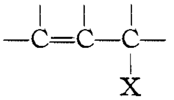
Thermal Decomposition of the Ozonides.—The solution of the ozonide (usually from about 2 g. of unsaturated material) in ligroin was warmed gently in a water-bath until no further reaction occurred. The effluent gases were passed through a Dry Ice trap and collected in a bulb. The gases were analyzed by Mr. Alvin Sellers, using the micro methods developed in the laboratory by Dr. F. E. Blacet, and were found to consist of carbon monoxide mixed with a small amount of carbon dioxide. Depending on the extent of abnormal ozonization, from 0-32% of the theoretical quantity of carbon monoxide was liberated. In those experiments where abnormal ozonization was the predominant reaction the residue from the thermal reaction gave no test for active ozonide with potassium iodide.

Summary

1. Abnormal products have been isolated from the ozonization of allylic isomers of the types R—CH=CH—CHR′X and RCHX—CH=CH-R′. The abnormalities were often such as to make the starting materials appear to be mixtures of allylic isomers. Carbon monoxide is liberated spontaneously or on gentle warming of abnormal ozonides.

2. Certain α,β-unsaturated carbonyl compounds also gave abnormal ozonization products.

3. For a series of compounds of the type  $-\overset{|}{C}=\overset{|}{C}-\overset{|}{\underset{\underset{X}{|}}{C}}-$ the extent of abnormal reaction appears to be related to the basicity of unshared electron pairs carried by group X. On this basis a mechanism for the abnormal reaction has been suggested involving the participation of group X in a rearrangement of the molozonide.

LOS ANGELES 24, CALIFORNIA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Diffraction of X-Rays by Aqueous Solutions of Hexanolamine Oleate

BY SYDNEY ROSS* AND J. W. MCBAIN

A number of papers published in Germany since 1937[1] have reported results on the diffraction of X-rays by soap solutions. The importance of these researches, in establishing the presence of lamellar micelles in aqueous soap solutions as well as in elucidating some of the mechanism of "solubilization,"[2] requires that independent confirmation and further investigation be forthcoming.

This paper presents results on a series of clear transparent aqueous systems of hexanolamine oleate at room temperature, ranging in concentration from 25 to 92% by weight of soap, a wider concentration range than any previously reported in detail. The most concentrated and the most dilute systems were fluid isotropic solutions. All others were anisotropic liquids ranging in consistency from oil to grease. X-Ray data are already available on the anhydrous crystalline material.[3] The X-ray diagrams obtained from these colloidal solutions differ from most photographs of liquids in that the inner spacing and its orders are sharp and definite and so render the reported measurement of more than customary accuracy.

Experimental

Materials and Methods

The hexanolamine oleate used is the same as that previously reported.[3] The series of aqueous systems was made by successive additions of conductivity water and prolonged stirring. The concentration in each case was obtained by weighing and is reported as weight per cent.

The source of X-rays was a General Electric beryllium window tube, with a copper target and nickel filter. The X-ray unit was the General Electric XRD 2.

The liquid was held in a stainless steel cell that had two thin mica windows. It was found that "Cenco Varniton" is useful in attaching the mica windows to the metal as, when dried, it is not affected by these solutions. The two halves of the cell were held together by pressure, with a thin film of Dow Corning stopcock grease between them. No leaking of liquid or evaporation of the solvent took place during the exposure time (six hours) when the cell was carefully put together.

The calibration of the sample-to-plate distance (50.0 mm.) was checked by using solid hexanolamine oleate. Once established it was not altered throughout the course of the experiments. It was checked at various times and found to remain constant.

Microphotometer records of each diffraction diagram were obtained, using the recording microphotometer designed by Leighton, Smith and Henson.[4] Care had to be taken in every case to obtain a diameter across the film that avoided spots arising from the mica windows.

