[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Diffraction of X-Rays by Sodium Oleate and Hexanolamine Oleate

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Although the oleates are of even greater commercial interest, their X-ray investigation has lagged behind that of the saturated soaps because of the difficulty of procuring pure samples. The oleates present the additional difficulty that they do not crystallize or form fibers as readily as the stearate, palmitate or laurate soaps. This paper records results on a carefully purified sample of sodium oleate, where a small amount of fiber formation was induced by extrusion through an orifice under pressure. Although the degree of fibrillation thus produced is not outstanding—it does not compare, for example, with the fibers obtained naturally from the saturated sodium soaps—yet the nature of the soap molecule is such that the long spacings are readily discriminated from the side spacings, and even a small degree of fiber formation is sufficient to determine the relation of the (001) planes to the direction of the fiber axis. The general advantage that fiber diagrams have over powder diagrams is for those reasons rendered even more striking in the case of such long chain carbon compounds.

Material.—The specially pure oleic acid, from which one sample of sodium oleate was prepared, was produced and kindly supplied to us by Professors Brown and Foreman of Ohio State University. A description of the method of purification has been published.[1a]

Other samples of sodium oleate were made from oleic acid obtained from the British Drug House, Kahlbaum, and Merck. The oleic acid of the British Drug House (BDH) was prepared by the Lapworth method.[2]

The hexanolamine oleate was prepared from Kahlbaum "purest" oleic acid by Dr. E. Gonick of the Stanford laboratories and is to be described in another publication. The amine used is 4-methyl-4-amino-pentanol-2 (mol. wt. 117.1).

Method.—The radiation was supplied by a 1944 model General Electric X-ray diffraction unit (XRD-1) and copper target tube, provided with two beryllium windows. A General Electric X-ray monochromator with a quartz crystal was used for the key powder photographs, to eliminate all beta and possible tungsten lines. Such exposures required about forty hours. For ordinary purposes of identification unfiltered radiation direct from the tube is satisfactory.

The Interpretation of Fiber Diagrams of Soaps

The technique employed for indexing crystals is an adaptation of the rotating single crystal technique to the examination of fiber photographs. Typical fiber and powder photographs have already been published and interpreted in this Journal[3] and reference should be made to the figures and diagrams there reproduced. Hexanolamine oleate gives better photographs than any other soap.

Definitive X-ray structural examination has been achieved by Buerger[4] for single crystals of a very few forms of soap. A very few single crystals have also been examined by Thiessen *et al.* Furthermore, these and other authors, including also other work published from the Stanford Laboratories, have shown that there are many polymorphic forms of each of such saturated sodium soaps as sodium stearate. All the studies of single crystal neutral soaps have shown them to be monoclinic. It is of interest to compare the present results with the already authenticated structures of other soaps.

It is, of course, impossible in general to determine crystal structure merely from a powder photograph. However, in the case of soap, the double molecules are so long in comparison with their width that in a powder photograph it is often possible to distinguish with certainty between long spacings, 001, on the one hand, and side spacings on the other.

If now, further, a fiber photograph can be obtained, a separation of the side spacings follows for some of the spacings, and this leads to probable values for a, b and c. The layer lines give the values of b, and the indices k. Spots on the equator begin with the various orders of the long spacing 001, because in soaps the molecules lie in pairs end to end at right angles to the fiber axis. Further out come the short spacings $h0l$ in which, as a numerical computation will show, values of l varying between 0 and small integers have only a minor influence upon the position of the Bragg spacing, because of the ten-fold disproportion in length and breadth of the double molecules. Values of h can therefore be assigned and checked by comparison with the similar and intervening positions in the first and second layer lines. The minor divergences from exact positions of $h00$ and $hk0$ spacings allow certain small values of l in the hkl spacings to be inferred for a number of the remaining observations.

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[1] Bristol-Myers Postdoctorate Fellow in Chemistry, Stanford University; now Associate Professor of Chemistry, University of Alabama.

(1a) J. B. Brown and G. Y. Shinowara, THIS JOURNAL, **59**, 6 (1937).

(2) A. Lapworth, L. K. Parson and E. N. Mottram, *Biochem. J.*, **19**, 7 (1925).

