JOURNAL OF SOLID STATE CHEMISTRY 9, 214–223 (1974)

Comparative Study of the Polymorphic Species of Strontium and Calcium Formates. II. X-Ray Diffraction

BERNARD F. MENTZEN AND CLAUDE COMEL

Laboratoire de Cinétique et Génie Chimiques, Institut National des Sciences Appliquées de Lyon, 20 avenue A.—Einstein, F-69621, Villeurbanne, France

Received January 30, 1973

The existence, in the temperature range 20–400°C, of three polymorphic species α, β, and δ of strontium formate, and of four polymorphic species α, β, γ, and δ of calcium formate is established by the means of X-ray diffraction. Crystal lattices of all these varieties are given, and the temperature ranges for their existence have been precisely stated. The importance of the role played by water vapor traces on some polymorphic transitions is pointed out.

Introduction

In the preceding article (*1*) of this series, it has been shown that strontium and calcium formates exhibit respectively two (α and δ) and four (α, β, γ, and δ) polymorphic species under atmospheric pressure and in the 20–400°C temperature range. This study will now be completed by relating the experimental results found by X-raying the powdered samples, and their interpretation. Occasionally, the existence of some polymorphic varieties of both formates has been confirmed by infrared spectrophotometry.

Experimental

The X-ray generator used was a SIEMENS, Kristalloflex II model, equipped with the following photographic cameras:

(a) a 57.3 mm radius camera for the investigations at room temperature; this camera may also be fitted with a heating device (*2*);

(b) a temperature regulating moving-film camera (T.R.M.F. camera), 38.2 mm in radius, which enables the continuous photographic recording of the diffraction lines against temperature (*3*).

In both cases, the powdered samples were introduced in glass capillaries. Filtered Cu*Kα* radiation was used throughout.

Experimental Results

Strontium Formate at Room Temperature

The structures of α-$Sr(HCOO)_2$ (*4*) and $Sr(HCOO)_2 \cdot 2H_2O$ (*5*) are known. Both crystallize in the orthorhombic system with four molecules per unit-cell, the space group being $P2_12_12_1$. The unit cell parameters are as follows:

	a (Å)	*b* (Å)	*c* (Å)	Ref.	*T* (°C)	*Z*
α-$Sr(HCOO)_2$ (Table V)	6.874	8.747	7.268	(*4*)	20.0	4
	6.86 ± 0.01	8.75 ± 0.01	7.26 ± 0.01	this work	25.0	4
$Sr(HCOO)_2 \cdot 2H_2O$ (values not mentioned)	7.30	11.99	7.13	(*5*)	—	4
	7.321 ± 0.006	12.07 ± 0.01	7.148 ± 0.006	this work	22.3	4

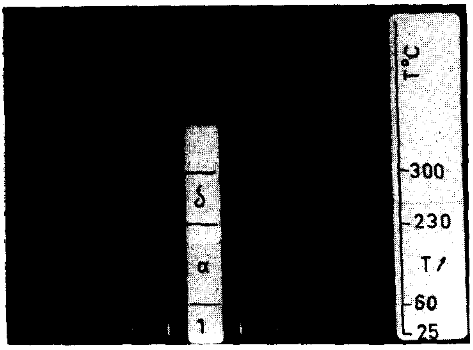

FIG. 1. $Sr(HCOO)_2 \cdot 2H_2O$ temperature regulating X-ray diffraction pattern—25°C hr^{-1} heating rate.

Strontium Formate At Higher Temperatures—T.R.M.F. Camera

(a). $Sr(HCOO)_2 \cdot 2H_2O$

Since α-$Sr(HCOO)_2$ is obtained by dehydration of the dihydrate, it was deemed relevant to investigate in situ formation of α-$Sr(HCOO)_2$ by using the T.R.M.F. camera. Figure 1 shows the X-ray diffraction pattern obtained with the dihydrate; in this experiment, the glass capillary was open, the heating rate 25°C hr^{-1} and the temperature range 25–300°C (within these limits the sample is not decomposed). Following observations can be made:

(1) Diffraction lines on the lower part of the pattern (zone 1) correspond to strontium formate dihydrate.

(2) The lines in the middle (α zone) are assigned to α-$Sr(HCOO)_2$: indeed, if the same sample is cooled and then heated again (Fig. 2), the lower part of Fig. 2 (α zone) and the middle part of Fig. 1 (α zone) are identical.

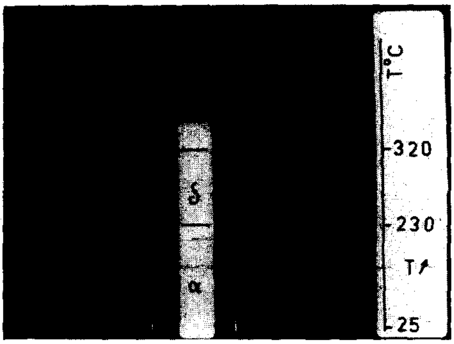

FIG. 2. α-$Sr(HCOO)_2$ temperature regulating X-ray diffraction pattern—25°C hr^{-1} heating rate.

