Thermochimica Acta, 133 (1988) 251–256
Elsevier Science Publishers B.V., Amsterdam

STUDIES ON ALKALINE EARTH METAL SULFITES. X[1] -THERMAL DEHYDRATION OF CALCIUM SULFITE HEMIHYDRATE: DEPENDENCE OF THE PRODUCTS ON DEHYDRATION CONDITIONS

Abr. COHEN[a] and M. ZANGEN, Soreq Nuclear Research Center, Yavne, Israel

ABSTRACT

Investigation of the thermal dehydration of various modifications of $CaSO_3 \cdot \frac{1}{2}H_2O$ using thermogravimetry and differential thermal analysis showed that different crystalline phases of anhydrous $CaSO_3$ are obtained. Differences in dehydration mechanisms which lead to these different crystalline structures, are due not only to the nature of the hemihydrate, but also to the conditions, e.g. water vapour pressure, under which the dehydration is performed.

INTRODUCTION

An X-ray power diffraction pattern (XPDP) for anhydrous $CaSO_3$ was reported in 1948 by Matthews and McIntosh [2], JCPDS* file No. 4-599. A similar, but more accurate, XPDP was reported in 1976 by Lutz and Suradi [3], JCPDS file No. 31-307. A completely different XPDP was reported in 1978 by Matsuzaki et al. [4], JCPDS file No. 31-306 which replaced file No. 4-599 , who presented it without comment next to Matthews pattern. The above authors' data include d-indexes and relative intensities only. In 1982 Arai et al. [5] claimed that the dehydration of the orthorhombic hemihydrate results in the formation of orthorhombic anhydride, whose XPDP differs from those previously reported.

EXPERIMENTAL

Sample preparation. Samples of $CaSO_3 \cdot \frac{1}{2}H_2O$ were prepared by 3 different methods at 25°C:

(a) Single crystals were obtained by slow diffusion of SO_3^{2-} and Ca^{2+} from solid Na_2SO_3 and $CaCl_2$ into a "bridge" containing pure water or an aqueous electrolyte solution.

(b) Powder samples were obtained by rapid precipitation upon mixing equivalent amounts of aqueous solutions of Na_2SO_3 and $CaCl_2$, in the concentration range 0.05 to 1.5 M and 0.05 to 6 M, respectively.

---

*JCPDS: Joint Committee on Powder Diffraction Standards - International Centre for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19081.

[a] present address: 41 R. Wolfson, Rishon Lezion, Israel

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

(c) Other powder samples were prepared by removing H_2O and SO_2, either rapidly (by pumping) or slowly (by drying over concentrated H_2SO_4), from aqueous solutions of $Ca(HSO_3)_2$ in the range 0.05 to 0.7M, obtained by passing gaseous SO_2 into aqueous suspensions of $CaCO_3$ or $Ca(OH)_2$.

The products obtained were examined by X-raydiffraction and chemical analysis. They underwent thermal dehydration in DTA/TG procedures up to 500°C in an inert atmosphere or in vacuum. The dehydrated products were studied by chemical analysis and X-ray powder diffraction.

Chemical Analysis. Sulfite was determined by iodometry and calcium by complexometry with EDTA using methylthymol blue as indicator.

Instrumentation. A Philips X-ray powder diffractometer with PW1380 horizontal goniometer and PW1152 X-ray focussing monochromator, and a DuPont-990 thermoanalytical system were employed in the experiments.

RESULTS AND DISCUSSION

The hydrated products, prepared using methods (a), (b) and (c), were identified as $CaSO_3 \cdot \frac{1}{2} H_2O$ by chemical analysis. They gave similar X-ray powder diffraction patterns (XPDP) which were in good agreement with the data reported by Matthews and McIntosh [2] for the hydrated salt, JCPDS file NO. 4-588. These data were related by Waerstad et al. [6] to the orthorhombic system, JCPDS file No. 26-1074.

The chemical analysis proved that all the products of the thermal dehydration are anhydrous $CaSO_3$, and that contamination with sulfate is insignificant (below 0.5 mole %).

An in depth analysis of the XPDP of the various samples of anhydrous $CaSO_3$ revealed the existence of 3 different crystalline phases. The XPDP of these phases are given in Tables I, II and III. It was found that the crystalline structure of anhydrous $CaSO_3$ depends on both the type of the hemihydrate, i.e. on the method employed for its preparation, and the dehydration conditions.

Anhydride I, Table I, is obtained upon dehydration in vacuum of hydrated calcium sulfite prepared using method (b). The XPDP of this phase is in agreement with the data reported by Matthews and McIntosh [2] for the anhydrous salt (they, too, prepared the hydrate using method (b) and performed the dehydration in vacuum), and also with the data reported by Lutz and Suradi [3].

