

ESTERIFICATION IN THE PRESENCE OF ANHYDROUS SALTS.

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The usual method of producing esters involves the removal of water, which is one of the products of the reaction between alcohol and acid. Equilibrium is shifted toward the production of ester by the removal of water. Sulphuric acid is often employed for this purpose, but hydrochloric acid is also frequently used.

The role that such an acid plays in promoting ester formation, although not well understood, cannot be wholly due to the combination of sulphuric or dry hydrochloric acid with water. Either the acid molecule, or some part of it, plays the role of catalyst. The question of the nature of acid catalysis and the active catalysing agent is still one that may be considered open for investigation.

Many salts crystallize from water in definite forms and combined with definite numbers of water molecules per molecule of compound. When such salts are dehydrated, they become excellent dehydrating agents, and, as such, they should promote esterification and all similar reactions in which water is one of the products. There are, however, several questions that arise in using anhydrous salts for this purpose. Do the salts act as catalysts? If so, is the catalytic effect due to the salt itself? Do the salts hydrolyse to produce acids which act as catalysts? Will the salts accelerate the reaction at temperatures above the dehydration temperatures of the crystalline substances? How does the temperature at which the salt is dehydrated affect its use in promoting esterification? How does the catalytic effect of the anhydrous salt compare with its efficiency in other instances of its use as an agent of dehydration and dessication? Is there any relation between the number of molecules of water in the crystalline substance and the effect of the anhydrous salt upon ester formation? What salts are most effective?

This paper does not attempt to answer all these questions. It is the hope of the writers, however, to add to the present knowledge of this reaction.

Various anhydrous salts have been used in the esterification of organic acids and ethyl alcohol by Bogojawlensky and Narbutt¹ and by Haberman and Brezina² and by Haberman and Kurtenacher.³ The salts employed by these workers were sulphates with few exceptions. Ferrous, nickel, copper, manganese and zinc sulphates were found effective. Sodium

¹ Bogojawlensky and Narbutt: Esterificierungsversuche, 38, 3344, (1905).

² Haberman and Brezina: Beiträge zur Darstellung und Kenntnis des Essigäthers. J. prakt. Chem., 80, 349, (1909).

³ Haberman and Kurtenacher: Beiträge zur Darstellung und Kenntnis des Essigäthers. J. prakt. Chem., 82, 541, (1910).

sulphate was found to have no effect. Potassium pyrosulphate gave very good results. Various aliphatic and aromatic acids were esterified with ethyl alcohol in the presence of these salts.

EXPERIMENTAL.

Apparatus. Most of the experiments of the writers were made in a thermostat of about fifteen gallons capacity; the water in it was continuously agitated, and the temperature was maintained at 45° C.

Some of the reactions were carried out in a water bath large enough to accommodate four flasks to which reflux condensers were attached. The temperature of this bath was kept at the boiling point of water.

Some experiments were made in which the anhydrous salts were placed in an electric furnace which was heated to a temperature above that of the dehydration point of the salts. The vapors of the acid and alcohol were passed over the catalyst very slowly. Both reactants were introduced into an auxiliary furnace, where they were vaporized. The vapors were then passed through the second furnace, where the reaction occurred. The gaseous products were led through a condenser. Each reaction was run as long as any product could be condensed. The tube which contained the salts and through which the reacting vapors were made to pass was of quartz.

Materials. Absolute alcohol was prepared by treating 96 per cent stock alcohol with quicklime. Calcium hydroxide was heated slowly to a dull red heat. About 300 grams of the product were added to 500 cc. of alcohol, and the mixture was refluxed for four hours. The alcohol was then distilled with great care to prevent overheating. Anhydrous copper sulphate was used to test for water in the product. The alcohol was not used unless the sulphate remained colorless after two hours.

About three liters of C. P. acetic acid were placed in a freezing mixture of salt and ice. After the solid acid had collected on the walls of the bottle, the liquid was poured off and placed in another freezing mixture, where it was left for two hours. The final liquid fraction was poured off, and the two solid portions were mixed. The specific gravity was measured with a pycnometer.

The normal hydrochloric acid solution was standardized against potassium acid phthalate. The normal potassium hydroxide solution was made up in 50 per cent redistilled stock alcohol.

The salts were dehydrated in an iron container, which was carefully cleaned and sanded after each dehydration. This container and its contents were heated in an electric furnace. The temperature was noted and carefully controlled in every case.

Experimental Procedure. Alcohol and acid were placed in separate burettes, care being taken that no more than the unavoidable amount of air should come into contact with them at any time. Ten ml. of the acid was run into a long necked flask of about 50 ml. capacity; 10.5 ml. of absolute alcohol was added. Ten grams of the anhydrous salts were added, since this amount was well above the amount that is theoretically required to combine with the water which is produced by the reaction of the amounts of acid and alcohol indicated above. These salts were all

dehydrated at temperatures slightly above that which is necessary to drive off all the water which is combined with them in the crystalline state.

After the proper mixtures were prepared, the flasks and their contents were weighted and suspended from a wire that extended across the constant temperature bath. The flasks were completely submerged, with the exception of the extreme ends of the long necks.

