

ester. The formates are considerably more active than the acetates and from then on the decrease in activity is much smaller as the length of acid increases. In this series the exception to the above statement is methyl *n*-butyrate.

It is interesting to note that esters having a total of five carbons have higher equilibrium constants. Methyl *n*-butyrate and *n*-butyl formate have constants much higher than would be expected. *n*-Propyl acetate does not vary as much but even here the constant is the same as the preceding ester instead of decreasing. The one exception to this observation is *n*-butyl acetate, which is even higher than *n*-propyl acetate. No equilibrium constant has been run for ethyl propionate.

Hatch and Adkins⁶ in their displacement series for alcoholysis observed that the values decreased until the normal amyl group was reached. A marked increase was then noticed which gradually decreased in going up the series, but all values were higher than those preceding the normal amyl group. They rationalized these anomalies by the assumption that the effect of a methyl or methyl-

ene group may be transferred directly as well as through the chain. By stereochemical considerations the methyl group of the amyl group should be close to the oxygen and act directly.

This explanation might be used for the above anomalies but it is difficult to see why *n*-amyl formate should have a smaller constant than *n*-butyl formate. If the activation is due to both ends of the ester being close together, then the observation that it occurs only in esters having five carbons would be logical. This, however, does not explain why *n*-butyl acetate should have a large constant.

Summary

The equilibrium constants for the reaction of several alkyl formates and alkyl acetates with stearic acid have been determined. Increasing the length of the alkyl group of the ester decreases the value of the constant. However, when the total number of carbons in the ester reaches five, higher values are obtained. Secondary and branched-chain alkyl esters give lower values than the normal alkyl esters.

LEXINGTON, KY.

RECEIVED FEBRUARY 14, 1940

(6) Hatch and Adkins, *THIS JOURNAL*, **59**, 1694 (1937).

[CONTRIBUTION FROM THE PENNSYLVANIA STATE COLLEGE]

Optical Constants of Benzamide, its Homologs, and Some Aliphatic Amides¹

BY M. L. WILLARD AND CHARLES MARESH²

Two homologous series of organic amides, namely, an aromatic series based on benzamide and an aliphatic series based on acetamide, were studied optically by means of the petrographic microscope and the Fedorow universal stage as modified by R. C. Emmons.

Materials.—The derivatives and reagents used in this study were obtained from the Eastman Kodak Company. Acetamide was recrystallized from 95% alcohol. Propionamide and butyramide were used as obtained. *n*-Valeramide was recrystallized from fusion giving flat plates suitable for optical study. Isovaleramide was prepared from isovaleryl chloride and concentrated ammonia solution and purified by sublimation.

Benzamide, *o*-, *m*-, and *p*-toluamides were prepared by the hydrogen peroxide hydrolysis³ of the corresponding

nitriles. *o*-Ethylbenzamide, *p*-ethylbenzamide, and 1,3-dimethylbenzamide-2 were prepared from the corresponding amines, using the method of Clarke and Read⁴ in the preparation of the nitriles followed by the hydrolysis to the amides. The dimethyl compound, however, required refluxing for seventy-two hours with a saturated alcoholic potassium hydroxide solution for the hydrolysis to the amide.

The melting point of *p*-ethylbenzamide (see Table I) was found to be different from that reported in the literature. Upon hydrolysis, the acid was obtained melting at 112–113.5°. The amide was likewise prepared from the acid by treating with thionyl chloride followed by treatment with concentrated ammonia solution. The amide so obtained melted at 162.9–164.4°.

The amides, *p*-propylbenzamide, *p*-*n*-butylbenzamide, and *p*-isobutylbenzamide were prepared from bromobenzene and the corresponding bromides (obtained from the alcohols) by means of the Wurtz-Fittig synthesis. The alkyl benzenes were nitrated and reduced according to the method of R. R. Read and D. B. Mullin.⁵ The

(1) Abstracted from a thesis submitted by C. Maresh to The Graduate School of The Pennsylvania State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Presented before the Division of Microchemistry at the 97th meeting of the American Chemical Society, Baltimore, Md.

(2) Present address: Calco Chemical Division, The American Cyanamid Company, Bound Brook, New Jersey.

