trolyte contamination, immaculate cleanliness was always observed. The collodion bags used in dialysis were always thoroughly rinsed with distilled water before being put into use. All glassware was steamed and rinsed.

A subsequent paper will deal with the properties of chloride free ferric oxide hydrosols.

Summary

Stable ferric oxide hydrosols giving no test for chloride have been prepared by hydrolysis and hot dialysis of ferric chloride.

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THE RELATION BETWEEN THE HYDROLYSIS EQUILIBRIUM CONSTANT OF ESTERS AND THE STRENGTHS OF THE CORRESPONDING ACIDS

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The relationship has previously been mentioned[1] in comparing esters with mixed acid anhydrides, that esters of stronger acids are in general more completely hydrolyzed under like conditions than the esters of weaker acids. This generalization was based upon rather limited and in some cases questionable data, and it was therefore hoped to test out the generalization by obtaining more data on the hydrolysis equilibrium constants of esters of different acids.

It was planned to determine the equilibrium constants by the simple, direct method of heating the acid and alcohol together until equilibrium was established and analyzing the original and final mixtures. Unfortunately experimental difficulties prevented the determination of very many values by this direct method. The reactions are so slow even at 100° that it is necessary in order to reach equilibrium within any reasonable time to have a fairly high concentration of acid to act as catalyst in the final equilibrium mixture. Especially is this true in case a weak acid is being used. One of the principal difficulties introduced by reason of this fact is that of obtaining a homogeneous solution at equilibrium. In many cases sufficient acid for the catalysis will not remain dissolved. Another more or less obvious difficulty limiting the application of this direct method is the fact that "side reactions" are likely to occur. Many acids, for example, decompose under the conditions used before equilibrium in the esterification reaction is attained.

In spite of the fact that the work was not extended as far as it was at first hoped, some data contributing to the question were obtained and are here reported.

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[1] Williams and Truesdail, This Journal, 45, 1348 (1923).

Experimental Results and Discussion

Ethyl Esters of Halogen Acids.—Hydriodic acid is the strongest of the halogen acids, hydrobromic acid is next and hydrochloric acid is not as strong as the other two as determined by the ordinary methods. It was accordingly thought desirable to determine the hydrolysis equilibrium constants of the ethyl esters of these acids. Euler[2] had previously determined the value for the hydrochloric acid ester, using essentially the method we had in mind. However, the formation of ether takes place too readily to allow a satisfactory determination of these constants by this direct method. Ether formation is especially noticeable when alcohol is heated with hydrobromic acid. The results obtained, in so far as they can be relied upon at all, indicate that the hydrolysis equilibrium constants of the three ethyl esters are in the same order as the strengths of the corresponding acids, in accordance with the generalization mentioned above. However, the values which were obtained are subject to errors of unknown magnitude due to ether formation and, therefore, are not recorded here. In order to arrive at the true constants it will probably be necessary to make independent measurements of the rates of hydrolysis and esterification in each case and to compute the constants from these data. We are not prepared at present to carry out these more extensive experiments.

Esters of Fatty Acids.—The only fatty acids which show distinct and consistent differences in their acid strengths at all temperatures at which they have been studied are formic, acetic and propionic acids. They are, therefore, the only ones which could be used to throw light on the problem under consideration. The equilibrium "constants" of the methyl esters of these acids were determined under one set of conditions and the values for the ethyl esters were determined for two different sets of comparable conditions.

TABLE I

ETHYL ESTERS OF FATTY ACIDS

A

	Acid		Alcohol		Water		Ester			
	Initial concn.	Final concn.[a]	Initial concn.	Final concn.	Initial concn.	Final concn.	Initial concn.	Final concn.	K_E	$K_A \times 10^{-5}$
Formic	9.95	6.33	9.95	6.33	4.00	7.62	0	3.62	1.45	21.4
Acetic	9.00	3.17	9.00	3.17	0	5.83	0	5.83	.296	1.8
Propionic	7.75	2.77	7.75	2.77	.35	5.33	0	4.98	.289	1.34
B										
Formic	7.25	2.53	12.50	7.78	0	4.72	0	4.72	.883	
Acetic	7.07	1.81	10.31	5.05	0	5.26	0	5.26	.332	
Propionic	7.11	2.12	8.24	3.25	0	4.99	0	4.99	.294	

[a] The "initial" concentration refers to the molar concentration in the original acid–alcohol mixture before reaction has taken place. The "final" concentration refers to the corresponding value after equilibrium is established.

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[2] Euler, *Z. physik. Chem.*, **36**, 405 (1901).

In the experiments summarized in Table IA, equimolecular quantities of the concentrated acid and absolute alcohol were heated together in a boiling water-bath in sealed glass tubes filled nearly full with the mixture, allowing only for thermal expansion. A sample tube was removed from time to time, cooled to 0° and portions titrated with standard alkali. The pipets used were calibrated for this purpose. When the titrations of successive samples became practically constant, it was assumed that equilibrium had been reached.