Anhydride II, Table II, is obtained upon dehydration, both in vacuum and in the presence of water vapour, of hydrated calcium sulfite prepared using method (c). The XPDP of this phase is in agreement with the data reported by Matsuzaki et al. [4]. They, too, prepared the hydrate using method (c) but compared the XPDP of their anhydride to that of anhydride I without giving any explanation for the great differences observed.

Anhydride III, Table III, is obtained upon dehydration in the presence of water vapour, of hydrated calcium sulfite prepared using methods (a) and (b). The XPDP of this phase has not been reported in the literature.

TABLE I

$2\theta(^{o})$[a], relative intensity[b], d-spacings (Å) and indexes[c] of X-ray powder diffraction lines of $CaSO_3$, anhydride I[d].

$2\theta_{exp}$	I/I_o	d_{exp}	d_{calc}	h	k	ℓ	$2\theta_{exp}$	I/I_o	d_{exp}	d_{calc}	h	k	ℓ
28.31	100	3.150	3.149	1	2	1	56.10	6	1.638	1.638	1	1	3
30.67	71	2.913	2.913	2	2	0	56.42	6	1.630	1.630	4	2	1
			2.909	1	3	0	58.80	6	1.569	1.570	1	2	3
35.01	39	2.561	2.560	0	0	2				1.548	1	6	0
35.42	64	2.532	2.532	2	2	1	59.74	3	1.547	1.547	3	3	2
			2.530	1	3	1	63.06	11	1.473	1.473	2	2	3
36.52	8	2.458	2.459	3	0	0				1.472	1	3	3
38.36	16	2.345	2.344	1	1	2	66.71	5	1.401	1.401	4	4	1
			2.155	1	2	2	69.10	2	1.358	1.358	5	2	1
41.92	8	2.154	2.154	0	4	1	73.92	8	1.281	1.281	4	5	1
42.54	38	2.123	2.103	2	0	2	75.28	1	1.261	1.261	1	0	4
47.23	23	1.923	1.923	2	2	2	82.15	3	1.172	1.172	1	8	0
			1.922	1	3	2				1.172	2	2	4
50.23	9	1.815	1.816	3	3	1	85.37	1	1.136	1.136	5	5	1

[a] Obtained by using $CuK\alpha_1$ radiation (λ = 1.5406Å). Scan speed $0.25^{o}(2\theta)$ min^{-1} with elemental Si as internal standard. 2θ values were determined at 80% of peak intensity.

[b] Intensities were measured as peak heights above background and are expressed as a percentage of the strongest line.

[c] Indexed using a computer program (version 8) written by J.W. Visser (J. Appl. Cryst., 2, 2(1969)). The unit-cell dimensions were refined using a least-squares computer program (D.E. Appleman, H.T. Evans and D.S. Handwerker, Indexing and least-squares Refinement of Powder Diffraction Data, Geological Survey, Washington, 1973, distributed by National Technical Information Service, Springfield, document no. PB-216188).

[d] Orthorhombic with a = 7.376(1)Å, b = 9.498(2)Å, c = 5.121(1)Å, V = 358.8Å^3, Z = 6, D_X = 3.335 gcm^{-3}, Bravais lattice = P. Figure of merit M_{20} = 24.8 (P.M. de Wolff, J. Appl. Cryst., 1, 108 (1968)).

It is interesting to note that the dehydration, both in vacuum and in the presence of water vapour, of hydrated calcium sulfite prepared using method (c), gave identical products. This fact suggests the assumption that the presence of minute amounts of NaCl or of the starting materials in the hydrates prepared using method (b), which are absent from hydrates prepared using method (c), are among the kinetic factors responsible for the differences between dehydration in vacuum and in the presence of water vapour.

TABLE II

$2\theta(^{o})^{a}$, relative intensity, d-spacings (Å) and indexes[c] of X-ray powder diffraction lines of $CaSO_3$, anhydride II[d].