(3) C. R. Noller, "Organic Syntheses," Vol. 13, 1933, p. 94.

(4) H. T. Clarke and R. R. Read, "Organic Syntheses," Vol. 4, 1925, p. 69.

(5) R. R. Read and D. B. Mullin, *THIS JOURNAL*, **50**, 1763 (1928); D. B. Mullin, Thesis "The Disinfectant Power of Phenols," U. of Vermont, 1924.

TABLE I
 ANALYSES AND PHYSICAL AND OPTICAL PROPERTIES OF AMIDES

Amides	Nitrogen, % Calcd. Found	M. p., °C.	n_D	n_D	n_D	Birefr.	Sign	2V	Optical orientations	Cryst. syst.	Habit
Acet-		81.1 ± 0.5	1.461 ^b			0.046	-	0°	X = c	Hex.	Short, prismaticine.
Butyr-		114.1 ± .5	1.465 ^b			.065	+	61° ^g , 63° ^h	X = a, Y = b, Z = c	Orth.	Mica-like pl.
Propion-		78.0 ± .5	1.445 ^b			.085	+	52° ^g , 53° ^h	X = a, Y = b, Z = c	Orth.	Mica-like pl.
Isovaler-		125.9 ± .5	1.458 ^b			.040	+	57° ^h	Ax. pl. (010)	Mono.	Mica-like pl.
n-Valer-		101.0 ± .7	1.466 ^b			.064	+	75° ^g , 74° ^h	Ax. pl. (010)	Mono.	Mica-like pl.
Aromatic Amides, $\lambda = 5461 \text{ \AA}$.											
Benz-		127.1 ± 0.5	1.541			0.289	+	87° ^g , 88° ^h	Ax. pl. (010)	Mono.	Prism. pl. ^g
p-n-Butylbenz-	7.91 7.89	121.5 ± .4	1.547			.153	+	55° ^g , 56° ^h	Ax. pl. (010) ^m	Mono.	Prism. ne. ^g
p-s-Butylbenz-	7.91 7.99	117.2 ± .5	1.596	1.72 ± 0.01		.294	-	85° ^g , 86° ^h	M. p. 128.4 ± 1.5 ^f	Mono.	Ne. + long rect. pl. ^{g, n}
2-Cyano-1,3-dimethylbenz-		89.5 ± .5	1.454			.293	-	20° ^{g, h}	X = a, Y = b, Z = c	Mono.	Long rect. cryst. ^g
1,3-Dimethyl-benz-(2)		137.3 ± .4	1.565			.108	+	61° ^{g, h}	Ax. pl. (010) ^t	Mono.	Long rect. pl. ^g
p-Ethylbenz-	9.49 9.62	164.2 ± .5	1.505			.221	-	72° ^{g, h} , 73° ^h	Ax. pl. (010)	Mono.	Tabular ^{g, o}
o-Ethylbenz-		153.0 ± .5	1.547			.146	+	71° ^{g, h} , 73° ^h	Ax. pl. (010)	Mono.	Rect. cryst. ^{g, o}
p-Isobutylbenz-	7.91 7.80	151.2 ± .2	1.464			.260	+	79° ^{g, h} , 78° ^h	Ax. pl. (010)	Mono.	Rect. cryst. ^{g, o}
p-Propylbenz-	8.59 8.58	128.4 ± .5	1.526			.163	-	33° ^{g, h} , 32° ^h	X Δ c = ca. 40°, Y = b	Mono.	Rect. cryst. ^{g, o}
o-Tolu-		141.2 ± .2	1.470			.291	-	44° ^g , 42° ^h		Tri.?	Tablets ^g
m-Tolu-		93.7 ± .5	1.468			.284	-	23° ^g , 20° ^h	Ax. pl. (010)	Mono.	Prisms ^g
p-Tolu-		159.6 ± .5	1.510			.224	-	35° ^g , 38° ^h , 36° ^h	Z = b = Bx ₀	Mono.	Square pl. ^g