TABLE I

δ-$Sr(HCOO)_2$ X-RAY DIFFRACTION PATTERN $-T=$ 280°C – 38.2 mm RADIUS T.R.M.F. CAMERA—Cu$K\alpha$ RADIATION

I^a	$10^5 \sin^2\theta$ Obsd	$10^5 \sin^2\theta$ Calcd	d_{obs}	$h\,k\,l^c$
vs	1729 ± 17^b	1742	5.87	1 0 1
s_b	4662 ± 28	4707 4618	3.57	1 1 2 2 0 0
m	6296 ± 32	6270	3.072	1 0 3
vvw	6439 ± 32	6450	3.058	2 1 1
mw	9055 ± 38	9055	2.561	0 0 4
w	9415 ± 38	9414	2.511	2 2 0
mw	11143 ± 41	11157	2.309	3 0 1
w	13801 ± 45	13762	2.075	2 0 4
mw	14070 ± 46	14032	2.055	3 1 2
w	15844 ± 48	15864	1.937	3 2 1
vvw_b	18636 ± 51	18829 18469	1.786	4 0 0 2 2 4
vw_b	20505 ± 53	20571 20391	1.702	4 1 1 3 2 3
vvw	22768 ± 55	22728	1.616	1 1 6
vw	23541 ± 56	23536	1.589	4 2 0

[a] v, very; s, strong; m, medium; w, weak; b, broad.

[b] these values correspond to an experimental error of ±0.1 mm on the diffraction pattern.

[c] *hkl* extinctions correspond to the two possible space groups $I4_1/a(C_{4h}^6)$ or $I4_1/amd(D_{4h}^{19})$.

(3) Diffraction lines on the upper parts (δ zones) of Figs. 1 and 2 are assigned to the new δ-$Sr(HCOO)_2$ variety, existence of which has been precendently recognized (*1*) and can be checked also by ir spectroscopy according to the method already described by one of us (*6*).

Table I summarizes the results obtained at 280°C on the anhydrous strontium formate. The relationship between the diffraction lines observed before and after the $\alpha \rightarrow \delta$ transition enables us to ascribe Miller indices to the lines of the higher temperature variety δ-$Sr(HCOO)_2$, the quadratic form being:

$$10^5 \sin^2\theta = 1176.8(h^2 + k^2) + 565.94l^2$$

This relation corresponds to a body-centered tetragonal lattice; the unit-cell has the following parameters: $a = b = 7.106 \pm 0.006$ Å, $c = 10.25 \pm 0.01$ Å; it contains four $Sr(HCOO)_2$ formulas ($Z = 4$) and the c/a ratio (1.442) is close to $(2)^{1/2}$.

TABLE II

COMPARED X-RAY DIFFRACTION PATTERNS OF β-Sr(HCOO)$_2$ AND β-Ca(HCOO)$_2$ ROOM TEMPERATURE (25°C)—57.3 mm RADIUS CAMERA—CuKα RADIATION

β-Sr(HCOO)$_2$					β-Ca(HCOO)$_2$				
	$10^5\sin^2\theta$					$10^5\sin^2\theta$			
I	Obsd	Calcd	*d*	*h k l*	*I*	Obsd	Calcd	*d*	*h k l*
vs	1813 ± 12	1817	5.72	0 1 1	vs	1960 ± 13	1961	5.51	0 1 1
vvw	2973 ± 15	2980	4.47	1 1 1					
vw	3780 ± 17	3780	3.96	0 1 2	vw	3943 ± 17	3945	3.88	0 1 2
vs	4648 ± 18	4649	3.573	2 0 0	vs	5203 ± 20	5197	3.386	2 0 0
w	4948 ± 19	4943	3.463	1 1 2					
m	5300 ± 20	5304	3.346	0 2 1	m	5840 ± 20	5859	3.189	0 2 1
vvw	5795 ± 20	5812	3.199	1 2 0					
w	6463 ± 21	6467	3.030	1 2 1					
s	7052 ± 22	7053	2.900	0 1 3	s	7270 ± 22	7253	2.859	0 1 3
vvw	8422 ± 24	8430	2.654	1 2 2					
					vvw	8538 ± 24	8552	2.639	1 1 3
vw	9289 ± 25	9299	2.527	2 2 0					
vw	9934 ± 26	9954	2.443	2 2 1	w	10586 ± 27	10586	2.370	0 0 4
mw	10474 ± 27	10473	2.380	0 0 4	vw	11071 ± 27	11056	2.320	2 2 1
m	11110 ± 27	11116	2.310	0 3 1	ms	12363 ± 29	12355	2.196	0 3 1
w	11687 ± 28	11703	2.253	1 2 3					
vw	12284 ± 29	12279	2.198	1 3 1	vw	13665 ± 30	13654	2.085	1 3 1
m	13063 ± 29	13079	2.131	0 3 2	m	14343 ± 31	14339	2.036	0 3 2
ms	14239 ± 31	14242	2.042	1 3 2	m$_b$	15744 ± 32	15783 15638	1.943	0 2 4 1 3 2
m	15119 ± 31	15111 15122	1.981	2 3 0 0 2 4					
w	15747 ± 32	15766	1.941	2 3 1	vvw	17033 ± 32	17082	1.868	1 2 4
mw	16339 ± 32	16285 16352	1.905	1 2 4 0 3 3	m	17627 ± 33	17647	1.836	0 3 3
w$_b$	17624 ± 33	17527 17515 17729	1.835	0 1 5 1 3 3 2 3 2	vvw vw	19008 ± 34 19593 ± 35	18946 19536	1.786 1.742	1 3 3 2 3 2
vw	18609 ± 34	18598	1.785	4 0 0	vw	20781 ± 36	20787	1.691	4 0 0
w	19241 ± 34	19253	1.756	0 4 1	vw	21421 ± 36	21449	1.666	0 4 1
vw	19791 ± 35	19772 19760	1.732	2 2 4 1 4 0					
vvw	20374 ± 35	20415	1.706	1 4 1					
w	20979 ± 36	21014 21002 20922	1.682	0 2 5 2 3 3 3 3 0	vw	22867 ± 36	22844	1.612	2 3 3
vvw	21507 ± 36	21577	1.661	3 3 1	vvw	23976 ± 37	24048	1.574	3 3 1
vvw	22167 ± 36	22177	1.636	1 2 5	vvw	24683 ± 37	24732	1.552	1 4 2
vw	23537 ± 37	23540	1.588	3 3 2	w	26013 ± 38	26032 25984	1.512	3 3 2 2 4 0
vvw	24488 ± 37	24489	1.558	0 4 3	w	26623 ± 39	26643	1.494	2 4 1
vw$_b$	25752 ± 38	25664 25651 25865 25890	1.518	2 2 5 1 4 3 2 4 2 1 1 6	vvw	27476 ± 39	27476	1.471	2 3 4
vw	26816 ± 39	26826 26813	1.488	0 3 5 3 3 3	vvw	28295 ± 39	28233	1.450	0 3 5