Results

In the more concentrated systems (above 40% hexanolamine oleate) the water halos do not appear. A halo that appears at all concentrations is observed at d = 4.5 to 4.6 Å., calculated from the Bragg formula. This halo corresponds in position to that portion of the diagram of the crystalline soap where the most intense side-spacings occur, more especially that provisionally

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[1] (a) K. Hess and J. Gundermann, *Ber.*, **70**, 1800 (1937); (b) W. Philippoff and K. Hess, *ibid.*, **70**, 1808 (1937); (c) K. Hess, H. Kiessig and W. Philippoff, *Naturwissenschaften*, **26**, 184 (1938); (d) H. Kiessig and W. Philippoff, *ibid.*, **27**, 593 (1939); (e) K. Hess, W. Philippoff and H. Kiessig, *Kolloid-Z.*, **88**, 40 (1939); (f) J. Stauff, *ibid.*, **89**, 224 (1939); (g) H. Kiessig, *ibid.*, **96**, 252 (1941); (h) W. Philippoff, *ibid.*, **96**, 255 (1941); (i) K. Hess, *Fette u. Seifen*, **49**, 81 (1942); (j) H. Kiessig, *Kolloid-Z.*, **98**, 213 (1942).

[2] J. W. McBain, "Advances in Colloid Science," Vol. I, New York, 1942, pp. 99-142.

[3] S. Ross and J. W. McBain, THIS JOURNAL, in press.

[4] P. A. Leighton, F. Smith and F. C. Henson, *Rev. Sci. Instruments*, **5**, 431 (1934).

indexed in the preceding paper as the 300 spacing at $d/n = 4.53$ Å. With the crystalline soap the most intense long spacing is that ascribed to the 002 planes (unlike all metallic soaps yet reported the even orders are more intense than the odd).

In the X-ray photographs of some of the aqueous systems of this soap (Fig. 1E and those following) two long spacings are revealed, which appear to be two orders of the same spacing. Had these spacings been taken as the first and second orders of a long spacing, the calculated values would have corresponded to those produced by single molecules separated from each other by layers of water. The improbability of single molecules being separated from each other by layers of water; the examples provided by other soaps both in the crystalline form and in isotropic solutions, always showing double molecules as the repeating unit; and the type of intensity variation of the long spacings in crystalline hexanolamine oleate, with which the solutions of that substance may be expected to show some correspondence; these considerations lead toward the interpretation that the two orders of long spacing here observed are the second and fourth, respectively (with the first and third too weak to be observed), rather than the first and second.[5]

Figure 1 reproduces the microphotometer records of the diffraction diagrams. As the long spacing increases with increasing dilution the diffraction effect moves closer to the center of the diagram. For the 25% isotropic solution a long spacing was not distinguishable, even in its computed fourth order, from the diffuse blackening around the center. Increasing the crystal-to-plate distance did not resolve the spacing because of the air-scattering of the central beam.

At a concentration of 30.55% hexanolamine oleate, X-ray diagrams were made at sample-to-plate distances of both 50.0 and 100.0 mm. Even in the latter film, however, the determination of the value of the long spacing could not be made with an accuracy of better than ±3%. The accuracy of measurement increased as the concentration increased.

It was found that, for determining the values of the spacings, the inner (long spacing) halo is more accurately obtained from the original film, as in the microphotometer plate it is often cut off by the shadow of the lead button along the particular diameter that was microphotometered. The outer halo is better measured from the microphotometer plate as there the position of maximum film-blackening is easily discovered.

