are indebted also to the Massachusetts Institute of Technology for the use of the spectroscopic equipment and to Dr. G. R. Harrison and Mr. A. Knudsen of the Physics Department of that institution for their kind and helpful coöperation.

Summary

The behavior of lignins as absorbers of energy in the ultraviolet region has been compared with that of known compounds in the same region and certain conclusions drawn from such comparison. These have been enumerated above and may be briefly summarized as follows:

1. The spectra of amorphous lignins can be explained satisfactorily on the assumption that they are derived from lignin precursors of the types exemplified by hydroxy derivatives of 1-(4-hydroxy-3-methoxyphenyl)-1-propanone and 1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone.
2. The absorption curves indicate that lignin is aromatic in nature.
3. The evidence suggests that a carbonyl group or an ethylenic double bond is present in conjugation with the aromatic nucleus to some at present unknown extent.

MONTREAL, CANADA RECEIVED MARCH 11, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

X-Ray Diffraction of Sodium Laurate, Palmitate and Stearate at Room Temperature

BY JAMES W. MCBAIN, O. E. A. BOLDUAN AND SYDNEY ROSS

In a previous communication[1] the characterization of different phases of sodium stearate was made on the basis of X-ray powder diffraction photographs. In the present paper fiber photographs of sodium laurate, sodium palmitate and sodium stearate are interpreted, yielding further information with regard to different soap phases.

Materials.—The soaps used throughout the present investigation were prepared from the corresponding fatty acids of the greatest purity supplied by Kahlbaum. Dr. R. D. Vold had prepared fibers of sodium palmitate by sealing a mixture of 25% water, 75% soap in an Erlenmeyer flask in an oven at 90° for a few weeks. It was found that soap fibers could be more easily prepared by placing a mixture of 25% water and 75% soap in an open beaker, under a bell jar without seal, in an oven at 90°. After about twelve hours it was observed that inside the porous mass of soap there were fine bundles of fibers about 3 mm. long and about 0.1–0.2 mm. in diameter. The sodium laurate fibers were much better formed than those of the sodium palmitate and stearate.

Mounting of Soap Fibers.—Fine glass capillary tubing, with an outer diameter of 1.5 mm. and an inner diameter of about 0.1–0.2 mm., is used. A small bundle of fibers, three or four millimeters long, having a diameter slightly greater than the internal diameter of the capillary and with a pointed end, is placed in the capillary and gently forced into it for a distance of about 1 mm. until it is firm. The fiber bundle is examined under a lens and all fibers not in line with the main bundle are carefully removed. Examination with a telescope having a cross-hair is made to ascertain that the fiber is aligned along the axis of the capillary. The capillary, with the fiber, is mounted at the end of a steel shaft which fits into the camera and is rotated at a speed of one revolution per minute by a Telechron motor.

Method.—The radiation used was Cu Kα ($\lambda = 1.537$ Å.), filtered through nickel foil. All the data were examined for possible Cu Kβ lines and also for lines due to the L radiation of tungsten from the filament ($\lambda = 1.675$ Å.).

1. **Results with Sodium Laurate.**—Sodium laurate fibers, prepared and mounted as previously described, were photographed in a cylindrical camera with a radius of 50 mm. The photograph obtained is shown in Fig. 1a and Fig. 1b. Using a different fiber and the cylindrical camera designed for high temperature,[2] with a radius of 57.3 mm., the photograph shown in Fig. 2 was obtained. Powder photographs taken with the flat casette camera and high temperature camera are reproduced in Figs. 3 and 4, respectively. With the casette camera the soap was pressed into a hole in a brass washer 1.0 mm. thick which was mounted on the end of the collimating tube. The soap sample for the cylindrical camera was "cast" in the form of a stick which was mounted on the end of a rotating shaft. This method uses the same technique as de Bretteville.[3] The powder photographs obtained by these two methods are identical.

Previous investigations have shown that soaps crystallized from water are monoclinic and that in soap fibers and crystals the *b* axis of the unit cell

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(1) J. W. McBain, A. de Bretteville and S. Ross, *J. Chem. Phys.*, **11**, 179 (1943).

(2) A. de Bretteville, *Rev. Sci. Instruments*, **13**, 481 (1942).

