chloride, something of the nature of association can be ascertained.

3. It was found that hexanol-3 in concentrated solutions consists chiefly of dimers and that its rate of dissociation with dilution is greater than that for the other alcohols. Hexanol-1 and 3-methylpentanol-1 show the presence of higher polymers down to and including a concentration of 0.1 molar. The rate of change of association with dilution is least for hexanol-1. The remainder of the alcohols form intermediate cases between hexanol-1 and hexanol-3, both in respect to the presence of higher polymers and rate of dissociation with dilution.

4. The difference in behavior of the hexyl alcohols has been interpreted in terms of the structural environment of the —OH group.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KENTUCKY]

The Equilibrium Constants for the Systems Alkyl Formates and Alkyl Acetates with Stearic Acid

BY CHAS. BARKENBUS, C. A. ROSWELL AND A. ELEANOR MITTS

Ester interchange with alcohols or alcoholysis has received considerable attention in the last few years. A similar type of interchange between ester and acid and called acidolysis has not been so extensively studied. Since very little work has been done from a quantitative viewpoint it was thought advisable to determine the equilibrium constants for a series of alkyl esters with stearic acid and to see how these constants varied with change of alkyl group.

The general reaction, *i. e.*

$$RCO_2R + R'CO_2H \longleftrightarrow R'CO_2R + RCO_2H$$

has been used to prepare certain esters where the conditions were favorable.[1] The first quantitative study of acidolysis was made by Reid[2] who determined the equilibrium constants for the systems benzoic acid–benzyl acetate and *p*-bromobenzoic acid–ethyl benzoate. The equilibrium mixture was analyzed by determining the density and the constants obtained checked within 5% with those calculated from the esterification constants.

Sudborough and Karve[3] obtained an equilibrium constant of unity for the two systems trichloroacetic acid–methyl acetate and trichloroacetic acid–ethyl acetate.

Gault and Chablay[4] have recently studied the system methyl palmitate–acetic acid. They determined the time needed to reach equilibrium and found that fifty hours were necessary at 100° when sulfuric acid was used as a catalyst. In their latest paper they give the equilibrium constants for methyl palmitate with acetic acid, propionic acid, *n*-butyric acid, *n*-valeric acid, and *n*-caproic acid. The analysis of equilibrium mixtures of this type is simplified by the determination of the water soluble or water insoluble acids.

Sowa[5] has determined the rate of reaction using acetic acid with various alkyl esters of propionic, benzoic and salicylic acids. He was able to show that the main reaction was one of straight interchange but that larger normal alkyl groups of esters rearrange to secondary alkyl groups when changing to the other acid. This is probably due to the intermediate formation of an olefin. It was stated that only 4% of the new ester was due to this type of reaction. To see whether this observation held for the higher fatty acids, a large scale run was made using *n*-butyl stearate and acetic acid. The butyl acetates when separated and fractionally distilled through a ten-plate Podbielniak column showed that only 2% of the esters was *s*-butyl acetate.

In this work the equilibrium was obtained by heating in a sealed glass tube at 100° about 0.02 mole of stearic acid, 0.1 mole of the ester and 0.1 g. of *p*-toluenesulfonic acid as a catalyst. The tubes were heated at various lengths of time and equilibrium was considered established when the tubes heated the longest checked with those heated next in length of time. From seventy-two to one hundred and twenty hours were usually required.

(1) Lowig, *J. prakt. Chem.*, [1] **83**, 130 (1861); Lorin, *Bull. soc. chim.*, [2] **49**, 344 (1888); Norman, *Chem. Umschau*, **30**, 250 (1924); Forneau, *Bull. soc. chim.*, **45**, 834 (1929); Pistor, *Z. angew. Chem.*, **38**, 1118 (1925); Graves, U. S. Patent 1,882,808.

(2) Reid, *Am. Chem. J.*, **45**, 479 (1911).

(3) Sudborough and Karve, *Indian Inst. Sci.*, **5**, 1 (1922).

(4) Gault and Chablay, *Compt. rend.*, **203**, 729 (1936); **207**, 293 (1938).

(5) Sowa, THIS JOURNAL, **60**, 654 (1938).

The contents were dissolved in benzene and extracted at least ten times with cold water to remove the water soluble acids. It was rather difficult to completely remove acetic acid from the benzene solution. The time consumed in the extraction caused some hydrolysis of the lower esters which made it impossible to determine the water soluble acids produced by the acidolysis. The stearate esters due to their insolubility in water were not hydrolyzed during the extraction, as was determined by running blanks.

