, at 125–130°, corresponds to the initial decomposition of the dihydrate as in equation 1; the second to the decomposition of CuOHF as in equation 3 and the third to the decomposition of the $CuOHF \cdot CuF$ formed in the first two stages.

The nature of the decompositions depends on the presence or absence of air. In the presence of air, copper(II) oxide is the final product and no well-defined steps in the decomposition series can be observed. If the decompositions are carried out, however, in a closed system, so that the hydrogen fluoride produced prevents contact with the air, the final products are the oxide and fluoride, and the stages are shown clearly.

The new X-ray powder data are given in Table I. It is of interest to note that the "d"-spacings listed for the dihydrate in the ASTM diffraction catalog[11] appear to include values for the basic fluoride, CuOHF. This illustrates the difficulty of preparing and keeping a pure sample of the hydrate. An attempt is being made to grow single crystals of the hydrate for X-ray structural studies.

TABLE I

X-RAY POWDER DATA

$CuF_2 \cdot 2H_2O$		$CuOHF \cdot CuF_2$		CuOHF	
d	Relative intensity	*d*	Relative intensity	*d*	Relative intensity
4.78	100	4.22	100	4.68	100
3.71	25	3.54	85	2.65	8
3.15	12	3.45	70	2.55	40
3.10	12	2.71	70	2.43	25
2.98	12	2.61	30	2.34	5
2.71	45	2.58	20	2.14	15
2.55	18	2.47	12	1.97	35
2.35	15	2.34	45	1.88	20
2.29	18	2.25	12	1.63	5
2.18	9	2.20	25	1.59	15
2.02	15	2.10	3	1.56	3
1.96	12	1.99	3	1.54	10
1.92	17	1.87	12	1.51	5
1.85	13	1.84	18	1.49	3
1.75	8	1.79	6	1.48	3
1.70	8	1.77	45	1.44	3
1.60	20	1.72	30	1.43	1
1.58	5	1.70	45	1.36	1
1.55	5	1.63	6	1.33	1
1.53	5	1.55	25	1.30	2
1.49	5	1.51	12	1.28	1
1.43	6	1.43	6	1.26	1
1.33	8	1.41	3	1.24	1
				1.21	2
				1.17	1

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(11) "X-Ray Diffraction Data Cards," American Society for Testing Materials," Philadelphia, Pa.