(3) A. de Bretteville, Ph.D. Dissertation, Stanford University, 1941. May be ordered copied in bibliofilm or photoprint form by the Bibliofilm Service, United States Department of Agriculture Library, Washington, D. C.

is along the fiber axis.[4] From the position of the first layer lines in the fiber photograph the repeating distance, *b*, along the fiber axis was calculated. The value of $c \sin \beta$ was readily determined from the position of the spots on the equator line corresponding to the 002, 003, 005 reflections. Similarly $a \sin \beta$ was determined from the positions of the spots on the equator line corresponding to the 100, 200 and 300 reflections. The indices are obtained from the positions of the diffraction effects (see chart in Fig. 1b). The 200 effect is the most intense spot on the equator line while the 100 and 300 are quite weak.

Table I

The "Hydrated Gamma" Form[a] of Monoclinic Sodium Laurate at Room Temperature

	Powder photograph			Fiber photograph		
Indices	$\sin^2\theta$ (calcd.)	$\sin^2\theta$ (obs.)	Intensity	$\sin^2\theta$ (obs.)	d/n (obs.)	Intensity
			Equator line			
002	0.00235	0.00232	s.	0.00235	15.9	s.
003	.00528	.00532	v.s.	.00527	10.6	s.
100	.00939			.00939	7.95	w.
005	.0147	.0147	m.	.0147	6.35	m.
006	.0211			.0210	5.29	v.w.
				.0338	4.18	w.
200	.0376	.0374	v.s.	.0376	3.95	v.s.
		.0433	w.	.0432	3.70	w.
				.0475	3.53	w.
				.0584	3.18	w.
		.0700	m.	.0711	2.88	w.
300	.0845	.0852	w.	.0850	2.64	w.
		.101	w.	.0994	2.44	w.
		.115	w.	.115	2.27	m.
				.181	1.81	v.w.
				.277	1.46	v.w.
			First layer line			
012	0.0231			0.0231	5.06	w.
013	.0260	0.0262	v.s.	.0260	4.76	v.s.
110	.0301	.0302	m.	.0301	4.43	m.
015	.0354			.0354	4.08	s.
016	.0419	.0422	m.	.0420	3.75	w.
017	.0495	.0491	w.	.0496	3.45	w.
210	.0583	.0586	w.	.0587	3.17	w.
				.0669	2.97	s.
				.0797	2.72	w.
				.0911	2.54	w.
310	.105			.105	2.37	w.
				.119	2.22	w.
				.135	2.09	w.
				.154	1.96	v.w.
410	.171			.171	1.86	v.w.
				.189	1.77	w.
			Second layer line			
				0.112	2.30	m.
220	0.121			.121	2.21	m.
				.130	2.13	m.

[a] See later, under sodium stearate.

The dimensions of the unit cell which were thus obtained for sodium laurate are as follows: $a \sin \beta = 7.94$ Å., $b = 5.34$ Å., $c \sin \beta = 31.8$ Å. Those values were substituted in the monoclinic equation

$$\sin^2\theta = \frac{\lambda^2}{4}\left[\frac{h^2}{(a \sin \beta)^2} + \frac{k^2}{b^2} + \frac{l^2}{(c \sin \beta)^2} - \frac{2hl \cos \beta}{a\,c \sin^2 \beta}\right]$$

giving

$$\sin^2\theta = 0.00937h^2 + 0.0208k^2 + 0.000585l^2 - 0.00468hl \cos \beta \quad (1)$$

Since β cannot be unambiguously determined from fiber photographs alone, $\sin^2\theta$ values can only be calculated with certainty for those indices in which either *h* or *l*, or both, is equal to zero. In Table I all the $\sin^2\theta$ values obtained from the powder and fiber photographs are compared with those calculated from equation 1 for various values of *h*, *k*, *l*. The agreement between the observed and calculated values of $\sin^2\theta$ is very good and in all cases within the error of measurement. The powder photograph values of $\sin^2\theta$ are in agreement with those of the fiber.

2. Results with Sodium Palmitate

Fiber and powder photographs of sodium palmitate were obtained in a manner similar to that described for sodium laurate. They are shown in Figs. 5a, 5b and 6, respectively.