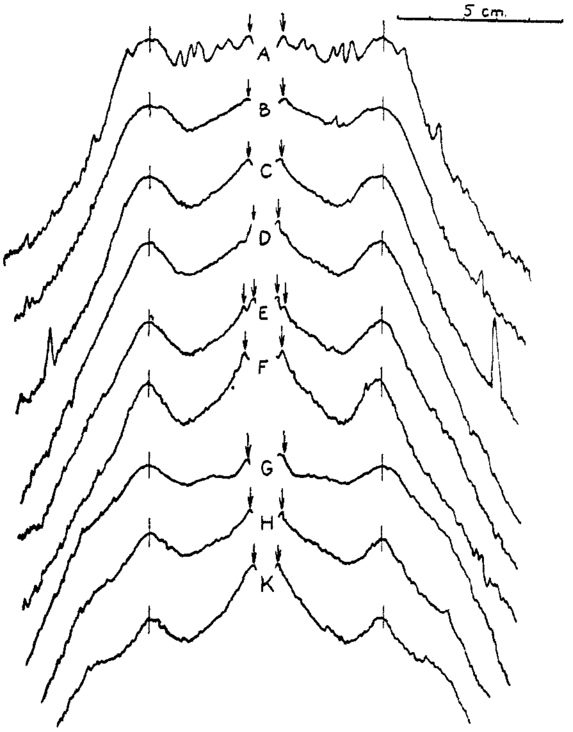

Fig. 1.—Microphotometer records of X-ray powder diagrams of aqueous solutions of hexanolamine oleate: A, 100% hexanolamine oleate by weight; B, 92%; C, 82%; D, 67%; E, 61%; F, 55%; G, 45%; H, 39%; K, 30.5%.

Figure 2 is a graphical representation of the variation of long spacing with concentration of hexanolamine oleate. The points lie nearly on

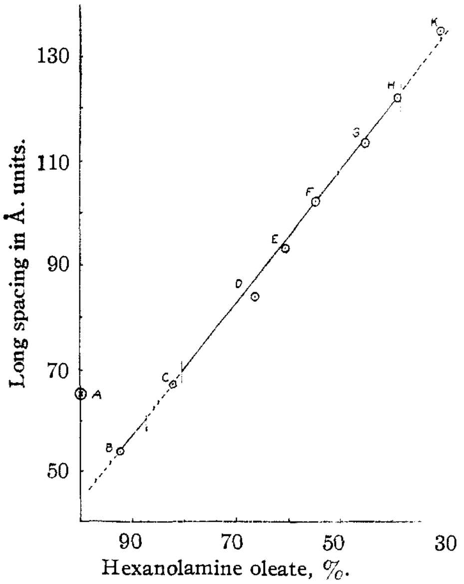

Fig. 2.—The variation of the long spacing in ångström units with weight concentration of hexanolamine oleate. The capital letters refer to the same solutions designated in Fig. 1.

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[5] Prof. W. D. Harkins was good enough to check at the University of Chicago the measurement of the 50% solution. Both he and Prof. Zachariasen hold the opinion that the two orders observed are the first and second rather than the second and fourth. If so, the values given in Fig. 2 would have to be halved with the exception of the value marked A for the anhydrous hexanolamine oleate and then the structure for the X-ray micelles in hexanolamine oleate solution would have to be, for some unexplained reason, quite different from that found for sodium oleate and all other soap and detergent solutions.

a straight line throughout the complete concentration range investigated.

The position of the side-spacing remains constant and therefore is independent of variations in concentration.

Discussion

The remarkable increase in long spacing with dilution of a soap solution, as here observed, provides independent confirmation of the results reported from Germany,[1] and by Hughes, Sawyer and Vinograd[6] of this country, and now also communicated by Harkins, Mattoon and Corrin.

All observers concur in interpreting these results as establishing the existence of layers of water many molecules deep between the successive layers of double molecules of soap, which lie side by side and end to end at right angles to the alternate layers of water and soap. Such polymolecular layers of water very many ångströms in thickness have also been found in studies of tactoids, such as Bernal's tobacco mosaic virus, and of clays, such as Bentonite. The general importance and significance of such thick polymolecular layers was particularly emphasized by Sir Wm. Hardy[7] before completely convincing evidence of their existence became available.

Kiessig gives data for different concentrations of aqueous sodium oleate solutions (only over the narrow range 6 to 18%) and his points were represented by a straight line. Apparently this linear relation is applicable to solutions of colloidal electrolytes. If the straight line of Kiessig were extrapolated to 100% sodium oleate, the long spacing resulting would have a negative value, showing that the increase of long spacing on addition of water is not continuous throughout the phase diagram.

The hexanolamine oleate of the present investigation is soluble throughout the complete range of concentration here examined and the approximately linear relation of Fig. 2 is found down to a concentration of 30% soap. It is, of course, a requirement of the phase rule that there must be discontinuities in any graph, whether linear or otherwise, whenever a heterogeneous region is traversed. Either the spacing might remain constant or a new value appear for the new phase. The data for systems of hexanolamine oleate are insufficient to exhibit such discontinuities, perhaps because the heterogeneous regions are narrow and the change in spacing not pronounced or perhaps because the break is approximately compensated by a shortening of the spacing in the new phase. The portions of the empirical straight line passing through the heterogeneous regions, as reported by Gonick,[8] are dotted in Fig. 2, for lack of more complete and accurate information.