TABLE II—(*continued*)

β-Sr(HCOO)$_2$					β-Ca(HCOO)$_2$				
	$10^5 \sin^2\theta$					$10^5 \sin^2\theta$			
I	Obsd	Calcd	d	$h\,k\,l$	I	Obsd	Calcd	d	$h\,k\,l$
vw	27972 ± 39	27989	1.456	1 3 5	vw	29520 ± 40	29532	1.420	1 3 5
vw	29063 ± 40	29071	1.429	0 4 4	vvw	31363 ± 41	31376	1.377	0 4 4
vvw	29680 ± 40	29714	1.414	0 5 1 3 4 1	vvw	33112 ± 41	33142	1.340	0 5 1 3 4 1
					vvw	33932 ± 41	33972	1.323	3 3 4
mw	31634 ± 41	31677	1.370	0 5 2 3 4 2	vw	35090 ± 42	35126 35016	1.301	0 5 2 3 4 2 1 1 7
vw	35123 ± 42	35189	1.300	1 3 6	vw_b	36764 ± 42	36810 36570	1.271	1 3 6 2 4 4
vw	36159 ± 42	36125 36112	1.281	1 4 5 1 5 3					
vvw_b	39626 ± 43	39599 39612	1.224	2 5 3 2 4 5					

(*b*). *α-Sr(HCOO)$_2$*

Sample previously heated and sealed at 280°C in a glass capillary. Since the DTA study has shown that the $\delta \rightarrow \alpha$ transition does not occur in the absence of water traces (*1*), we had to prepare in situ at 280°C a sample of strontium formate and to seal the glass capillary at this temperature in order to obtain an anhydrous sample which has never been in the presence of water vapor. After cooling, the sample prepared in this way was investigated by X-ray diffraction. Results represented in Fig. 3 can be summarized in the following way:

(a) Diffraction lines of the middle section (230–320°C) are the same as those observed on the upper part (δ zone) of Fig. 2; therefore they correspond to δ-Sr(HCOO)$_2$.

(b) The whole set of diffraction lines located in the lower part of Fig. 3, especially at 25°C, does not belong either to α-Sr(HCOO)$_2$ or to the dihydrate. Accordingly, we are in the presence of a new polymorphic species of strontium formate. This variety has been called β-Sr(HCOO)$_2$, since, as it will be shown further on, it is isomorphous with β-Ca(HCOO)$_2$. Table II allows the comparison of crystallographic data of β varieties of strontium and calcium formates.

(c) Above 360°C (upper section), the lines of SrCO$_3$ appear.

Diffraction lines of β-Sr(HCOO)$_2$ are indexed on the basis of a primitive tetragonal unit-cell

TABLE III

X-RAY DIFFRACTION PATTERN OF THE FACE-CENTERED CUBIC FORM OF δ-Sr(HCOO)$_2$ AT 230°C—38.2 mm RADIUS T.R.M.F. CAMERA—CuKα RADIATION