(3) J. W. McBain, O. E. A. Bolduan and S. Ross, *ibid.*, **65**, 1873 (1943).

(4) K. W. Gardiner, M. J. Buerger and L. B. Smith, *J. Phys. Chem.*, **49**, 417 (1945).

Finally, many authors have inferred, for soap and for other aliphatic compounds, the monoclinic angle β from the relation of the observed long spacing to that calculated from the known dimensions of the molecule.[5]

In view of the foregoing we have assigned provisional indices to some of the spacings recorded in the present paper because it is illuminating to have this comparison between the different soaps. We have also indicated briefly the reasons for some of the conclusions drawn.

Part I. Results with Sodium Oleate.—Powder diagrams of different samples of sodium oleate reveal at least two different forms, which we shall call 1 and "2." The first form has a long spacing of 44.6 Å. and the "second" form or forms has a long spacing of 41.9 Å. Useful side spacings to distinguish the forms, a practice introduced for the sodium soaps by Ferguson, Rosevear and Stillman,[6] are Bragg spacing $d/n = 2.95$ for the former, and $d/n = 2.80$ or 2.87 for the latter. The soap prepared from the oleic acid supplied by Brown and Foreman, an outstandingly crystalline specimen, belongs to the first category; soaps prepared from Kahlbaum oleic acid and from the B. D. H. oleic acid (Lapworth method) belong to the second. A mixture of the forms was obtained in one sample prepared from Merck oleic acid. Table I gives the spacings obtained from typical monochromatic X-ray powder diagrams of the two forms.

TABLE I

X-RAY DIFFRACTION (POWDER) DATA FROM TWO POLYMORPHS OF SODIUM OLEATE[a]

No. 1 Source: Brown and Foreman's oleic acid				No. 2 Sources: Kahlbaum oleic acid and B. D. H. oleic acid	
d/n	Int.	hkl	Calcd. d/n	d/n	Int.
2.95	m			2.80	w
3.21	w	210	3.20	2.87	w
3.50	w			3.40	w
4.01	s	200	4.01	4.17	m
4.34	v.s. (halo)[b]	110	4.42	4.56	m
4.79	e	014	4.70	10.6	w
5.29	v.v.w.	010	5.29	13.8	s
6.38	m	007	6.37	Av. long spacing = 41.9 Å.	
8.91	s	005	8.92		
11.15	m	004	11.15		
14.7	v.s.	003	14.9		
22.0	s	002	22.3		

Av. long spacing = 44.6 Å.

[a] The analyses of the different samples of oleic acid from which sodium oleate is prepared (see references in Table II) show no sufficient differences in composition to account for the differences in the X-ray spacings, which are presumably due to polymorphism of the sodium oleate.

[b] From 4.2 to 4.5 Å.

In order to obtain the further structural information a sample of the polymorph no. 1 was forced through an orifice of 1 mm. diameter, emerging as a coherent fibrous string. An X-ray diffraction diagram showed a degree of orientation, from which the following information was obtained.

1. The long spacings are found to lie perpendicular to the direction of the extrusion of the fiber. The molecules therefore lie as usual transversely to the fiber axis, as already found by Thiessen[7,8,9] for sodium oleate as well as for the saturated sodium soaps. The same type of orientation has been revealed by the electron microscope.[10]

2. Along the fiber axis there were apparently two periodicities, $d = 5.29$ Å., intensity = w, and $d = 4.79$ Å., intensity = s. These lines also appear on the monochromatic photograph. The first of these spacings, $d = 5.29$ Å., is close to the value of b found for the saturated soaps,[3] so it is probably the true 010 spacing. It is interesting that a 010 spacing has not been observed in the saturated sodium soaps, with the exception of the alpha form. However, the oleate here observed has a long spacing too small to permit of its being in the alpha form. The other side spacing, although at first sight a fiber periodicity, on closer examination appeared due to spots on the first layer line that are joined by a circular arc because of the small degree of fibrillation.

3. The side spacing that has intensity maxima definitely and solely on the equatorial line is $d = 4.01$ Å. It appears to arise from the 200 plane.