^a Melting points determined by usual capillary tube method with thermometer calibrated against Bureau of Standards' thermometers. The \pm indicates the range, as: 127.1 \pm 0.5 = 126.6–127.6°. ^b (n_D). ^c 1.464 = 0.005, Universal Stage. ^d 1.44 = 0.01, Universal Stage. ^e 1.45 = 0.01, Universal Stage. ^f 1.47 = 0.01, Universal Stage. ^g Cryst. from H₂O. ^h Universal Stage. ⁱ Calcd. from 2V. ^j Cryst. from petroleum ether. ^k Indices. ^l X Δ c = ca. 8°. ^m X Δ c = 40°. ⁿ Elongated to β . ^o Mica-like plates crystallized from 50% ethyl alcohol; rect. plates from water. ^p Prisms from xylene-Canada balsam. ^q Melatopes.

amines were then diazotized, the nitriles prepared, and the amides formed by the hydrogen peroxide hydrolysis.

The Wurtz-Fittig synthesis was not successful in the preparation of *s*-butylbenzamide, and Eastman Kodak Co. *s*-butylbenzene was the starting material in the preparation of secondary butyl benzamide. The melting points from water and petroleum ether differed, and there is a possibility that the optical activity of the secondary butyl group is the explanation. The product from water was studied.

In nitrating, the position of the nitro group was in all cases checked by the preparation of the corresponding nitrobenzoic acid. The amides, *p*-propylbenzamide, *p*-butylbenzamide, *p*-isobutylbenzamide, and *p*-*s*-butylbenzamide, have not been reported in the literature.

The fractionations of the intermediates in the preparation of the aromatic amides were carried out with two columns packed with glass helices of the total condensing variable take-off type with electrically heated jackets 40 and 64 cm. long.

Apparatus and Technique.—A Spencer 35 petrographic microscope was used in all of the work except that involving the universal stage. In addition to the usual accessories, the microscope was fitted with a 1.8-mm. oil immersion (N. A. = 1.25) objective used in conjunction with an aplanatic wide angle condenser (N. A. = 1.40). A removable ocular micrometer in a Spencer 8x ocular was calibrated with both the 4-mm. and 1.8-mm. objectives for optic axial angle measurement against standardized mineral thin sections. As illustrated by W. M. D. Bryant,⁶ the use of an oil immersion objective permits the measurement of the entire range of acute axial angles as well as smaller obtuse axial angles.

A Bausch and Lomb modified Fedorow universal stage was fitted on a Bausch and Lomb LC petrographic microscope for the measurement of optic axial angles and indices of refraction beyond the limit of the index oils as well as n_D in the case of the platy aliphatic amides. The universal stage was fitted with three pairs of hemispheres of refractive indices, 1.649, 1.559, and 1.516.

The indices of the liquids beyond the limit of the Abbé refractometer were determined by the method of minimum deviation using a constant temperature hollow prism⁷ in conjunction with a single circle reflecting goniometer made by the R. Fuess Company. Monochromatic light was furnished by an 85-watt high intensity Westinghouse mercury vapor lamp Type H-3 along with suitable Corning filters ($\lambda = 5461 \text{ \AA}$).

(6) W. M. D. Bryant, *THIS JOURNAL*, **60**, 1394 (1938).

(7) M. S. Buerger, *Am. Mineral.*, **18**, 325 (1933).

The principal refractive indices, α , β , and γ at $25^\circ \pm 3^\circ$ for $\lambda = 5461 \text{ \AA}$. were determined by the immersion method with axial illumination using interference figures in selecting the correct orientation for a given index.⁸

The optical study involved the examination of the crystals obtained from various solvents and from xylene-Canada balsam. In some cases crushed material was mixed with powdered glass preparatory to the examination. The determination of the optic axial angles by means of the universal stage was done on preparations made up in Canada balsam.

The universal stage was used in the determination of n_γ in the case of benzamide and n_α in the case of the platy aliphatic amides using the methods worked out by R. C. Emmons.⁹ In the determination of the optic axial angles, the graphical method of T. A. Dodge¹⁰ was used.

Optical Data.—Although metastable forms were encountered in this research, no attempt was made to determine their optical constants. $2V$ values were (a) obtained from melatope distances, (b) measured on the universal stage, and (c) calculated from the indices of refraction. The accuracy of the $2V$ values is given by the agreement of the values obtained by the three methods. The indices of refraction are given with an accuracy of ± 0.003 except where indicated.