	$10^5 \sin^2\theta$			
I	Obsd	Calcd	d_{obs}	$h\,k\,l$
vs	1755 ± 17	1759	5.87	1 1 1
s	4690 ± 28	4693	3.57	2 2 0
m	6439 ± 32	6453	3.043	3 1 1
mw	9358 ± 38	9386	2.518	4 0 0
m	11143 ± 41	11146	2.309	3 3 1
ms	14094 ± 46	14079	2.052	4 2 2
mw	15868 ± 48	15839	1.934	3 3 3–5 1 1
mw	18789 ± 51	18772	1.775	4 4 0
w	20558 ± 53	20532	1.699	5 3 1
w	23486 ± 55	23466	1.589	6 2 0
vw	25170 ± 57	25225	1.535	5 3 3
vw	28121 ± 59	28158	1.453	4 4 4
vw	29903 ± 60	29918	1.409	7 1 1–5 5 1
w	32817 ± 61	32852	1.344	6 4 2
vw	34611 ± 62	34612	1.309	7 3 1–5 5 3

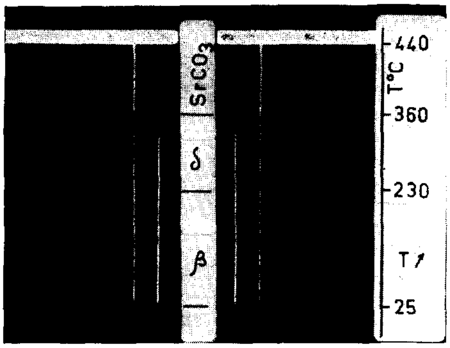

FIG. 3. β-Sr(HCOO)$_2$ temperature regulating X-ray diffraction pattern—25°C hr^{-1} heating rate.

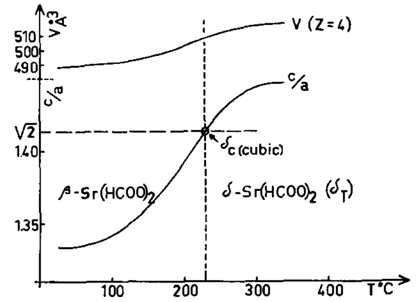

FIG. 4. Modification of the c/a ratio and the unit-cell volume for $Z = 4$ with temperature during $\beta \rightarrow \delta_c \rightarrow \delta_T$ structural changes.

with $a = b = 7.150 \pm 0.006$ Å; $c = 9.54 \pm 0.01$ Å; $Z = 4$ formulas per unit-cell. The pertaining quadratic form is:

$$10^5 \sin^2\theta = 1162.36(h^2 + k^2) + 654.58l^2,$$
$$T = 25°\mathrm{C}$$

(space groups $P4_12_12(D_4{}^4)$ or $P422(D_4{}^8)$).

(d) In the temperature range 25–230°C, β-Sr(HCOO)$_2$ diffraction lines are shifted and at 230°C pass over into a simpler pattern pertaining to a face-centered cubic unit-cell with $a_0 = 10.07 \pm 0.01$ Å (δ_c) (Table III), with $Z = 8$ and $F4_132(O^4)$ space group.

(e) Beyond 230°C, some lines of the above cubic phase split into doublets and the lines thus obtained are indexed on the basis of a body-centered tetragonal unit-cell (δ_T), the transformation matrix from the tetragonal I cell to the cubic F cell being:

$$\begin{array}{cc} & \text{cubic } F \\ \text{tetragonal } I & \boxed{\begin{matrix} 1 & \bar{1} & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{matrix}} \end{array}$$

Table IV summarizes the modification of β-Sr(HCOO)$_2$ unit cell parameters in the investigated temperature range (25–360°C), and Fig. 4 shows how the c/a ratio and the unit cell volume for $Z = 4$ change as a function of temperature. These curves let us look upon a progressive polymorphic transition, the order of which, according to the DTA results (*1*), is higher

TABLE IV

UNIT-CELL PARAMETER MODIFICATION DURING THE $\beta \rightarrow \delta_c \rightarrow \delta_T$ STRUCTURAL TRANSITIONS

Unit-cell volume for $Z = 4$ (Å^3)	T (°C)	Species	Lattice	Parameters		
				a (Å)	c (Å)	c/a
487.5	25	β	tetragonal P	7.150	9.54	1.334
489.6	50	β	tetragonal P	7.16	9.55	1.334
492.1	100	β	tetragonal P	7.16	9.60	1.342
495.7	145	β	tetragonal P	7.13	9.75	1.367
499.2	190	β	tetragonal P	7.13	9.82	1.378
506.9	210	β	tetragonal P	7.12	10.00	1.406
510.6	230	δ_c	cubic F or tetragonal I	10.07 7.121	 10.07	 $2^{1/2}$
511.1	260	δ_T	tetragonal I	7.11	10.17	1.430
517.6	280	δ_T	tetragonal I	7.106	10.25	1.442
517.2	340	δ_T	tetragonal I	7.10	10.26	1.446

TABLE V

$Sr(HCOO)_2$ X-RAY DIFFRACTION PATTERN AFTER THE $\delta \rightarrow \alpha$ TRANSITION—57.3 mm RADIUS CAMERA—CuKα RADIATION $T = 25°C$