4. If, like all other neutral soaps, sodium oleate is monoclinic, the parameters of the unit cell for this Form 1 of sodium oleate would then be:

$$\begin{aligned} a \sin\beta &= 8.02\ \text{Å.} \\ b &= 5.29\ \text{Å.} \quad {}^1\!/_2\, ab \sin\beta = 21.2\ \text{Å.}^2 \\ c \sin\beta &= 44.6\ \text{Å.} \end{aligned}$$

These bear a close similarity to the known parameters of the monoclinic gamma forms of the saturated soaps, with four molecules per unit cell, and the density is similar. Form 1 may therefore be termed gamma sodium oleate.

Previous investigators of the properties of solid sodium oleate have occasionally uncovered discrepant behavior, *e. g.*, in solubility behavior,[11] which has been attributed to a chemical change "as yet unknown." The difficulty of procuring reliably pure oleic acid has been pointed out by M. E. L. McBain.[12] The X-ray diffraction photograph therefore becomes of value in the identification of specimens.

Many papers contributed from this Laboratory

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(5) Karl Herrmann, *Trans. Faraday Soc.*, **29**, 972–976 (1933).

(6) R. H. Ferguson, F. B. Rosevear and R. C. Stillman, *Ind. Eng. Chem.*, **35**, 1005 (1943).

(7) P. A. Thiessen and R. Spychalski, *Z. physik. Chem.*, **156**, 435 (1931).

(8) P. A. Thiessen and Eva Erhlich, *ibid.*, **165**, 453 (1933).

(9) P. A. Thiessen and J. Stauff, *ibid.*, **176**, 397 (1936).

(10) Sydney Ross, *J. Phys. Chem.*, **46**, 414 (1942).

(11) K. Hess, W. Philippoff and H. Kiessig, *Kolloid Z.*, **88**, 40 (1942).

(12) M. E. L. McBain, unpublished work, partially quoted by R. D. Vold, *J. Phys. Chem.*, **43**, 1214 (1939).

have discussed physico-chemical properties of sodium oleate and its solutions. As the original samples were still available it seemed advisable to identify them according to the distinction in crystal structure afforded by X-ray diffraction. The two forms of sodium oleate are referred to in Table II as the gamma or first, and the second forms.

TABLE II

SODIUM OLEATE PREPARED FROM DIFFERENT SAMPLES OF OLEIC ACID

Oleic acid				
Source	Mol. wt.	Iodine no.	Literature reference	X-ray form
Brown and Foreman	282.3	89.8	1, 13	1 (gamma)
British Drug House (by Lapworth method)	285.0	85	2, 14	2
British Drug House (by Lapworth method)	288.3	85.8	15	2
British Drug House (by Lapworth method) (recovered)	284.1	87.1 81.2	16	2
Merck	288.5	93.4	17, 18	1 and 2
Theoretical	282.2	90.00		

Previously published reports on the diffraction of X-rays by sodium oleate are not in agreement with each other nor do they all agree well with the results presented in this paper. A fiber diagram obtained by Thiessen and Spychalski[7] led to the following parameters of the unit cell

$$c \sin \beta = 42.9°$$
$$a \sin \beta = 7.6°$$
$$b = 4.9°$$

These parameters are not those of the gamma form (no. 1) nor do they yield values of the 200 and 010 spacing that agree with any spacings here reported for the no. 2 form. It must therefore be regarded as still another form, with an exceptionally small cross-sectional area ($^1/_2\ ab \sin \beta$ = 17.2 sq. Å.).

Hess and Gundermann[19] report for solid sodium oleate a value of $c \sin \beta = 41$, and two principal side spacings of 4.27 and 4.76 Å. This bears an approximate resemblance to our no. 2 form. The spacings reported by Krishnamurti[20] lead to a value of $c \sin \beta = 36.6$ Å., smaller than any yet observed elsewhere. M. de Broglie and Friedel[21] report a long spacing of 43.5 Å. and cite previous investigations that reported values from 42 to 44 Å. These larger values would seem to refer to the gamma form, although no short spacings are reported.