$2\theta_{exp}$	I/I_o	d_{exp}	d_{calc}	h	k	ℓ	$2\theta_{exp}$	I/I_o	d_{exp}	d_{calc}	h	k	ℓ
17.94	9	4.940	4.944	1	1	0	45.18	26	2.005	2.004	2	1	$\bar{2}$
21.37	4	4.155	4.155	1	0	$\bar{1}$	45.43	22	1.995	2.001	2	3	0
22.57	7	3.936	3.955	1	0	1	46.15	15	1.965	1.967	3	1	$\bar{1}$
23.32	8	3.812	3.808	0	2	0				1.963	3	0	1
24.40	11	3.644	3.648	1	1	$\bar{1}$	47.50	19	1.913	1.914	2	1	2
25.35	15	3.510	3.510	1	1	1	47.76	16	1.903	1.904	0	4	0
27.43	46	3.249	3.249	2	0	0				1.901	3	1	1
29.05	100	3.071	3.069	0	2	1	48.27	17	1.884	1.883	3	2	0
29.88	52	2.988	2.989	2	1	0	49.28	8	1.848	1.847	2	3	1
31.85	62	2.808	2.808	1	2	$\bar{1}$	49.87	32	1.827	1.827	1	4	0
32.61	61	2.744	2.743	1	2	1	51.05	13	1.788	1.787	0	4	1
33.93	62	2.640	2.643	2	1	$\bar{1}$	52.82	4	1.732	1.731	1	4	$\bar{1}$
34.56	35	2.593	2.591	0	0	2				1.731	1	3	2
			2.539	0	3	0	53.71	4	1.705	1.705	3	0	$\bar{2}$
35.33	67	2.538	2.538	2	1	1	55.26	12	1.661	1.664	3	1	$\bar{2}$
36.31	13	2.472	2.472	2	2	0				1.649	1	0	3
			2.366	1	0	2	55.74	17	1.648	1.648	3	3	0
38.04	12	2.364	2.365	1	3	0	56.60	7	1.625	1.625	4	0	0
38.57	16	2.332	2.332	1	1	$\bar{2}$	58.11	11	1.586	1.586	3	1	2
39.86	11	2.260	2.259	1	1	2	59.82	6	1.545	1.545	1	2	$\bar{3}$
43.52	6	2.078	2.078	2	0	$\bar{2}$	60.62	11	1.526	1.527	2	1	$\bar{3}$
43.89	6	2.061	2.060	1	2	$\bar{2}$	63.40	7	1.466	1.466	2	1	3
44.60	12	2.030	2.036	3	0	$\bar{1}$							

[a] See footnote a to Table I.
[b] See footnote b to Table I.
[c] See footnote c to Table I.

[d] Monoclinic with a = 6.507(2)Å, b = 7.617(2)Å, c = 5.188(1)Å, β = 92.91(1)°, $V = 256.8 Å^3$, Z = 4, D_x = 3.106 gcm^{-3}, Bravais lattice = P. Figure of merit M_{20} = 45.9 (P.M. de Wolff, J. Appl. Cryst., 1, 108 (1968)).

Another factor which may have an effect on the mechanism of the dehydration and therefore on the type of anhydride formed is the pH of the solution in which the hydrated calcium sulfite is obtained. Possibly, this effect also is due to minute residues of acidity or basicity in the hydrate. In the present work, the pH of the mother solution was basic when methods (a) and (b) were employed, acidic when method (c) was used.

These assumptions are supported by the fact that the dehydration of hydrated samples prepared by method (b) and washed many times with oxygen-free distilled water gave a mixture of anhydride II with either anhydride I or III, depending on the water vapour pressure which prevailed during the dehydration. Furthermore, dehydration of the above hydrated samples after several days of equilibration with distilled water gave pure anhydride II.

TABLE III

$2\theta(^{\circ})^{a}$, relative intensity, d-spacings (Å) and indexes[c] of X-ray powder diffraction lines of $CaSO_3$, anhydride III[d].

$2\theta_{exp}$	I/I_o	d_{exp}	d_{calc}	h	k	ℓ	$2\theta_{exp}$	I/I_o	d_{exp}	d_{calc}	h	k	ℓ
17.97	3	4.933	4.936	1	0	$\bar{1}$	46.76	7	1.941	1.942	0	1	3
19.73	8	4.496	4.497	0	1	1				1.941	1	3	1
22.37	6	3.971	3.981	1	0	1	47.64	27	1.907	1.908	2	1	2
			3.968	1	1	$\bar{1}$	49.92	12	1.825	1.827	2	1	$\bar{3}$
26.70	5	3.335	3.335	0	2	0	50.62	39	1.802	1.803	2	3	$\bar{1}$
28.26	11	3.155	3.156	2	0	0				1.801	3	1	1
29.29	100	3.046	3.045	0	0	2	52.75	14	1.734	1.734	0	2	3
30.54	100	2.925	2.925	0	2	1	54.37	17	1.686	1.686	2	3	1
31.33	50	2.853	2.853	2	1	0	55.04	7	1.667	1.668	0	4	0
31.97	33	2.797	2.797	2	1	$\bar{1}$	55.62	15	1.651	1.652	2	3	$\bar{2}$
32.29	39	2.770	2.770	0	1	2				1.651	2	2	$\bar{3}$
32.66	11	2.739	2.738	1	1	$\bar{2}$	56.34	3	1.632	1.631	3	2	1
35.07	5	2.557	2.557	1	2	1	57.24	4	1.608	1.608	0	4	1
36.38	13	2.467	2.468	2	0	$\bar{2}$	57.56	3	1.600	1.600	1	2	3
37.25	3	2.412	2.412	2	1	1	58.44	3	1.578	1.578	4	0	0
37.91	2	2.372	2.374	1	1	2	60.06	5	1.539	1.539	3	3	$\bar{1}$
38.88	28	2.314	2.314	2	1	$\bar{2}$				1.539	3	1	2
40.33	2	2.234	2.231	1	2	$\bar{2}$	60.21	4	1.536	1.535	4	1	0
42.34	11	2.133	2.133	3	0	$\bar{1}$	60.80	5	1.522	1.522	0	0	4
43.12	10	2.096	2.097	1	3	0				1.522	2	1	3
44.82	14	2.021	2.021	1	2	2	61.77	7	1.501	1.501	2	0	$\bar{4}$
45.15	5	2.006	2.006	3	1	0				1.501	4	1	$\bar{2}$
45.99	3	1.972	1.972	1	1	$\bar{3}$	63.53	7	1.463	1.463	0	4	2