As in the case of sodium laurate, values for $a \sin \beta$, *b*, and $c \sin \beta$ were calculated. From these values the coefficients of the first three terms of the monoclinic equation were calculated. The values obtained are: $a \sin \beta = 7.79$ Å., $b = 5.27$ Å., $c \sin \beta = 42.1$ Å. The monoclinic equation is

$$\sin^2\theta = 0.00973h^2 + 0.0211k^2 + 0.000333l^2 - 0.00360hl \cos \beta \quad (2)$$

In Table II all the $\sin^2\theta$ values, both from the fiber and powder photographs, are compared with the calculated values.

On the basis of the long spacings, obtained by de Bretteville[5] and by Thiessen and Stauff,[6] this may be identified as the beta-form of monoclinic sodium palmitate. Thiessen and Stauff's Fig. 12 likewise indicates a value of $b = 5.27$ Å. for beta sodium stearate, when the spots of that figure are identified by means of the powder photographs already described.[1] Furthermore, the value of *a*

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(4) P. A. Thiessen and R. Spychalski, *Z. physik. Chem.*, **A156**, 442 (1931); L. Marton, J. W. McBain and R. D. Vold, This Journal, **63**, 1990 (1941); S. Ross, *J. Phys. Chem.*, **46**, 414 (1942).

(5) A. de Bretteville and J. W. McBain, *Science*, **96**, 470 (1942).

(6) P. A. Thiessen and J. Stauff, *Z. physik. Chem.*, **A176**, 397 (1936).

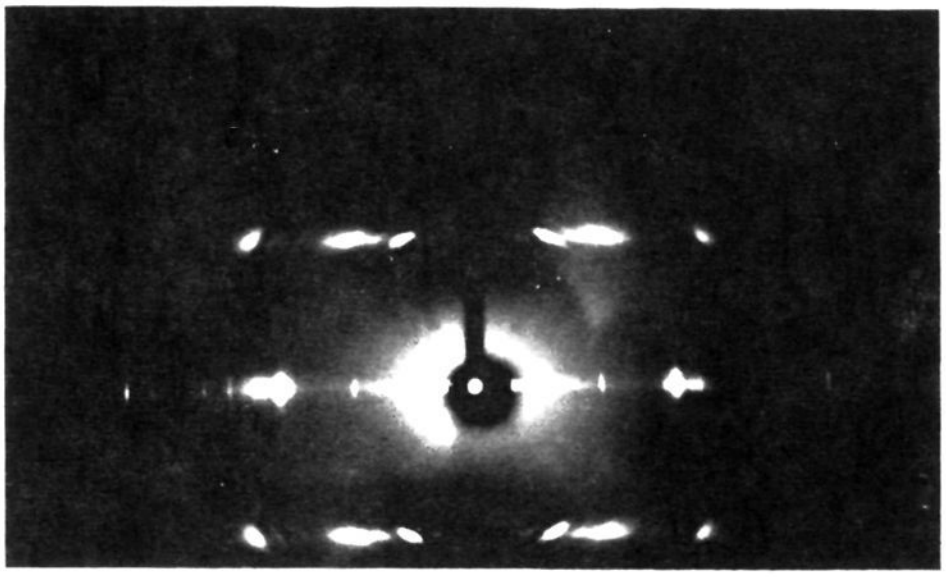

Fig. 1a.—Sodium laurate fiber at room temperature, radius of camera 50.0 mm.

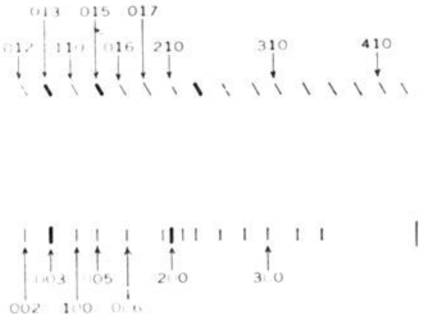

Fig. 1b.—Chart showing indices (left half omitted).