I	$10^5 \sin^2\theta$		d_{obs}	$h\,k\,l$[a]
	Obsd	Calcd		
w	1890 ± 12	1899	5.64	0 1 1
s	2034 ± 13	2038	5.40	1 1 0
w	3106 ± 16	3100	4.37	0 2 0
vw	3431 ± 17		4.16	
w	4484 ± 18	4499	3.64	0 0 2
w	5060 ± 19	5050	3.42	2 0 0
s	5469 ± 20	5488	3.30	1 2 1
vw	5791 ± 20	5825	3.20	2 1 0
vw	6227 ± 21		3.09	
s	6547 ± 21	6537	3.013	1 1 2
m	6941 ± 22	6950	2.926	2 1 1
s	8114 ± 23	8101	2.706	0 3 1
m	9549 ± 25	9549	2.495	2 0 2
w	10897 ± 26	10897	2.335	0 1 3
w	12150 ± 28	12139	2.211	3 1 0
w	13166 ± 29	13151	2.125	2 3 1
m	14552 ± 31	14485	2.021	1 2 3
mw	14861 ± 31	14790	2.000	1 4 1
m	15582 ± 32	15589	1.953	3 2 1
vw	15996 ± 32	15947	1.928	2 1 3
mw	16641 ± 32	16640	1.890	3 1 2
vw	17098 ± 32	17098	1.864	0 3 3
w	20084 ± 35	20032	1.720	1 1 4
w	22149 ± 36	22148	1.638	2 3 3

[a] The hkl values are obtained on the basis of the unit cell dimensions described in *Strontium Formate at Room Temperature.*

than one. Thus, $\beta \rightarrow \delta$ transition corresponds to the passage from a simple tetragonal P lattice (β species) to a body-centered tetragonal I lattice (δ_T species—the P and I unit-cells have the same volume) through the intermediary of a face-centered cubic F lattice (δ_c species) at about 230°C.

Sample previously heated at 280°C without sealing the capillary. If α-$Sr(HCOO)_2$ is heated for one hr at 280°C and then cooled down in an open glass capillary, the diffraction lines indicated on Table V are observed at room temperature. They belong to α-$Sr(HCOO)_2$, but two of them, which are of very weak intensity (at 4.16 and 3.09 Å), and cannot be indexed on the basis of the unit cell described in *Strontium Formate at Room Temperature.* By assuming that α-$Sr(HCOO)_2$ issued from the cooling of δ-$Sr(HCOO)_2$ in the presence of water vapor crystallizes in a superstructure with $a' = 2a$, $b' = 2b$ and $c' = c$, the two extra lines at 4.16 and 3.09 Å may be indexed as (140) and (321), respectively. These two lines progressively vanish, and completely disappear 4 days after the sample preparation.

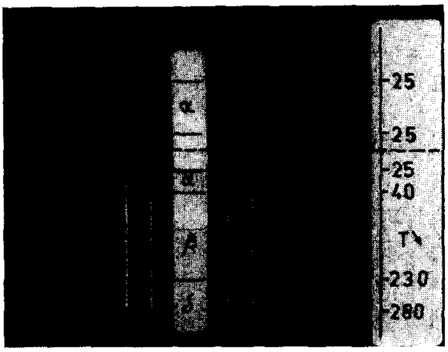

FIG. 5. δ-$Sr(HCOO)_2$ temperature regulating X-ray diffraction pattern—25°C hr^{-1} cooling rate. (Lower pattern) $\delta \rightarrow \beta \rightarrow \alpha$ transitions during the cooling of the sample in an open glass capillary. (Upper pattern) α-$Sr(HCOO)_2$ diffraction lines at 25°C, the film moving for 4 hr without any heating.

Reversibility of the $\beta \rightleftharpoons \delta_c \rightleftharpoons \delta_T$ Structural Evolution

The reversibility of the $\beta \rightleftharpoons \delta_c \rightleftharpoons \delta_T$ progressive transition has been checked in the following two cases:

(a) In a sealed glass capillary (cf. *Sample Previously Heated and Sealed at 280°C in a Glass Capillary* and Fig. 3).

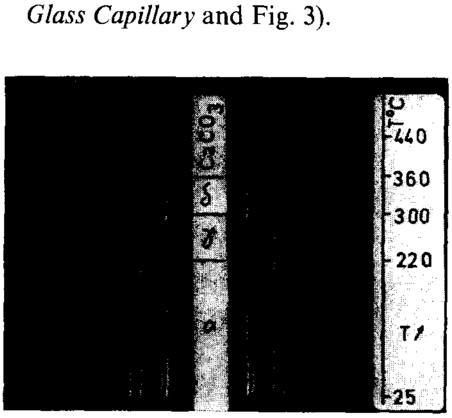

FIG. 6. α-$Ca(HCOO)_2$ temperature regulating X-ray diffraction pattern—25°C hr^{-1} heating rate.

(b) In an open glass capillary: in the presence of atmospheric water vapor $\delta_T \rightarrow \delta_c \rightarrow \beta \rightarrow \alpha$, transitions are observed on cooling (Fig. 5); the $\beta \rightarrow \alpha$ passage takes place at 40°C.