[a] See footnote a to Table I.
[b] See footnote b to Table I.
[c] See footnote c to Table I.

[d] Monoclinic with a = 6.458(2)Å, b = 6.670(2)Å, c = 6.231(2)Å, β = 102.22(2)°, V = 262.3Å^3, Z = 4, D_x = 3.041 gcm^{-3}, Bravais lattic = P.
Figure of merit M_{20} = 30.9 (P.M. de Wolff, J. Appl. Cryst., 1, 108 (1968)).

It should be noted that the dehydration of calcium sulfite hemihydrate prepared using methods (a) and (b) frequently gave mixtures, in different proportions, of anhydrides I, II and III. In thermogravimetric analysis the dehydration is generally performed in an open boat from which most of the water vapour, released during the dehydration, is removed by the flow of dry nitrogen. Under these conditions the main product is anhydride I, which is usually obtained in a mixture with anhydrides II or/and III. Contrary to TG, during the dehydration in a DTA cell, where the sample is compressed in a tube with a narrow opening, the water of crystallization released is trapped and causes a high vapour pressure. Under these conditions the main product is anhydride III, which may be received contaminated with anhydride II.

The fact that mixtures of anhydrides may be obtained during the dehydration of orthorhombic $CaSO_3 \cdot ½H_2O$ could explain the experimental results of Arai et al. [5]. They claimed that the dehydration of orthorhombic $CaSO_3 \cdot ½H_2O$ gave an anhydride whose X-ray pattern agreed generally with that reported by Lutz et al. [3], but showed many additional diffraction peaks. An examination of this XPDP shows that it belongs to anhydride I, as a major component in a mixture with anhydride II. As a result, the intensity of the X-ray diffraction lines of the latter is much lower than it would be in pure anhydride II, and only the lines of highest intensity appear in the XPDP of the mixture.

Finally, it may be noted that the differences observed in our system between dehydration in vacuum and in the presence of water vapour are similar to those found during the dehydration of $CaSO_4 \cdot 2H_2O$. Barriac [7] reported the existence of 3 different modifications of $CaSO_4 \cdot ½H_2O$ (α, β and low-pressure α), obtained upon dehydration of $CaSO_4 \cdot 2H_2O$ under different water vapour pressures. Recently, these modifications were proved to be definite crystalline phases with different lattice structures [8-10]. It may therefore be worthwhile to pay special attention to water vapour pressure conditions, whenever thermal dehydration is investigated.

REFERENCES

1 Part IX: A. Cohen and M. Zangen, J. Chem. Soc. Dalton Trans. (1987) 235.
2 F.W. Matthews and A.O. McIntosh, Can. J. Res., 26B (1948) 747.
3 H.D. Lutz and S. El-Suradi, Z. Anorg. Allg. Chem., 425 (1976) 134.
4 R. Matsuzaki, H. Masumizu, N. Murakami and Y. Saeki, Bull. Chem. Soc. Jpn., 51 (1978) 121.
5 Y. Arai, T. Yasue, N. Nagata and H. Shiino, ibid, 55 (1982) 738.
6 K.R. Waerstad, R.M. Scheib and G.H. McClellan, J. Appl. Cryst., 7 (1974) 447.
7 P. Barriac, Ph.D. Thesis, Lyon University, Lyon, France, 1968.
8 A. Bachiorrini and M. Murat, Cemento, 13 (1976) 151.
9 N.N. Bushuev, N.G. Frolova, V.N. Nosov and V.F. Karmyshov, Russ. J. Inorg. Chem., 23 (1978) 1767.
10 N.N. Bushuev, Sov. Phys. Dokl., 25 (1980) 957.