Were the straight line of Fig. 2 to be extrapolated to a value corresponding to 100% soap, the spacing for the double molecule would be given as 44 Å. In the crystalline soap, however, the long spacing has been determined as 61.5 Å.[3] In solutions, therefore, the soap molecules are either not fully extended, or are inclined at a more acute angle to the layers. This contradicts the assumption made by the German writers that soap molecules are extended at right angles to the lamellae. If they are not normal to the layers then the thickness that must necessarily be ascribed to the water layers is correspondingly increased, and must be even greater than reported by the other workers in this field.

The empirical straight line in Fig. 2 is represented by the equation

$$\lambda = -1.26c + 170 \qquad (1)$$

where λ is the long spacing in Å. and c is the weight per cent. of hexanolamine oleate. This can readily be converted to an equation showing the relation between the spacing and the number of molecules of water added per molecule of soap, by converting to μ, where μ is the ratio of the number of moles of water to the number of moles of soap in solution; then

$$\lambda = \frac{976 + 170\,\mu}{22.17 + \mu} \qquad (2)$$

Examination of equation 2 shows that in the 95% soap system, addition of one molecule of water per molecule of soap causes an expansion in the long spacing of about 10 Å., whereas in 70% soap, the expansion falls off to half this value, and so on progressively with dilution. The initial rate of increase of λ is so large that it must be supposed that *at first* much of the water added enters the micelle, or the angle at which the soap molecules are inclined to the basal plane must rapidly increase. Anhydrous liquid crystalline sodium stearate is known to exhibit a much shorter long spacing than any crystalline form.[9] Similarly here, it probably would be more logical to compare the long spacings in the solutions with the liquid crystalline anhydrous hexanolamine oleate, which has not yet been measured.

The straight line of Fig. 2 pursues its course through a range of concentration in which great changes in viscosity and anisotropy are taking place. At 92% soap the solution is isotropic and fluid; at 70% soap it is anisotropic and has the consistency of a grease; at 35% soap it is once more fluid and partly isotropic. It is therefore conclusively shown that all the changes in soap solutions are due to rearrangements of the gross micelles with respect to each other. The internal structure of the primary micelle itself is meanwhile independently maintained and shows no

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(6) E. W. Hughes, W. M. Sawyer and J. R. Vinograd, *J. Chem. Phys.*, **13**, 131 (1945).

(7) W. B. Hardy, "Colloid Symposium Monograph," Vol. VI, Chemical Catalog Co., New York, N. Y., 1928.

(8) E. Gonick, "The Constitution of Hexanolamine Oleate and Related Colloidal Electrolytes," Ph.D. Dissertation, Stanford University, 1945.

(9) A. de Bretteville, Jr., and J. W. McBain, *J. Chem. Phys.*, **11** 426 (1943).

marked discontinuities throughout a wide range of concentration.

Acknowledgment—The authors wish to thank Dr. E. Gonick for the hexanolamine oleate from which the solutions were made.

Summary

1. Transparent aqueous systems of hexanolamine oleate have been examined by X-ray diffraction over the wide range of concentration from 30 to 92% soap. The more dilute systems exhibit a water halo. All exhibit a well-marked halo with the Bragg spacing of 4.5 to 4.6 Å., as well as a long spacing often in two orders.

2. This confirms similar results from Germany and this country, which have uniformly been interpreted as proving the presence of lamellar micelles in aqueous solutions of colloidal electrolytes.

3. The lamellar micelles consist of alternate layers of soap and of water. The soap molecules are packed side by side (giving rise to the side spacing) and end to end, the long spacings being due to the alternate layers of water and soap.

4. The long spacing increased approximately linearly over the range of systems studied, some of which were fluid and isotropic, others fluid and anisotropic and others semi-solid and anisotropic. Hence throughout the aqueous systems the essential structure of the primary micelle appears to be maintained and the variations in properties caused by changing relations of these micelles to each other.