Calcium Formate at Room Temperature

The crystal lattices of α- and β-$Ca(HCOO)_2$ are known. The α species is orthorhombic and the β tetragonal, the unit-cell parameters being as follows:

	a (Å)	b (Å)	c (Å)	Z	Space group	Ref.	T (°C)
α-$Ca(HCOO)_2$ (values not mentioned)	10.163	13.381	6.271	8	*Pcab*	(*7*)	18.0
	10.16 ± 0.01	13.38 ± 0.01	6.28 ± 0.01	8	*Pcab*	this work	21.0
β-$Ca(HCOO)_2$	6.77	6.77	9.46	4	$P4_12_12$	(*8*)	—
(isomorphous with β-$Sr(HCOO)_2$ (Table II))	6.763 ± 0.006	6.763 ± 0.006	9.48 ± 0.01	4	$P4_12_12$ or $P422$	this work	25.0

Calcium Formate at Higher Temperatures

(*a*). α-$Ca(HCOO)_2$

Diffraction pattern in the range 25–440°C is represented by Fig. 6. On this pattern four distinct zones are observed:

(1) α zone (25–220°C) corresponds to α-$Ca(HCOO)_2$;

(2) γ zone (220–300°C) corresponds to γ-$Ca(HCOO)_2$ species, the existence of which has been precedently recognized by DTA (*1*) and is ascertained by ir spectroscopy. Some doublet lines on the diffraction pattern of this variety are progressively modified and finally yield a single line at 300°C;

(3) δ zone (300–360°C) corresponds to a new crystal lattice and thus reveals the existence of the δ-$Ca(HCOO)_2$ species, which has already been found by DTA (*1*);

(4) the upper zone pertains to rhombohedral calcite $CaCO_3$.

(*b*). β-$Ca(HCOO)_2$

X-ray diffraction patterns of the species issued from β-$Ca(HCOO)_2$ are represented on Fig. 7, and the following four zones are observed:

(1) β zone (25–180°C) for β-$Ca(HCOO)_2$;
(2) γ zone (180–300°C) for γ-$Ca(HCOO)_2$;
(3) δ zone (300–360°C) for δ-$Ca(HCOO)_2$;
(4) upper zone (360–440°C) for calcite $CaCO_3$.

δ-$Ca(HCOO)_2$ Crystal Lattice

Comparison of diffraction patterns of the δ varieties of strontium and calcium formates enables us to assign *hkl* indices to the lines observed for δ-$Ca(HCOO)_2$. Table VI summarizes the results concerning this species, the quadratic form at 330°C being as follows:

$$10^5 \sin^2\theta = 1296(h^2 + k^2) + 586l^2$$
$$\text{(tetragonal system)}$$

with $a = b = 6.77 \pm 0.01$ Å; $c = 10.05 \pm 0.02$ Å; $Z = 4$; $c/a = 1.485$ – possible space groups ($I4_1/a$ or $I4_1/amd$).

The first intense diffraction lines of δ-$Ca(HCOO)_2$ seem to indicate that, as in the case of δ-$Sr(HCOO)_2$, the lattice is body-centered. Unfortunately the following ones are weak and broad, and at these temperatures (~360°C) the presence of some parasitic lines belonging to $CaCO_3$ are observed, the formate having already undergone partial decomposition. Accordingly, it is not possible to state the $h + k + l = 2n$ rule for all indices of the three last very weak and broad lines of the δ species. However, it may reasonably be admitted that the δ species of both calcium and strontium formates are isomorphous.

FIG. 7. β-$Ca(HCOO)_2$ temperature regulating X-ray diffraction pattern—50°C hr^{-1} heating rate.

TABLE VI

δ-$Ca(HCOO)_2$ X-Ray Diffraction Pattern at 330°C—38.2 mm Radius T.R.M.F. Camera—Cu*Kα* Radiation

	$10^5 \sin^2\theta$			
I	Obsd	Calcd	d_{obs}	*h k l*
s	1877 ± 18	1888	5.62	1 0 1
vs	5185 ± 29	5185	3.38	2 0 0
w	9472 ± 38	9472	2.503	0 0 4
vvw	10412 ± 40	10368	2.387	2 2 0
vw	12365 ± 43	12256	2.190	3 0 1
w_b	13507 ± 45	13552	2.096	3 1 1
vw_b	15964 ± 48	16096 15952	1.928	1 0 5 2 1 4
vw_b	16738 ± 49	16992 16848	1.883	3 0 3 3 2 0
vvw_b	17428 ± 52	17392 17440	1.845	1 1 5 3 2 1

TABLE VII

γ-$Ca(HCOO)_2$ X-Ray Diffraction Pattern at 260°C—38.2 mm Radius T.R.M.F. Camera—Cu*Kα* Radiation

	$10^5 \sin^2\theta$			*h k l*	
I	Obsd	Calcd	d_{obs}	*B* mode	*P* mode
s	1704 ± 17	1719	5.90	1 0 $\bar{1}$	1 0 0
ms	2078 ± 19	2097	5.34	1 0 1	1 0 $\bar{1}$
vs	5273 ± 29	5273	3.324	2 0 0	2 0 $\bar{1}$
m	6059 ± 31	6061	3.129	1 0 $\bar{3}$	1 0 1
mw	7198 ± 34	7195	2.870	1 0 3	1 0 $\bar{2}$
m	9472 ± 38	9440	2.503	0 0 4	0 0 2
vw_b	10013 ± 39	10002 9707	2.43	(1 0 $\bar{4}$) 2 1 2	2 1 $\bar{2}$
vw	11308 ± 41	11334	2.288	1 2 $\bar{3}$	1 2 1
w	11937 ± 42	11887 12150	2.229	3 0 $\bar{1}$ 2 2 $\bar{2}$	3 0 $\bar{1}$ 2 2 0
w	13063 ± 44	13021	2.135	3 0 1	3 0 $\bar{2}$
vw_b	13641 ± 45	13662 13583	2.09	2 2 2 1 3 $\bar{1}$	2 2 $\bar{2}$ 1 3 0
w_b	15535 ± 47	15469	1.95	3 0 $\bar{3}$	3 0 0
w_b	16446 ± 49	16442 16226	1.90	1 1 $\bar{5}$ 2 0 4	1 1 2 2 0 $\bar{3}$
w_b	18891 ± 51	18879 18332	1.77	3 0 3 1 1 5	3 0 $\bar{3}$ 1 1 $\bar{3}$