TABLE II

METHYL ESTERS OF FATTY ACIDS

	Acid		Alcohol		Water		Ester			
	Initial concn.	Final concn.	Initial concn.	Final concn.	Initial concn.	Final concn.	Initial concn.	Final concn.	K_E	$K_A \times 10^{-5}$
Formic	7.10	1.98	18.81	13.69	0	5.12	0	5.12	1.03	21.4
Acetic	7.05	0.93	15.1	8.98	0	6.12	0	6.12	.224	1.8
Propionic	7.11	1.20	12.15	6.24	0	5.91	0	5.91	.214	1.34

The experiments summarized in Tables IB and II were carried out in a similar fashion except that sufficient of the anhydrous acids were dissolved in the absolute alcohols to make the initial concentrations of the acids approximately 7 *N*. The initial normalities of the acids were checked both by weighing and by titration. (Anhydrous formic acid could not be evaluated by titration in alcoholic solution, because esterification takes place too rapidly. In this case the weighed samples of acid were titrated after dilution with water.) The final concentrations of formic acid could not be determined with a high degree of accuracy even at 0° because of the relative rapidity of the hydrolysis of ethyl and methyl formates. The first experiments carried out with formic acid were discarded because of this difficulty. However, the results obtained in these preliminary experiments checked approximately those obtained in the more carefully controlled experiments here reported.

The time of heating necessary to produce approximate equilibrium varied from about one day (twenty-four hours) when formic acid was concerned, to eight or ten days when propionic acid was used.

In order to test whether ether might be formed when a fatty acid is heated continuously with alcohol, a mixture of 30 cc. of glacial acetic acid and 120 cc. of absolute alcohol was heated to 100° for 144 hours in a sealed tube. At the end of this time the mixture was fractionated using a three foot column, and no trace of liquid came over below 70°, indicating that no ether was formed.

Euler[2] previously made determinations of the hydrolysis equilibrium constants of fatty acids in accordance with the results given in Table III. He started in each case with a solution 2 *N* in both acid and alcohol, but in addition the solution was 0.25 *N* in hydrochloric acid. Our principal objection to his work is the fact that the hydrochloric acid which was introduced as a catalyst was present at the start in a concentration one-eighth as great as the concentration of the acid investigated. This introduced an error due to the formation of the ester of the hydrochloric acid as well as the formation of the ether mentioned above.

TABLE III

HYDROLYSIS EQUILIBRIUM CONSTANTS (EULER)

	Methyl alcohol	Ethyl alcohol
Formic acid	0.20	0.36
Acetic acid	.15	.27
Propionic acid	.15	.27

A study and comparison of the values obtained emphasizes the fact that they are not "constants" since they vary with the conditions. In the case of the weakest acid (propionic) the variations in the value are the least, but the discrepancies in the case of the strongest acid (formic) are very great. The results show that under all the comparable conditions studied the esters of formic acid are most completely hydrolyzed, the esters of acetic acid are next and the esters of propionic acid are least hydrolyzed. This order is the same as that of the strengths of the acids concerned. It is also noteworthy that the hydrolysis equilibrium constants of the esters as well as the ionization constants of the acids are nearly the same in the case of acetic and propionic acids, but in the case of formic acid both values are much higher.

Esters of Hydroxy Acids.—Hydroxy acids are materially stronger than the corresponding fatty acids as indicated by the values given in Table IV. In this table are also given the results obtained for the ethyl esters of glycolic and lactic acids and (for comparison) the values for the corresponding esters of acetic and propionic acids.

TABLE IV

ETHYL ESTERS OF GLYCOLIC AND LACTIC ACIDS

	Acid		Alcohol		Water		Ester			
	Initial concn.	Final concn.	Initial concn.	Final concn.	Initial concn.	Final concn.	Initial concn.	Final concn.	K_E	$K_A \times 10^{-5}$
Acetic	..	..	..	..	..	..	.	..	0.296	1.8
Glycolic	5.46	2.52	9.75	6.81	10.3	13.24	0	2.99	(.44)	15.2
Propionic	..	..	..	..	..	..	.	..	.289	1.34
Lactic	6.45	3.80	6.45	3.80	11.7	14.35	0	2.65	(.38)	14.0

These values for the esters of the hydroxy acids, because of some "lactide" formation, do not represent true esterification equilibrium values. In spite of this fact the results are not meaningless, since the values obtained indicate hydrolysis equilibrium constants for the esters of the hydroxy acids higher than for the esters of the corresponding fatty acids, and any correction which might be introduced to correct for lactide formation would increase rather than decrease the constants.

Although the results here presented are not very extensive, when considered in relation to other available information which is of a qualitative nature, they are sufficient to convince us that one of the most important factors which govern the stability (in the thermodynamic sense) of esters toward water, and probably other reagents, is the so-called "negative" character of the acid group. In terms of electronic structures it seems likely that a group which is capable of exerting a pull on electrons distorts the electron shells of nearby atoms and causes the compound to be less stable. A more "negative" group should then be capable of causing more distortion and consequently more instability. The situation is quite complex, however, and it does not seem possible at present to picture with any certainty the nature of the distortion, if it exists, or to know which particular atomic shell is distorted in such a way as to cause instability.

That the "negative" character of the acid group is not the only factor which governs instability is shown by the fact that when esters with quite different structures are compared there may be no relationship between the hydrolysis equilibrium constants of the esters and the ionization constants of the acids.

Summary

An attempt was made to determine by a direct method the hydrolysis equilibrium constants of several esters to see if these constants have any relation to the ionization constants of the corresponding acids. The results seem to bear out the generalization that when esters of not too dissimilar structure are compared, the esters of stronger acids are more completely hydrolyzed under like conditions than are the esters of weaker acids. The hydrolysis equilibrium constants were directly determinable in only a very limited number of cases and were found to vary with the conditions.

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