Powder diagrams of sodium oleate were obtained in 1941 in this Laboratory by Alex de Bretteville, Jr., and are in agreement with the measurements here reported.

Part II. Results with Hexanolamine Oleate.—The hexanolamine oleate is a white, waxy material, melting at about 58° to an isotropic liquid. The measurements corrected from the monochromatic powder diagram are given in Table III.

TABLE III

DIFFRACTION OF X-RAYS BY HEXANOLAMINE OLEATE

Spacing, d/n in Å.	Intensity	hkl	Calculated d/n
30	v.v.s.	002	30.7
15.3	m	004	15.4
13.6	m	100	13.6
12.3	w	005	12.3
10.3	m	006	10.2
7.58	s	$h0l$	
6.82	s	200	6.80
6.02	s	$h0l$	
5.75	v.w.	010	5.75
5.32	v.w.	110	5.30
5.00	m		
4.75	v.s.		
4.53	s	300	4.53
4.25	s		
3.89	s		
3.55	v.v.w.		
3.40	v.v.w.	400	3.40
3.24	v.w.		

As was the case with sodium oleate the hexanolamine oleate could be fibrillated to a slight extent by extrusion through a 1-mm. orifice under pressure. The layer line separation was more marked than for sodium oleate, and the periodicity along the fiber axis was calculated.[22] This periodicity is perpendicular to the long spacings, as in the case of sodium oleate, and has the value of $b = 5.8$ Å. A weak spacing of $d = 5.75$ Å. is observed in the monochromatic powder diagram and is ascribed to 010 planes.

A spacing of 13.6 Å. has its position between the fourth and fifth orders of the long spacing. It does not arise from the basal planes, as it is not a sub-multiple of the long spacing and since second, third and fourth orders of the 13.6 Å. spacing all occur as equatorial diffractions. These spacings are most probably due to the ($h00$) planes. The parameters of a monoclinic unit cell of hexanolamine oleate are taken as

$$a \sin \beta = 13.6$$
$$b = 5.75$$
$$c \sin \beta = 61.5$$

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(13) J. W. McBain and W. W. Lee, *Oil & Soap*, **20**, 17 (1943).

(14) S. A. Johnston and J. W. McBain, *Proc. Roy. Soc.* (London), **A181**, 119 (1942).

(15) J. W. McBain, M. J. Vold and S. A. Johnston, THIS JOURNAL, **63**, 1000 (1941).

(16) R. D. Vold, *J. Phys. Chem.*, **43**, 1214 (1939).

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

(18) J. W. McBain, R. D. Vold and K. Gardiner, *Oil & Soap*, **20**, 221 (1943).

(19) K. Hess and J. Gundermann, *Ber.*, **70B**, 1800 (1937).

(20) P. Krishnamurti, *Ind. J. Phys.*, **3**, 307 (1929); *C. A.*, **23**, 4116 (1929).

(21) M. de Broglie and E. Friedel, *Compt. rend.*, **176**, 738 (1923).

(22) W. P. Davey, "Study of Crystal Structure and its Applications," 1st ed., McGraw-Hill Book Co., New York, N. Y., 1934, p. 181.

Assuming the cross sectional area of the molecule to be about 20 sq. Å., then *ab* sin β must be divided by four to give a value of 19.5 sq. Å. This unit cell, therefore, has eight molecules. Within a few tenths of an ångström, the calculated length of two fully extended molecules of hexanolamine oleate, based on analogous work on the saturated fatty acids, sodium soaps and sodium acid soaps, agrees with the value of *c* sin β here reported. The value of sin β is therefore close to unity. By analogy with the sodium salts of the fatty acids, this form may appropriately be called the alpha form.

The density, calculated from the unit cell parameters and sin β of unity, is 1.096 g./cc.—a result in agreement with known data on sodium soaps.

Summary

1. Two forms of sodium oleate are distinguished by X-ray powder diagrams.

2. The unit cell parameters of a pure sample of one of these forms of sodium oleate are obtained after fibrillation of the sample, produced by extrusion through a small orifice under pressure. The parameters agree with values previously found for the gamma forms of saturated sodium soaps.

3. Samples of sodium oleate used in previously published physicochemical investigations in this laboratory are identified by X-ray diffraction.