STANFORD UNIVERSITY CALIF. RECEIVED MAY 14, 1945

[CONTRIBUTION FROM THE POLYMER RESEARCH INSTITUTE, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Copolymerization of Styrene and Allyl Chloride

BY TURNER ALFREY AND JOHN G. HARRISON, JR.

It is well known that allyl halides exhibit markedly lower polymerization reactivities than do vinyl halides and many other substituted ethylene derivatives, such as styrene. This low polymerization tendency may be the result of a low rate of activation, a low rate of propagation, or a high rate of chain termination.

A number of investigators[1,2,3] have demonstrated that copolymerization experiments make it possible to isolate the chain propagation step, and determine quantitatively the relative rates at which different monomers add to a specific free radical chain end. This investigation of the system styrene–allyl chloride leads to the conclusion that allyl chloride exhibits a very low relative rate of addition to a growing free radical chain of either type.

Both Lewis and Mayo[1] and Alfrey and Goldfinger[2] arrived independently at the following equation, which relates the chemical composition of a copolymer with that of the monomer mixture from which it is formed.

$$\frac{b}{a} = \alpha \cdot \frac{B}{A}\,\frac{\beta B + A}{\alpha B + A}$$

where

b/a = the molar ratio of the monomer units in the copolymer,

B and A = molar concentrations of the unpolymerized monomers,

α = the ratio of the respective rate constants for addition of monomer B and A, respectively, to type A radical; *i. e.*, k_2^{ab}/k_2^{aa}

and

β = the ratio of the respective rate constants for addition of monomer B and A, respectively, to type B radical; *i. e.*, k_2^{bb}/k_2^{ba}

In this investigation styrene has been selected as monomer A and allyl chloride as monomer B.

Experimental

Reagents.—Styrene, pure grade, from the Dow Chemical Co. was shaken with four successive portions of 10% sodium hydroxide solution and four portions of distilled water, dried with calcium chloride and distilled under 20-mm. pressure. Allyl chloride, b. p. 44.9° (from the Shell Chemical Division of the Shell Union Oil Corporation) was stated to be 99% pure, the impurities being by spectrographic evidence 1-chloro-1-propene (b. p. *cis*- 32–32.2° and *trans*- 36.7°) and isopropyl chloride, b. p. 36.5°. The lower boiling points of the impurities indicated that no purification beyond a very careful fractionation was necessary. An efficient column with a reflux ratio of 3:1 was used, the first and last 10% being rejected.

Procedure and Results.—The copolymerization equation discussed above is in the differential form and has been integrated by Lewis and Mayo. In this work, however, the degree of conversion was small, and the relative concentrations of the unreacted monomers did not essentially change throughout the reaction, as will be shown in Table I. Therefore, the differential form of the equation was quite satisfactory, particularly when average, rather than initial, monomer ratios were used.

A series of copolymers with varying amounts of each component was prepared by heating the mixtures in sealed glass vessels immersed in a water-bath held at 70 ± 0.1°. Benzoyl peroxide (0.5%) was used as a catalyst. Polymerization was stopped at a low degree of conversion.

The "initial polymers" so obtained were purified by precipitating in methyl alcohol and reprecipitating from methyl ethyl ketone solution. The resulting powders were dried in a vacuum oven overnight at 50° and weighed. The polymers were microanalyzed in duplicate for chlorine

TABLE I

Conversion, %	Cl, %		Mole fraction allyl chloride: Monomers, Initial	Monomers, Residual	Monomers, Av.	Polymer	Rate of polymer production, % per min.	$[\eta]$
2.50	0.26	.25	0.15	0.15_7	0.15_4	0.007_5	0.081	0.43
2.80	0.39	.35	.30	$.31_6$	$.30_8$	$.010_9$	.061	.34
1.34	1.01	1.30	.50	$.51_1$	$.50_6$	$.033_6$	.036	.26
1.19	2.30	2.40	.70	$.72_0$	$.70_9$	$.067_8$	.019	.17
0.93	4.98	4.87	.85	$.87_0$	$.86_0$	$.139_3$	.0075	.10

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[1] Lewis and Mayo, THIS JOURNAL, **66**, 1594 (1944).

[2] Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).

[3] Alfrey and Merz, *Polymer Bulletin*, **1**, 86 (1945).