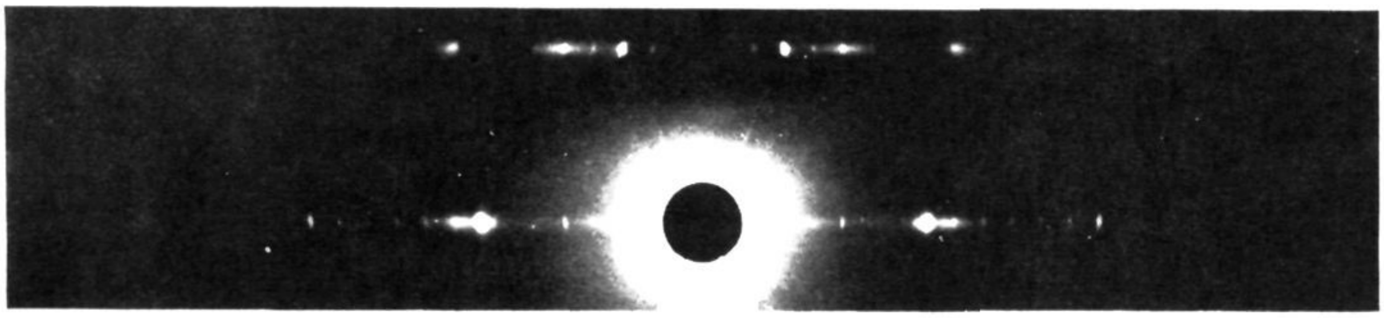

Fig. 2.—Sodium laurate fiber at room temperature, radius of camera 57.3 mm.

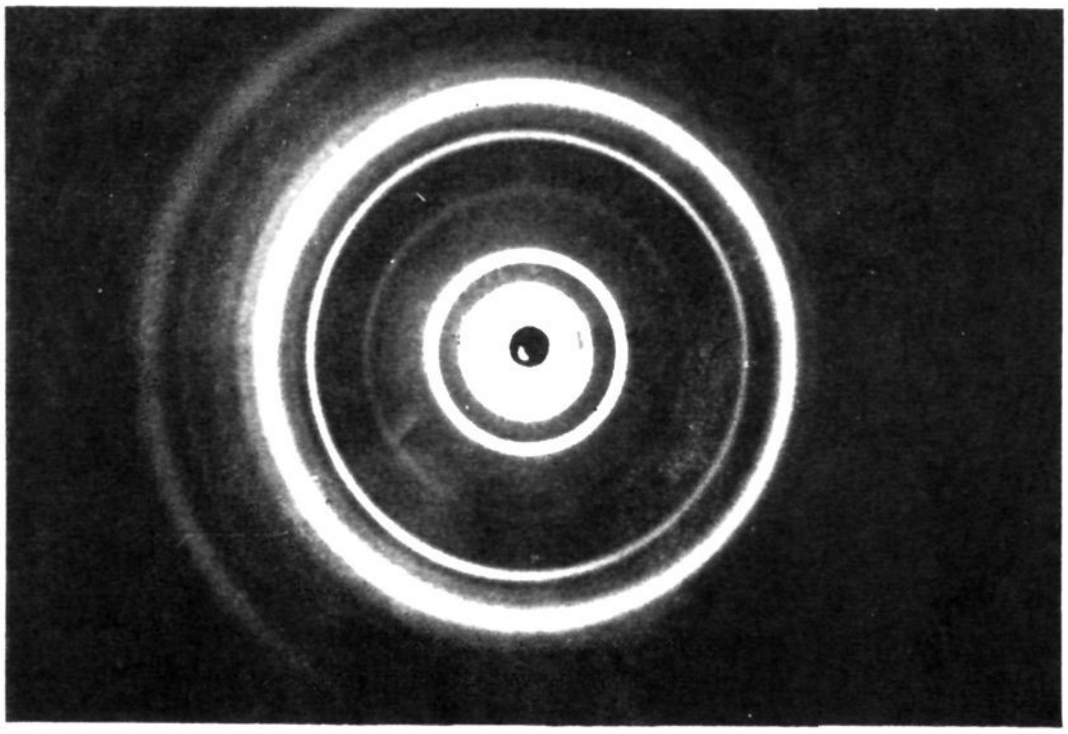

Fig. 3.—Sodium laurate powder at room temperature, sample to plate distance 65.2 mm.

Fig. 4.—Sodium laurate powder at room temperature, radius of camera 57.3 mm.