After extraction, the benzene was evaporated and the last traces of the more volatile ester were removed under vacuum. The residue was then taken up in neutral hot alcohol and titrated. It was found that the most consistent and accurate results were obtained by titrating the insoluble acid instead of the water soluble acid. The equilibrium constants obtained never varied more than 2% and most of them checked within less than 1%.

It was found that formic acid could be more readily extracted with water and a few of the constants were determined by the quantitative oxidation of formic acid with potassium permanganate. In this case the small amount of formate esters dissolved in the water had to be removed by aeration before oxidation. This made the analysis long and great care had to be used in keeping the solutions cold to prevent hydrolysis.

The stearic acid used was a highly purified product obtained by fractional distillation of methyl stearate and by crystallization of the acid. All the esters used were fractionally distilled through a Widmer column and only those fractions having indices corresponding to those in the literature were used. The *p*-toluenesulfonic acid was prepared in the usual way except that stirring was used during the sulfonation, which gave a whiter product. The acid was not crystallized but was triturated several times with toluene and filtered. This last procedure gave a product which was completely soluble in water and, after drying in a desiccator over phosphorus pentoxide, analyzed for approximately one water of hydration.

Gault and Chablay[4] have shown for the reversible reaction $CH_3COOH + CH_3(CH_2)_{14}COOCH_3 \rightleftarrows CH_3COOCH_3 + CH_3(CH_2)_{14}COOH$ that the equilibrium can be approached from both directions. They determined the time necessary to obtain equilibrium starting from both sides and, though the time varied, the concentrations at equilibrium were the same. It was also necessary to have some comparison between the systems using palmitic acid with those using stearic acid. The equilibrium constant for methyl palmitate–acetic acid was redetermined and an average value of 1.034 for four determinations was obtained. The average value obtained by Gault and Chablay,[4] who approached the equilibrium from the other side, was 1.070. Since the above data indicate clearly that a true equilibrium is obtained in acidolysis reactions, the equilibrium constants reported in this paper were obtained by approaching the equilibrium from one direction only.

The equilibrium constants

$$K = \frac{[CH_3(CH_2)_{16}COOR][RCOOH]}{[R—COOR][CH_3(CH_2)_{16}COOH]}$$

are collected in Table I. The values all represent the mean of three independent measurements.

TABLE I

EQUILIBRIUM CONSTANT K IN THE PRESENCE OF STEARIC ACID

	Formates		Acetates	
Esters	K	Av. dev. ±%	K	Av. dev. ±%
Methyl	1.287	0.1	1.019	0.4
Ethyl	0.845	.2	0.902	.5
n-Propyl	.794	.0	.912	.6
s-Propyl	.693	.9	...	...
n-Butyl	.869	.5	.964	.5
i-Butyl	.782	.4	...	...
n-Amyl	.750	.9	.731	.6

Similar measurements were made with methyl acetate using palmitic acid instead of stearic. The corresponding value of K for this system was 1.034 ± 0.4%. This is interesting in showing that there is no significant difference between the palmitate and the stearate system.

We have also calculated similar equilibrium constants from the data of Gault and Chablay.[4] The values thus obtained were for methyl propionate, *n*-butyrate, *n*-valerate and *n*-caproate, 1.12 ± 4, 1.17 ± 10, 1.04 ± 4 and 1.02 ± 3%, respectively. These constants show a diminishing trend with increasing molecular weight of the acid, but the deviations of the individual measurements from the mean are so great as to raise some questions as to whether there was any real difference in these values of K.

It can be seen readily that the methyl group of an ester is more readily replaced by the acid hydrogen of stearic acid than are the other alkyl groups listed. The normal alkyl groups are more readily exchanged than the secondary alkyl groups or branched chain alkyl groups. Esters containing a tertiary alkyl group could not be used as they were decomposed by the acid catalyst. The extent of displacement decreases slowly with length of normal alkyl group at least as far as the normal amyl group. The only exception to this is the *n*-butyl group, which is higher.

From the data of Gault and Chablay and from Table I it can be seen that the length of the fatty acid which forms the ester does not affect the reactivity as much as does the alkyl group of the

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 Adkins[6] 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 methylene 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.

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

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.

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[CONTRIBUTION FROM THE PENNSYLVANIA STATE COLLEGE]

Optical Constants of Benzamide, its Homologs, and Some Aliphatic Amides[1]

BY M. L. WILLARD AND CHARLES MARESH[2]

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 hydrolysis[3] 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 Read[4] 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.

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(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.