Table I gives the data for the aliphatic amides. All of the aliphatic amides listed have been measured crystallographically, but only acetamide in its stable and metastable forms has been studied optically. The values recorded for the stable modification¹¹ ($n_e = 1.46$, $n_w = 1.54$) are not entirely in accordance with those reported here. The stable form of acetamide is trigonal uniaxial giving short prismatic needles from alcohol and does not fit in with the remainder of the series. The amides from propionamide through isovaleramide crystallize out in mica-like flakes which make it difficult to measure the lowest index.

E. Kahrs¹² states that the amides show good cleavage parallel to the front pinacoid (100), and the obtuse bisectrix is perpendicular to the prominent face of the crystals in the case of propionamide and butyramide, and leaning slightly toward (101) in the case of the two valeramides.

The first value for n_α given has been calculated from $2V$ values. The birefringence being small gives good results for the calculated index. The values given in footnotes are index values obtained on the universal stage by the method of

(8) K. E. Buck, "Outline for Examining Crystals," *Bull. Am. Ceram. Soc.*, **16**, 61 (1937).

(9) R. C. Emmons, *Am. Mineral.*, **14**, 441 (1929).

(10) T. A. Dodge, *ibid.*, **19**, 62 (1934).

(11) "International Critical Tables," Vol. I, p. 180.

(12) E. Kahrs, *Z. Kryst. Mineral.*, **40**, 475 (1905).

R. C. Emmons.⁹ They are good to ± 0.01 except where noted.

In Table I are given the data for the aromatic amides studied. Only benzamide has been measured crystallographically. According to Groth¹³ benzamide forms monoclinic prismatic crystals, $\beta = 90^\circ 38'$; the acute bisectrix forms an angle of 40° with the c axis; and $2H = 100^\circ 15'$ (red), $2H = 102^\circ 10'$ (violet).

The plates obtained from water give beautifully centered optic axis figures which are practically straight. Twinning is prominent on this face. Rapid cooling during crystallization causes the formation of the metastable triclinic needles having $2V = 44^\circ$.

o-Toluamide from water gives tablets exhibiting oblique extinction, good cleavage, and off-centered Bx_0 figures. *m*-Toluamide from water crystallizes as monoclinic prisms with a maximum extinction angle of *ca.* 43° . They are elongated parallel to the c axis. The material used for optical determinations was fused beneath a cover glass, then crushed, and mixed with powdered glass. *p*-Toluamide from water crystallizes on the microscope slide as monoclinic square plates showing very good rectangular cleavage. Careful recrystallization from water gives monoclinic crystals elongated parallel to γ . *o*-Ethylbenzamide gives crystals showing both parallel and oblique extinction. From the melt a metastable form giving a well centered Bx_a figure rapidly reverts to the stable monoclinic form. *p*-Ethylbenzamide from water forms monoclinic tablets giving good Bx_0 figures and parallel extinction. *p*-Propylbenzamide from water shows very prominent cleavage parallel to the plane of the optic axes. *p*-*n*-Butylbenzamide from xylene-Canada balsam forms monoclinic prisms elongated parallel to the c axis. From water the prominent face is parallel to the plane of the optic axes with an extinction angle of 40° . *p*-Isobutyl benzamide from xylene-Canada balsam forms monoclinic prisms elongated parallel to the c axis. From water small plates representing sections parallel to the plane of the optic axes with an extinction angle of *ca.* 37° and with v-shaped cavities running in from the two ends are formed. The interference figure usually obtained for *p*-*s*-butylbenzamide is that of the optic axis section, not centered, however. Although 2-cyano-1,3-dimethylbenzene crystals

(13) P. Groth, "Chemische Krystallographie," Vol. IV, Leipzig, 1917, p. 523.

show only parallel extinction, they are monoclinic. The monoclinic needles are elongated parallel to the c axis and give perfectly centered Bx_a figures. 1,3-Dimethylbenzamide-2 from water forms needle-like plates giving Bx_a figures, and elongated parallel to c .

In Fig. 1 are given the optic axial angles of the aromatic and aliphatic amides. The aromatic amides plotted are para-substituted homologs of benzamide, and the abscissa gives the length of the carbon chain in the para position. In the case of the aliphatic amides the abscissa gives the length of the carbon chain attached to the $-\text{CONH}_2$ group.