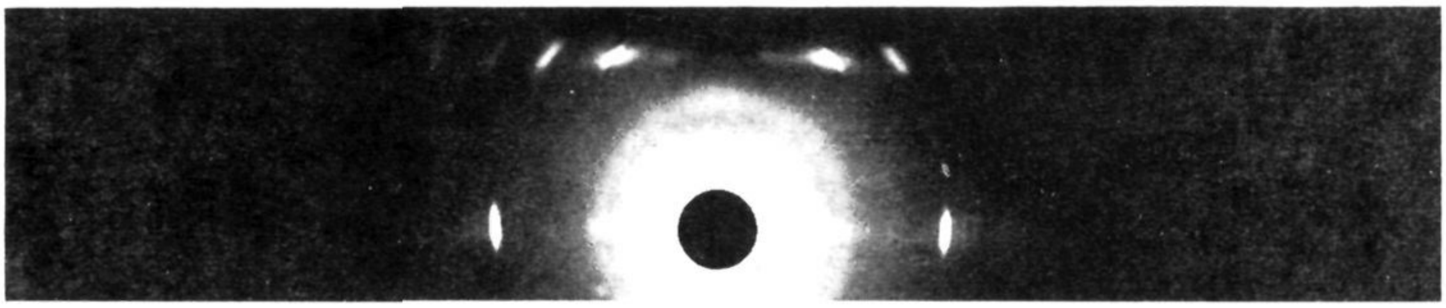

Fig. 5a.—Sodium palmitate fiber at room temperature, radius of camera 57.3 mm.

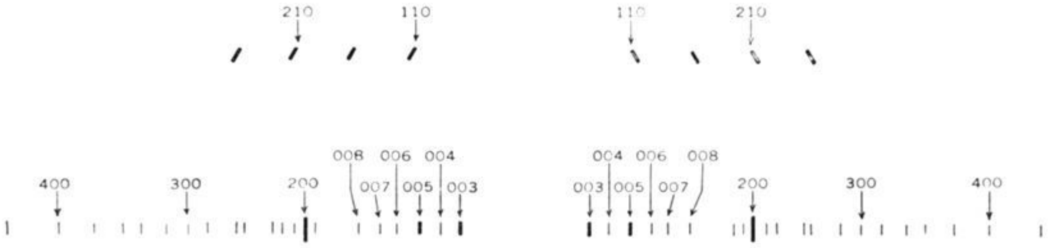

Fig. 5b.—Chart of sodium palmitate fiber at room temperature, radius of camera 57.3 mm.

Fig. 6.—Sodium palmitate powder at room temperature cooled slowly, radius of camera 57.3 mm.

Fig. 7.—Sodium palmitate powder at room temperature cooled rapidly, radius of camera 57.3 mm.

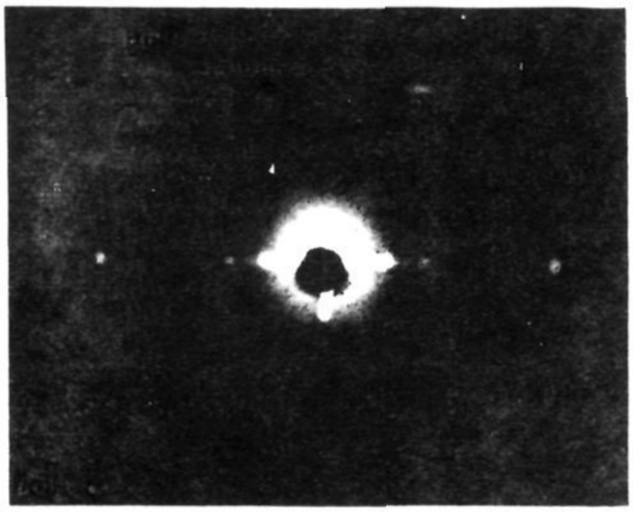

Fig. 8a.—Sodium stearate fiber at room temperature, sample to plate distance 55.7 mm.

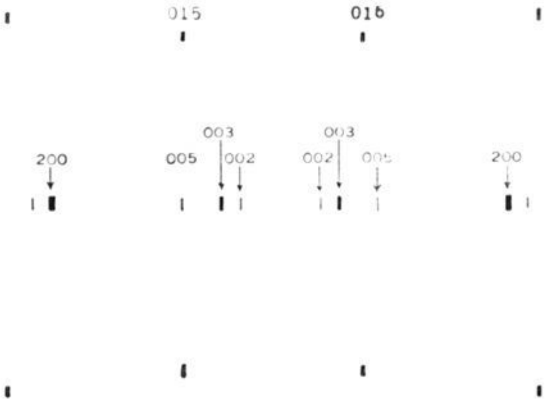

Fig. 8b. Chart of sodium stearate fiber at room temperature.