γ-$Ca(HCOO)_2$ Crystal Lattice

X-ray diffraction patterns represented on Figs. 6 and 7 show the relationship occurring between the diffraction lines during the $\gamma \to \delta$ transition. γ-$Ca(HCOO)_2$ *hkl* indices deduced from those of δ species yield the following parameters for the monoclinic unit-cell thus obtained: $a = 6.75$; $b = 6.705$; $c = 10.10$ Å; $\beta = 96°9'$; $Z = 4$; *B* mode ($T = 260$°C); and the quadratic form is:

$$10^5 \sin^2\theta = 1318.25(h^2 + k^2) + 590.03l^2 + 189.13hl.$$

For all the lines observed, the $h + l = 2n$ (*B* mode) extinction rule is satisfied, and accordingly the conventional *P* mode monoclinic lattice may be determined, the new parameters for γ-$Ca(HCOO)_2$ being as follows: $a = 6.75$; $b = 6.705$; $c = 5.78$ Å; $\beta = 119°28'$; $Z = 2$; *P* mode ($T = 260$°C); the new quadratic form is then:

$$10^5 \sin^2\theta = 1719.15h^2 + 1318.25k^2 + 2310.12l^2 + 1982hl.$$

Both indices for the *B* and *P* modes of the crystal lattice of γ-$Ca(HCOO)_2$ species are indicated on Table VII. The possible space groups for the *P* mode are $P2(C_2^{\,1})$, $Pm(C_s^{\,1})$ or $P2/m(C_{2h}^1)$.

Reversibility of $\beta \rightleftharpoons \gamma$ and $\gamma \rightleftharpoons \delta$ Transitions

The study of reversibility of these transitions gives the following results:

(a) During the first thermal cycle (50°C hr^{-1}) the following transitions are observed:

$$\beta \to 180°C \to \gamma \to 180\text{–}300°C \to \delta(+\gamma)$$
$$(\gamma +)\,\beta \leftarrow 90\text{–}100°C \leftarrow \gamma \leftarrow 300°C \leftarrow\!\lrcorner$$

with persistence of γ-$Ca(HCOO)_2$ phase as already mentioned elsewhere (*4*).

(b) During the next thermal cycles, the same transitions are observed, but after the second run γ phase no longer persists in the presence of the β or δ phases. The $\beta \rightleftharpoons \gamma$ and $\gamma \rightleftharpoons \delta$ transitions are then perfectly reversible.

The fact that the γ species is not completely transformed during the first two thermal cycles may be due to structural defects or impurities; for instance water traces which are only progressively eliminated during these runs, as shown by ir spectrophotometry.

(c) Diffraction patterns show that $\gamma \rightleftharpoons \delta$ transitions are progressive (this is not the case of the abrupt $\beta \rightleftharpoons \gamma$ transitions), and that they occur on a broad temperature range: the $10\bar{1}$–101, $30\bar{1}$–301 ... doublets of

γ-Ca(HCOO)$_2$ progressively yield the corresponding 101, 301 ... lines of δ-Ca(HCOO)$_2$ and vice-versa (cf. Figs. 6 and 7). Hence it is not possible to locate $\gamma \rightleftharpoons \delta$ transition other than by an average temperature of 300°C.

Discussion

The results obtained by X-ray diffraction are now to be compared to those obtained by DTA (*1*) with the help of ir spectrophotometry.

Firstly, the former technique gave us the crystal lattices of all the varieties investigated. Secondly, if the $\alpha \rightleftharpoons \gamma$ and $\beta \rightleftharpoons \gamma$ transitions of Ca(HCOO)$_2$ and the $\alpha \rightleftharpoons \delta$ transition of Sr(HCOO)$_2$ are rapid, this is not the case of the $\gamma \rightleftharpoons \delta$ transition of Ca(HCOO)$_2$ and the $\beta \rightleftharpoons \delta$ transition of Sr(HCOO)$_2$, which are both progressive. Thirdly, among the above polymorphic species, δ-Sr(HCOO)$_2$, γ-Ca(HCOO)$_2$ and δ-Ca(HCOO)$_2$ have been established by DTA and their existence has been verified by X-rays. The existence of the new β-Sr(HCOO)$_2$ phase could be established by X-ray diffraction only.