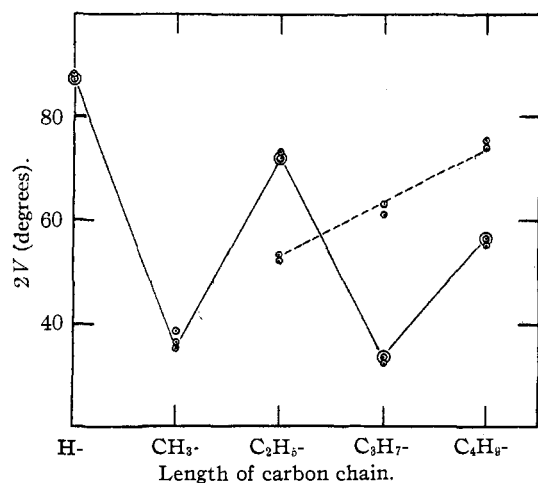


Fig. 1.—Optic axial angles: full lines represent $2V$ values of aromatic amides as a function of the carbon chain in the para position; dotted lines represent $2V$ values of aliphatic amides as function of the carbon chain.

The $2V$ value of acetamide has been omitted. Whereas the $2V$ values of the aliphatic amides vary in a regular manner, there is noted a fluctuation in the case of the aromatic para-substituted amides. The one with the odd number of carbon atoms in the aliphatic chain has a $2V$ value lower than the homolog containing the even number of carbon atoms. From the compounds investigated it appears that the evens and odds vary in a regular manner.

According to Müller and Shearer¹⁴ the natural saturated alcohols have a zigzag structure while the carbon atoms in the natural saturated aliphatic acids have the alternate structure. It appears that the same two types of structure are present in the aromatic and aliphatic amides. Possibly the benzene ring is the cause of the alternate structure.

(14) A. Müller and G. Shearer, *J. Chem. Soc.*, **123**, 3156 (1923).

In Fig. 2 are plotted the refractive indices of the para-substituted normal aromatic amides as a function of the carbon content. As can be seen from the curves, there is a step-like decrease in the birefringence with an increase of the carbon chain which is what would be expected. The substance takes on an aliphatic character as the aliphatic chain is increased, a low birefringence being associated with the aliphatic amides and a higher birefringence with the aromatic amides.

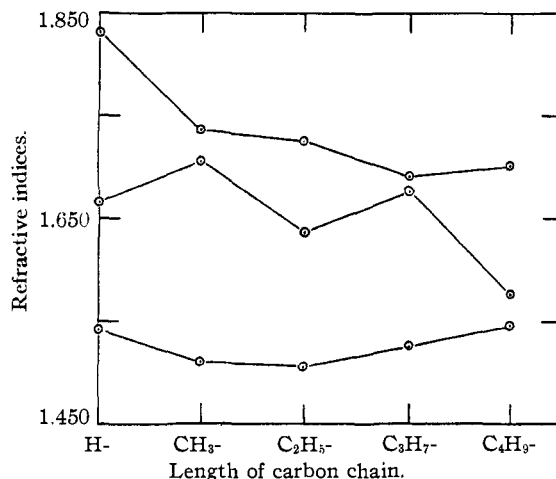


Fig. 2.—Refractive indices of benzamide and its para-substituted homologs: from top to bottom the lines represent n_γ , n_β and n_α ; the length of the carbon chain in the para position is plotted as the abscissa.

It is noted from the figure that it is n_β which causes the fluctuation of the $2V$ values.

Acknowledgment.—The authors thank Dr. C. D. Jeffries of the Agronomy Laboratory for his counsel in the use of the universal stage and Mr. E. F. Williams of the Geology Department for the use of the universal stage and his counsel with its application. Thanks are also due The Research Council of this College for making a part of this research possible.

Summary

1. A homologous series of aromatic acid amides based on benzamide was prepared. Four of these have not been reported in the literature and another was reported incorrectly.

2. The optical data including the principal refractive indices, $2V$ values, optical character, crystal system, etc., was worked out for the aromatic amides as well as for a homologous series of amides based on acetamide.