Table II

Sodium Palmitate Fiber, Monoclinic Beta-Form, at Room Temperature

Indices	Calcd. $\sin^2\theta$	Obs. $\sin^2\theta$	d/n	Intensity
		Equator line		
003	0.00302	0.00302	14.0	s.
004	.00537	.00549	10.4	v.w.
005	.00838	.00838	8.40	s.
006	.0121	.0128	6.97	v.w.
007	.0164	.0166	5.97	v.w.
008	.0214	.0213	5.26	v.w.
		.0341	4.16	v.w.
		.0372	3.99	v.w.
200	.0391	.0391	3.89	s.
		.0450	3.62	v.w.
		.0487	3.48	v.w.
		.0589	3.17	v.w.
		.0618	3.09	v.w.
		.0750	2.81	v.w.
300	.0879	.0855	2.63	v.w.
		.0955	2.49	v.w.
		.107	2.34	v.w.
		.120	2.22	m.
		.129	2.14	v.w.
400	.156	.156	1.95	v.w.
		.189	1.77	m.
		First layer line		
015	0.0294	0.0303	4.42	v.s.
110	.0308	.0311	4.36	s.
		.0327	4.25	m.
		.0435	3.68	s.
210	.0600	.0584	3.18	s.
		.0794	2.73	s.
		.133	2.10	w.

sin β for the beta monoclinic form of sodium stearate[1] was 7.77 Å.

Several phases were obtained in different powder photographs. Figs. 6 and 7 show two photographs of sodium palmitate, of which the first is cooled slowly from isotropic liquid, whereas the second was quenched from the same state. The strong line at $\sin^2\theta = 0.0265$, indicated by an arrow, has almost disappeared in Fig. 7. It was not observed in the fiber of the beta form.

3. Results with Sodium Stearate

The fibers used in the present investigation, and prepared in the manner already described, do not conform exactly in their principal diffraction effects with any of the polymorphs of the previous investigation,[1] although they closely resemble the fiber of sodium laurate.

The few spots observed have most in common with the side-spacings of the gamma-form of monoclinic stearate, but the long spacing, 45.6 Å., is half way between that of the beta- and gamma-forms. Possibly this is due to a small amount of water between the planes of the polar groups having lengthened the long spacing of the gamma-form, with a small but distinctive effect on the other spacings.[7] We have, therefore, designated this soap phase "hydrated gamma form."

It is possible definitely to settle some of the parameters of the unit cell of this form of sodium stearate. From the photograph in Fig. 8a and the descriptive chart appended to it (Fig. 8b), it will be seen that only a few of the principal diffraction effects are obtained in the fiber diagram; sufficient, however, to permit the calculation of the following parameters

$$a \sin \beta = 7.94 \text{ Å.},\ b = 5.34 \text{ Å.},\ c \sin \beta = 45.6 \text{ Å.}$$

In Table III the calculated spacings, based on these parameters, are compared with those observed.

Table III

A Fiber of the "Hydrated Monoclinic γ" Form of Sodium Stearate

Indices	Calcd. $\sin^2\theta$	Obs. $\sin^2\theta$	d/n	Intensity
		Equator line		
002	0.00113	0.00113	22.9	m.
003	.00255	.00255	15.2	v.s.
005	.00708	.00714	9.11	m.
200	.0376	.0376	3.97	v.s.
		.0437	3.68	m.
		First layer line		
015	0.0278	0.0276	4.63	s.
		.0690	2.93	w.

General Discussion

Although all the fibers were prepared in a similar manner, the different soaps form different phases under the same conditions. The spacings can be used to identify the samples as follows:

		$a \sin \beta$	b	$c \sin \beta$
Sodium laurate	Hydrated gamma phase	7.94	5.34	31.8
Sodium palmitate	Beta phase	7.79	5.27	42.1
Sodium stearate	Hydrated gamma phase	7.94	5.34	45.6

In previous communications from this Laboratory dealing with phase changes in the case of sodium stearate, the change in the long spacing of the unit cell has been primarily relied upon to distinguish between different phases. While the present work shows that there is but little change in the smaller dimensions of the unit cell, there are more noticeable changes in the "short spac-

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(7) Results of A. de Bretteville, quoted by J. W. McBain, "Advances in Colloid Science," Vol. I, 1942, p. 121.

ings" of the X-ray photograph, very useful for identification of phases.