4. The parameters of the unit cell of hexanolamine oleate are obtained after fibrillation of the sample, as already described.

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Isomerization Equilibria among the *n*-Butenes

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Knowledge of the equilibria among the three *n*-butenes at a series of temperatures is of value in the industrial use of these hydrocarbons, and also serves to verify and augment basic thermodynamic data. Equilibrium determinations for vapor phase isomerization over several catalysts, covering the range 200 to 630°, are reported in this paper. The measurements were greatly facilitated by an infrared absorption method of analysis, recently developed.[1] This method is a marked improvement over earlier methods of analysis such as distillation; the latter is difficult to do with precision because of the small differences in boiling points (1-butene, −6.3°; *trans*-2-butene, 0.9°, and *cis*-2-butene 3.6°).

Previous observations of the isomerization of *n*-butenes by McCarthy and Turkevich[2] at 400 and 450° using an alumina catalyst gave values for the 1-butene contents at equilibrium but did not show the amounts of *cis*- and *trans*- 2-butenes. Determinations of the *cis–trans*-equilibria in thermal isomerization at 347 and 390° were made by Kistiakowsky and Smith.[3] Twigg[4] gave a value of 7% for the equilibrium content of 1-butene at about 100° (65–126°) based on isomerization over nickel in the presence of hydrogen. Approximate equilibrium ratios of all three *n*-butenes at 350 to 450° were given by Frey and Huppke[5] on the basis of low temperature distillation analyses of the products from dehydrogenation of *n*-butane over chromic oxide. None of these studies, however, furnished accurate equilibrium distributions, or results over a wide range of temperature.

Experimental

Isomerizations were effected by flowing the *n*-butenes over granular catalysts in an electrically heated tube. Temperatures were automatically controlled, and were held within 3° of the specified values in the outlet portion of the catalyst bed. Catalyst volumes varied from 15 to 100 cc. Flow rates were chosen, with the help of experimental results not reported here in detail, to produce essentially equilibrium conversions. The pressure was atmospheric throughout. After the gases had passed through the catalyst they were separated from the small amount of liquid product, if there was any, and analyzed. In most runs a butene fraction for infrared analysis was separated by low temperature distillation, but in some experiments the amount of side reaction was so small that this proved to be unnecessary. Thus, products from experiments at 250° and LHSV 1, at 350° and LHSV 4, and at 450° and LHSV 8, were not usually distilled prior to analysis (LHSV = liquid hourly space velocity = flow rate, volumes *n*-butene as liquid per volume of catalyst per hour).

Side reactions observed were polymerization at the lower temperatures, cracking and isomerization to isobutene at the higher temperatures, and dehydrogenation at the highest temperature. The extent of side reactions was below 20%, and often below 2%, except in the experiments at 630°, where there was about 30% side reaction, chiefly dehydrogenation to butadiene. The extents to which these side reactions cause the apparent equilibria to differ from true equilibria are difficult to estimate without rate data. From unreported experiments in which isomerization was incomplete, it is estimated that the slowest of the six isomerization rates was at least ten times as fast as the rate of disappearance of *n*-butenes through side reactions Therefore, according to the considerations of Bates,[6] the equilibrium constants cannot be in error by more than 10%.

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[1] R. R. Brattain, R. S. Rasmussen and A. M. Cravath, *J. Applied Phys.*, **14**, 418 (1943); R. R. Brattain and O. Beeck, *ibid.*, **13**, 699 (1942).

[2] W. W. McCarthy and J. Turkevich, *J. Chem. Phys.*, **12**, 405 (1944).

[3] G. B. Kistiakowsky and W. R. Smith, THIS JOURNAL, **58**, 766 (1936).

[4] G. H. Twigg, *Proc. Roy. Soc.* (London), **A178**, 106 (1941).

[5] F. E. Frey and W. F. Huppke, *Ind. Eng. Chem.*, **25**, 54 (1933).

[6] J. R. Bates, "Effect of Side Reactions on Experimental Isomerization Equilibria," Petroleum Division Papers, American Chemical Society Meeting, New York, September, 1944.