3. The applicability of petrographic methods

including the use of the universal stage was shown.

4. Some attempt was made to explain the data

in terms of structure and chemical constitution.

STATE COLLEGE, PA.

RECEIVED DECEMBER 12, 1939

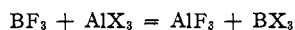
[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 80]

The Reaction of Boron Fluoride with Aluminum Chloride or Bromide

BY E. LEE GAMBLE, PAUL GILMONT AND JOHN F. STIFF

Discussion

The comparative lack of volatility of aluminum fluoride (melting point 1040°) with respect to the other halides of aluminum may be taken advantage of for the preparation of various volatile halides. For example, this paper describes the preparation of boron chloride and of boron bromide by the action of boron fluoride on the corresponding aluminum halide.



The ease with which the reactants are obtainable and the differences in volatility make this a simple means of preparation. It is possible that mixed fluorohalides of aluminum are intermediate products of this reaction, but they have not been isolated in a state of purity. The action of boron fluoride on aluminum iodide has produced small amounts of boron iodide but as yet the yields have been quite low. The development of this preparation is to be continued. Boron chloride or bromide is also produced when potassium fluoborate is heated with aluminum chloride or bromide but the yields obtained are not as satisfactory as when boron fluoride is used.

No fluorochlorides or fluorobromides of boron have ever been reported, nor have any been detected in this investigation. To determine whether the known fluorochlorides of silicon¹ could be prepared by this type of reaction, sodium fluosilicate was heated with aluminum chloride, the volatile products obtained proved to be only silicon tetrachloride and tetrafluoride, containing none of the fluorochlorosilanes.

The conversion of volatile fluorides into chlorides or bromides by means of aluminum chloride or bromide should prove to be somewhat general. From one point of view, the results of this reaction may be looked upon as the reverse of those of the Swarts reaction for the production of fluorides

or mixed fluorohalides by means of antimony fluoride.²

Many of the methods described in the literature for the preparation of the boron halides have been repeated in this Laboratory.³ It is felt that the preparation of boron bromide from boron fluoride and aluminum bromide is a simpler method than any hitherto described. Also, the preparation of boron chloride by this method may prove convenient.

Experimental

Reagents.—Potassium fluoborate was prepared by dissolving boric acid in 48% hydrofluoric acid and adding potassium carbonate. The product was recrystallized from hot water and dried at 110°. Boron fluoride was prepared by the action of hot concentrated sulfuric acid on a mixture of potassium fluoborate and boric oxide.⁵ The aluminum bromide was prepared by slowly adding bromine to an excess of aluminum, in an ordinary distilling flask cooled by water.

Reactions with Boron Fluoride.—The flask in which the reactions were carried on was dumbbell-like in appearance and was constructed by sealing a 1-liter round-bottomed flask to the bottom of a half-liter distilling flask by means of 25 cm. of 30-mm. tubing. The tube for the introduction of the boron fluoride passed through a one-hole cork stopper in the distilling flask and extended to the middle of the larger flask. The smaller flask served as a condenser to prevent large quantities of the aluminum halide from distilling over with the product. A weighed quantity of aluminum chloride was poured into the reaction flask, or aluminum bromide was distilled in from the flask in which it was prepared, and its weight determined by difference. The boron fluoride generator was connected to the reaction flask by means of a small bubbler containing concentrated sulfuric acid. The rate of flow of the boron fluoride was comparatively rapid, about thirty minutes for 2 moles of gas. After the apparatus was swept out with boron fluoride, the large flask containing the

(2) F. Swarts, *Acad. roy. de Belgique*, **24**, 309 and 474 (1892); *Bull. soc. chim.*, [4] **35**, 1557 (1924).

(3) An effort was made to see whether, in the preparation of boron trichloride [BCl₃] by relatively low temperature reactions, some B₂Cl₄ was not formed at the same time. Careful distillation of the reaction products produced only negative results.

(4) "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 24.

(5) Ref. 4, p. 23.

(1) W. C. Schumb and E. L. Gamble, *THIS JOURNAL*, **56**, 3943 (1932); H. S. Booth and C. F. Swinehart, *ibid.*, **57**, 1333 (1935).