Both beta and gamma curd phases are destroyed upon heating to nearly 100°. They are transformed into supercurd. For sodium stearate, dilatometric[8] and X-ray patterns show that the gamma phase is converted into supercurd at the first order transition point 89°, whereas the heat change shown by calorimetry[9] gave the value 90°. Upon cooling to room temperature gamma phase is reformed. Indeed, gamma phase is reformed at room temperature upon subsequent cooling, no matter how high the sodium stearate is heated, through the waxy and anisotropic liquid forms up to final melting to isotropic liquid above 288°.

General Conclusion

All crystals of soap consist of layers of double molecules placed end to end, hydrocarbon to hydrocarbon and carboxyl group to carboxyl group. As a first approximation c is the double length of the molecule, b is twice the thickness of the molecule and a is twice the width of the molecule in the plane of the hydrocarbon zig-zag chain. The different crystalline forms differ chiefly in the angle of tilt of the molecule, and in minor details of close packing in the a and b directions. Water lengthens the $c \sin \beta$ spacing, presumably by entering amongst and between the polar heads. Even the alpha form has been shown by Buerger[10] to be not strictly orthorhombic but to possess a slight monoclinic inclination. If the successive layers of double molecules do not fit exactly end to end but are staggered alternately, the unit cell naturally has to be doubled, as was shown for the special case of Buerger's crystal. Such modifications do not essentially alter the first statement of this paragraph. We therefore have a direct physical significance for the 001 spacing as being approximately $\sin \beta$ times the double length of the molecule, 020 being the thickness of the molecule and 200 approximately equal to $\sin \beta$ times the width of the zig-zag hydrocarbon chains.

Summary

Fiber as well as powder photographs of sodium laurate, palmitate and stearate have been made. They confirm the unit cell of the beta form of monoclinic soap and give the unit cell for a "hydrated gamma form" of monoclinic soap at room temperature.

Alpha, beta and gamma forms differ primarily in long spacings, but likewise to a lesser extent in the lines corresponding to side spacings. The strongest characteristic beta line in the powder diagram corresponds to $d/n = 4.28$ Å., whereas that of the hydrated gamma or gamma phase is $d/n = 4.00$ Å.

[8] M. J. Vold, M. Macomber and R. D. Vold, THIS JOURNAL, **63**, 168 (1941).

[9] R. D. Vold, *ibid.*, **63**, 2915 (1941).

[10] M. J. Buerger, *Proc. Nat. Acad. Sci.*, **28**, 529 (1942).

STANFORD UNIVERSITY, CALIFORNIA

RECEIVED FEBRUARY 8, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Induced Chlorination of Maleic Acid. Evidence for Chain Reaction Mechanisms

BY HENRY TAUBE

The results to be presented show that certain substances when added to a solution containing maleic acid, chlorine and hydrochloric acid, induce the addition of chlorine to maleic acid. It is observed that the induction factor can rise to large values (exceeding 200 in some cases) and that the effect continues only while the inductor is being consumed. Among the substances which induce the reaction are Fe^{++} and Ti^{+++}; it is assumed that these and other reducing agents which produce the effect, do so because they reduce chlorine by a one-electron change to produce atomic chlorine[1] in the first step as shown by the equation below for ferrous ion.

$$Fe^{++} + Cl_2 \longrightarrow FeCl^{++} + Cl \qquad (1)$$

Atomic chlorine can set up a chain reaction of the type[2]

[1] The substance present as the reactive intermediate in solutions of the chloride ion concentration employed is probably Cl_2^- (Taube and Bray, THIS JOURNAL, **62**, 3369 (1940)). For convenience in representing reactions, the simple formula Cl is employed throughout.

[2] Similar mechanisms are proposed for the photo addition of halogens to certain substances containing double bonds: Rollefson and Burton, "Photochemistry," Prentice-Hall, New York, N. Y., 1942.