

380. *The Thermal Decomposition of Oxalates. Part IV.¹ Interrelation of Crystalline Phases in the Thermal Decomposition and Dehydration of Zinc Oxalate*

By D. DOLLIMORE, J. DOLLIMORE, and D. NICHOLSON

The thermal dehydration and decomposition of zinc oxalate dihydrate is investigated by *X*-ray powder diffraction. A well defined diffraction photograph is obtained during dehydration along with the diffuse lines typical of a poorly crystalline anhydrous product. The existence of a second crystalline dehydration stage is considered and a comparison is made between these data and those of other oxalates for which various hydrated forms occur. The B.E.T. surface areas are used as an indication of the imperfection of the crystalline state for the anhydrous oxalate and the oxide prepared by low temperature isothermal decomposition. The rapid sintering of the final oxide stage at high temperature is demonstrated by the *X*-ray diffraction data, and electron micrographs.

THE oxalates of manganese, cobalt, nickel, and zinc all exist as dihydrates and according to thermogravimetric analysis thermal treatment in air results in dehydration directly to the anhydrous oxalate.² In particular the dehydration of manganese oxalate has been examined.^{3,4} According to Garner⁵ dehydration in a hard vacuum occurs by evaporation of water molecules from the surface, giving an unstable ionic network which has no clearly defined structure. Further rearrangement then occurs, particularly in the presence of water vapour, to give a crystalline anhydrous product.

Robin⁶ has shown that the anhydrous oxalates of cobalt, nickel, and zinc are poorly crystalline giving *X*-ray powder diffraction photographs containing mainly broad or diffuse lines. Preliminary experiments by us confirmed Robin's observation and emphasised the difference between these anhydrous oxalates and the much better crystallised manganese compound. The anhydrous zinc oxalate had slightly more diffraction lines than the other two anhydrous oxalates. It was therefore chosen as the material to study by *X*-ray diffraction methods both in the dehydration reaction and in subsequent decomposition to the oxide. The associated morphological changes were followed by low-temperature nitrogen adsorption surface areas by the B.E.T. method,⁷ by the determination of complete adsorption-desorption isotherms, and by electron microscopy.

EXPERIMENTAL

The experimental results were obtained using a powder camera of 114.6 mm. and filtered copper radiation. The thermogravimetric analysis and nitrogen adsorption data were determined using methods described previously.^{2,8} Dispersions of the aggregates for the electron

¹ Part III, Dollimore and Nicholson, *J.*, 1964, 908.

² Dollimore, Griffiths, and Nicholson, *J.*, 1963, 2617.

³ Smith and Topley, *Proc. Roy. Soc.*, 1931, *A*, **134**, 224; *J.*, 1935, 321.

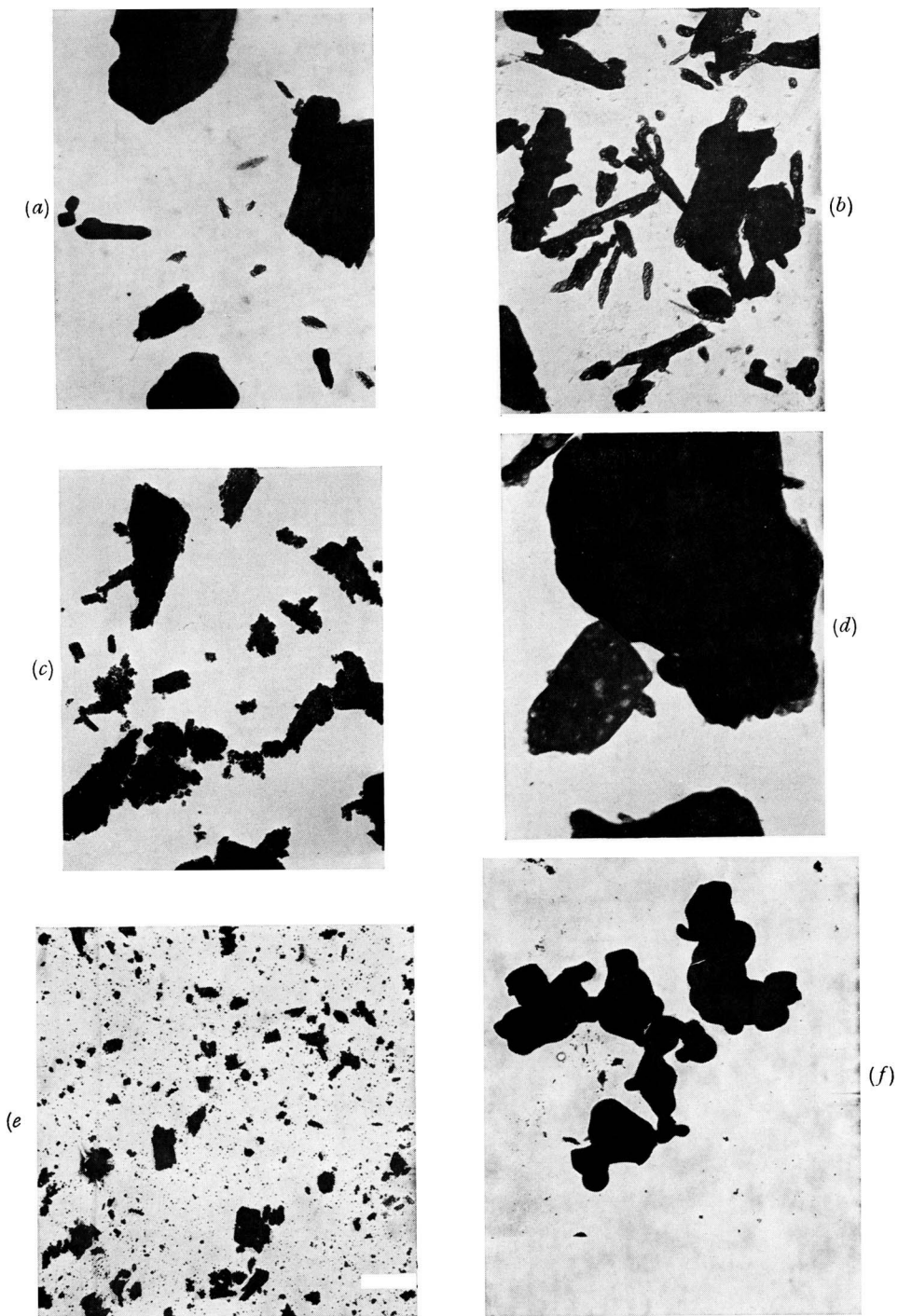
⁴ Colvin and Hume, *Discuss. Faraday Soc.*, Chemical Reactions involving Solids, 1938, 969.