The specific action of water traces on some polymorphic transitions has been firmly established by the three techniques. Accordingly, the β-Sr(HCOO)$_2$ species is transformed into α-Sr(HCOO)$_2$ only in the presence of water traces, and in the absence of water traces the higher temperature variety δ-Sr(HCOO)$_2$ (δ_c, δ_T) is reversibly transformed into β-Sr(HCOO)$_2$.

The progressivity of the $\beta \rightarrow \delta_c \rightarrow \delta_T$ structural evolution of strontium formate has clearly been observed by X-rays (cf. Fig. 5), and the continuity of this transition precludes its detection by DTA or ir spectroscopy. However, it can be mentioned that the ν_s(CO) (1366 cm^{-1}) and δ(OCO) (783 cm^{-1}) vibrations of δ-Sr(HCOO)$_2$ in the ir spectrum obtained at 262°C progressively split into doublets on cooling and yield respectively bands at 1366–1357 and 787–771 cm^{-1}, a fact which can be related to the progressivity of the δ(tetragonal I) $\rightarrow$ δ(cubic F) $\rightarrow$ β(tetragonal P) evolution which occurs with an increasing number of formula-units per elementary-cell: so, for each fundamental vibration of the formate ion, multiplets are to be expected on the ir absorption spectrum of β-Sr(HCOO)$_2$.

On the other hand, $\beta \rightarrow \alpha$ transition of calcium formate takes place only in the presence of water vapor; furthermore, it has been observed in the course of the ir investigation that both α and β calcium formates contain residual water. If it is assumed that this water is eliminated slowly during the heating, some experimental facts referred to above may now be interpreted in one of the two following ways:

(a) β-Ca(HCOO)$_2$ polymorphism occurs in the presence of adsorbed residual water according to following scheme:

$$\langle\beta\text{-Ca(HCOO)}_2\rangle + \varepsilon H_2O_{ads} \rightleftarrows \langle\gamma\text{-Ca(HCOO)}_2\cdot\varepsilon H_2O\rangle$$

$$\langle\gamma\text{-Ca(HCOO)}_2\rangle + \varepsilon H_2O_{ads} \rightleftarrows \langle\delta\text{-Ca(HCOO)}_2\rangle + [\varepsilon H_2O]^1.$$

The above reactions assume the presence of an intermediate solid solution $\langle\gamma$-Ca(HCOO)$_2$.εH$_2$O$\rangle$ before the $\gamma \rightarrow \delta$ transition. This mechanism accounts for the fact that the temperature range of the $\gamma \rightarrow \delta$ transition is broader during the first thermal cycle (230–300°C) than during the next one (270–300°C), since the water amount involved in this mechanism is related to the transition temperature.

(b) Water is kept within the structure of α, β, and γ formates, under a form which remains to be elucidated. Then, the progressive character of the $\gamma \rightarrow \delta$ transition, which is accompanied by a volume expansion of 1.41 %, would simply pertain to a progressive water evolution during the thermal expansion of the structure.

Summary and Conclusion

It has been established that the comparative study by the means of DTA, ir spectroscopy, and X-ray diffraction enable the detection and the characterization of the polymorphic species of strontium and calcium formates indicated on Fig. 8.

Among all the polymorphic phases established in the course of this study, β and δ varieties of both strontium and calcium formates are respectively isomorphous.

Finally, it can be seen that water traces accelerate the $\beta \rightarrow \alpha$ transitions of calcium and strontium formates, but slow down the $\gamma \rightarrow \delta$ transition of calcium formate. The mechanism of their action, unknown to date, is worth being

---

[1] The pure solid is noted ⟨S⟩. ⟨S.G⟩ designates a solid solution of G into the solid S. [G] is for a pure gas, G$_{ads}$ if the gas is adsorbed on S.

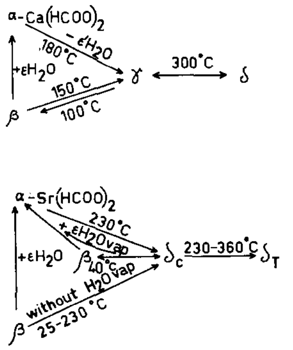

FIG. 8. "Anhydrous" Sr(HCOO)$_2$ and Ca(HCOO)$_2$ polymorphism.

investigated, and for this purpose the kinetic study of the influence of water vapor on the $\beta \rightarrow \alpha$-Ca(HCOO)$_2$ transition is presently in progress in our laboratory.

References

1. C. COMEL AND B. F. MENTZEN, *J. Solid State Chem.* **9**, 210–213 (1974).
2. B. MENTZEN, *Rev. Chim. Minerale* **6**, 713 (1969).
3. B. MENTZEN, *Bull. Soc. Fr. Mineral. Cristallogr.* **94**, 138 (1971).
4. *Structure Reports* **12**, 333 (1949).
5. J. FALGUEIRETTES, *C.R. Acad. Sc. Paris* (C) **253**, 994 (1961).
6. B. F. MENTZEN, *J. Solid State Chem.* **3**, 20 (1971).
7. *Structure Reports* **11**, 556 (1948).
8. C. J. H. SCHUTTE AND K. BUIJS, *Spectrochim. Acta* **20**, 187 (1964).
9. B. F. MENTZEN, *J. Solid State Chem.* **3**, 12 (1971).