⁵ Garner, "Chemistry of the Solid State," Butterworth, London, 1955, p. 215.

⁶ Robin, *Bull. Soc. chim. France*, 1953, 1078.

⁷ Brunauer, Emmett, and Teller, *J. Amer. Chem. Soc.*, 1938, **60**, 309.

⁸ Dollimore and Nicholson, *J.*, 1962, 960.



Electron micrographs of zinc oxalate dihydrate heated at (a) 160°, magnification 14,500; (b) 220°, magnification 14,500; (c) 300°, magnification 14,500; (d) 160°, magnification 24,000; (e) 350°, magnification 3,750; (f) 1000°, magnification 3,750.

Samples *a*—*d*, anhydrous zinc oxalate; *e*, *f*, zinc oxide.

a, *b*, *c* |-----| 1 μ
1.45 cm.

d |-----| 1 μ
2.4 cm.

e, *f* |-----| 1 μ
.375 cm.

micrographs were obtained by gently milling the samples between glass slides using light petroleum, and then placing the formvar filmed grid on the damp slide.

Material.—Zinc oxalate, of formula $\text{Zn}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ (based on chemical analysis for the zinc and oxalate ions), had been prepared by adding pure zinc to a boiling solution of oxalic acid. Analysis showed that up to 2% of zinc oxide could be present. The X-ray diffraction data however showed no lines due to zinc oxide and no carbonate or hydroxides could be identified. The layer spacing values (d) obtained for zinc oxalate dihydrate showed reasonable agreement with published values with additional values of 3.04 and 2.49 Å.

RESULTS AND DISCUSSION

Decomposition to the Oxide.—Thermogravimetric analysis of zinc oxalate dihydrate shows that it decomposes first to the anhydrous oxalate, which is complete at about 220°, and then to zinc oxide which is formed above 300°. The zinc oxide has been shown by nitrogen adsorption data to be in a finely divided form at low temperatures, but rapid sintering occurs at the higher temperatures. This sintering effect is apparent, as an increased resolution (particularly at back reflection), of the zinc oxide X-ray diffraction photographs. The clearest indication of the rapid sintering process is obtained from the electron micrographs, two extreme cases being shown in the Plate, *e* and *f*. The 350° product consisted largely of particles about 0.01 μ in size together with occasional aggregates and larger particles. This agrees with low-temperature nitrogen adsorption B.E.T. surface areas of about 50 m.²/g. found on a large number of samples heated for half an hour at this temperature. Samples heated for half an hour at 1000° had surface areas diminished by bulk diffusion to below 1 m.²/g. (N₂ B.E.T.) and the electron micrographs confirmed this behaviour. The particles previously showing corners have now agglomerated into smoothly contoured masses of much greater particle size.

Dehydration: X-Ray Diffraction Data.—All the techniques employed show clearly that above 300° zinc oxide is formed. X-Ray diffraction photographs below 300°, however, show that the dehydration is more complex than the weight-loss data would indicate. Diffraction photographs were obtained for samples heated for half an hour at 125, 160, 220°, and at 220° for three hours. Zinc oxide was the only substance formed above 300°, and it also appeared in all the samples down to 125°. At 125, 160, and 220° five additional lines appeared. These were rather diffuse, suggesting a poorly crystalline dehydrated oxalate. On the sample heated for three hours at 220°, only these five diffuse lines and the lines of zinc oxide were obtained. The lines due to zinc oxalate dihydrate did not all disappear in order of decreasing intensity. The comparatively intense dihydrate line $d = 3.94$ Å decreased progressively with increased temperature whilst many other less intense lines had disappeared at 160°. This was not, however, due just to a reduction in dihydrate content since certain dihydrate lines remained with relative intensities similar to those in the original zinc oxalate dihydrate. In fact the reported diffraction lines of Robin⁶ for anhydrous zinc oxalate could be regarded as the summation of these persistent dihydrate lines and the five diffuse lines already noted (Table).

Mechanism of Dehydration.—Two possibilities exist as an explanation of the various diffraction patterns. First, the original oxalate could consist of two distinct crystal structures, possibly differently hydrated, and that one of these dehydrates at a higher temperature. Each structure could then dehydrate with the degradation–recrystallisation mechanism postulated for manganese oxalate. Various hydrated forms have in fact been suggested for calcium oxalate.⁹ The X-ray diffraction patterns, however, show many similarities and apart from a monoclinic dihydrate the same tetragonal unit cell has been suggested for anhydrous calcium oxalate and various hydrated forms.

This leads to a second possible structural mechanism for dehydration in which pseudomorphs are formed. The contraction of a layer or chain structure with various possible sites for water molecules seems to be a possible solution in view of the corrugated layer and

⁹ Lecomte, Pobeguïn, and Wyart, *Compt. rend.*, 1943, **216**, 808.

X-Ray diffraction lines on anhydrous zinc oxalate samples obtained by heating samples of the dihydrate for $\frac{1}{2}$ hr. at 125, 160, and 220°

d values Å		
Reported by Robin for Zn(COO) ₂	The 5 diffuse lines *	Persistent dihydrate lines
4.74		4.75
		3.93 †
3.80	3.8	
2.98		2.97
2.79		
2.56		2.56
2.36	2.38	
2.22		2.23
2.17	2.16	
	1.88	2.09
	1.77	

* The sample heated to 220° for 3 hr. showed only these 5 diffuse lines plus those due to zinc oxide.

† Variable intensity.

chain structures of α and β oxalic acids,^{10,11} and the different oxygen-water molecule linkages (2.49 and 2.88 Å) in oxalic acid dihydrate. No continuous transformation has however been postulated so far for the dehydration of oxalic acid dihydrate and since the crystal structures of the dihydrate oxalates are undetermined this is purely speculative.

Indirect evidence for a toptactic dehydration of zinc oxalate dihydrate can be found. Robin has commented on the difficulty of completely dehydrating the dihydrate. In recent work Dollimore and Nicholson¹ report that the dehydration plateau on thermogravimetric analysis occurs for a weight loss of 17.5, 17.7%, in air, and 19.7% in vacuum. Only extended heat treatments in air, or hard-vacuum conditions, remove the last traces of water and it would seem reasonable to associate the 5-line diffuse pattern with these conditions. Although the powder diffraction method gives an average result, the persistence of some original dihydrate interlayer spacings over such a wide range of dehydration could be regarded as indirect evidence for a toptactic change.

Morphological Changes.—If dehydration occurs without shattering the original particle of zinc oxalate dihydrate and the resultant crystal structure of the anhydrous oxalate is a pseudomorph of the dihydrate then the dehydration process might be expected to yield a porous solid. Nitrogen adsorption-desorption isotherms on anhydrous zinc oxalate samples prepared in this investigation by the thermal decomposition of the dihydrate in air showed no hysteresis loop indicating no pores between 20 and about 300 Å in radius. The upper limit is uncertain since the isotherms were Type II. Electron micrographs of samples of the oxalate dehydrated at 160, 220, and 300° in air are shown in the Plate. Numerous pores greater than 300 Å exist and these become so extensive that at 300° the decomposing material is fragmenting into fine particles. Although some further dehydration has probably occurred owing to the electron beam and hard vacuum in the microscope the extensive pore structure and its development with heat treatment show that the original samples themselves must have been porous. Rehydration followed by a complete dehydration at 150° under vacuum brings the pore sizes down into the range which produces a definite hysteresis loop in low-temperature nitrogen adsorption-desorption.¹

Conclusions.—Although the crystallographic data are not yet sufficient to postulate a detailed mechanism of dehydration for zinc oxalate dihydrate, powder diffraction data and other indirect methods indicate that the changes could be toptactic. This mechanism appears more likely than the accepted degradation recrystallisation mechanism put forward for the dehydration of manganese oxalate dihydrate.

ROYAL COLLEGE OF ADVANCED TECHNOLOGY,
SALFORD, LANCASHIRE.

[Received, June 11th, 1964.]

¹⁰ Hendricks, *Z. Krist.*, 1935, **91**, 48.

¹¹ Ahmed and Cruickshank, *Acta Cryst.*, 1953, **6**, 385.