When definite periods of time had elapsed, the flasks were removed; the contents were cooled; and a two cubic centimeter sample was pipetted and transferred directly to a flask, where a few drops of phenolphthalein were added. The sample was titrated immediately with potassium hydroxide solution. The potassium hydroxide, standardized in reference to the acid used, gave the amount of the free acid that the sample contained. From these results the per cent of esterified acid was calculated. To avoid errors that might be caused by the presence of small amounts of the salts, the ester was saponified by treatment with excess potassium hydroxide at 90°-100° C. for four hours. The amount of hydroxide used in the saponification permitted the calculation of the amount of ester and, hence, the per cent of the acid which had been esterified.

DATA.

A series of preliminary experiments was made with a mixture of 24.5 ml. of absolute alcohol and 16.1 ml. of glacial acetic acid. This mixture was refluxed in the presence of 10 grams of different anhydrous salts. The results listed in Table I were found after the mixture had

TABLE I. Preliminary Preparation of Ethyl Acetate (Temperature 100°C.)

Catalyst	Time Refluxed (in hours)	Time Allowed to stand after refluxing (in hours)	Yield (Per cent of Theory)
H ₂ SO ₄	1	0	70.00
Blank	10	14	Slight odor
Alum	10	14	5.50
CuSO ₄	10	14	7.60
MnSO ₄	10	2	10.00
MgSO ₄	10	2	19.00
MgSO ₄	10	14	25.00
Alum	10	10.5	62.00
ZnCl ₂	0	43.5	70.90
CuSO ₄	0	0	0.00
CuSO ₄	2	0	15.19
CuSO ₄	4	0	19.19
CuSO ₄	6	0	18.87
CuSO ₄	8	0	21.25
CuSO ₄	10	0	20.32
CuSO ₄	0	14	23.75
MgSO ₄	10	0	32.19
MgSO ₄	0	14	35.00
MnSO ₄	10	0	25.19
MnSO ₄	0	10	27.00



been allowed to react for the designated number of hours. These results were found by neutralizing the whole sample with a saturated solution of sodium carbonate. It was then placed in a separatory funnel. The ester was then salted out and separated from the water layer. The crude product was then distilled, and the portion that came over at 74°-76° C. was then collected and weighed.

The data presented in the following tables are arranged to show the effects of the different salts that were used. Table II gives the percentages of acetic acid that were esterified in different periods of time in the presence of various salts. These results are also represented graphically. The retarding effect of calcium sulphate is to be noted; all other salts in this series gave positive results. Copper sulphate was the most effective catalyst. All these salts were dehydrated at temperatures just slightly above the temperatures at which they are supposed to lose all their water of crystallization.

Table III shows the effect of the nature of the alcohol molecule upon the formation of the ester. The length of the chain of carbon atoms and the structure of the molecule are found to affect the reactivity of the molecule in the presence of anhydrous salts as elsewhere.

Table IV shows the effect of the structure of the acid molecule upon the formation of esters in the presence of anhydrous copper sulphate.

Table V shows the effect of the temperature of dehydration of the salts upon their action as catalytic agents. Cupric sulphate dehydrated at 130° C. is not as good a catalyst as the same salt after it has been dehydrated at 240° C. This salt does not lose all of its combined water until it has been heated above 130° C. The same is true of magnesium sulphate, which does not attain its full catalysing action until it has been dehydrated at temperatures above 200° C. It will also be noted that salts dehydrated at temperatures above those at which they are supposed to lose all water of crystallization are poorer catalysts than those which are dehydrated at the exactly required temperatures.

Table VI shows the amounts of esters formed when vapors of alcohol and acid were passed together over anhydrous salts in a quartz tube, which was heated to a temperature above the point at which the salt is completely dehydrated. The alcohol and acid were vaporized in an auxiliary furnace which was held at 130° C. The temperature of the furnace which contained the salt was held at 230° C. The marked differences in the catalytic influences of the different salts cause great variations in the amounts of ester formed in the different experiments.

TABLE II. Time-percentage Data With Reference to the Action of Various Anhydrous Salts on the Rate of Formation of Ethyl Acetate.

(Temperature 45°C.)

A. CuSO_4		C. CdSO_4	
Hours	Acid Esterified	Hours	Acid Esterified
12	47.43%	12.5	8.46%
30	64.76%	43	23.20%
48	70.97%	96	50.26%
120	76.63%	168	61.24%
168	82.67%	768	63.49%
264	84.11%		
360	84.11%		
B. $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4$		D. MnSO_4	
43	40.63%	12.5	6.42%
96	57.49%	96	41.10%
120	62.61%	168	43.33%
240	69.12%	264	47.70%
792	75.06%	336	53.42%
E. $\text{Fe}_2(\text{SO}_4)_3$		G. CaSO_4	
17	52.77%	72	16.33%
72	60.35%	115	23.33%
114	63.56%	264	36.45%
384	63.56%	384	38.72%
F. $\text{Al}_2(\text{SO}_4)_3$		H. Blank (No Catalyst)	
12.5	39.95%	24	9.72%
48	56.86%	118	34.12%
No samples could be obtained after 48 hours due to the absorption of all of the liquid by the solid.		552	47.32%

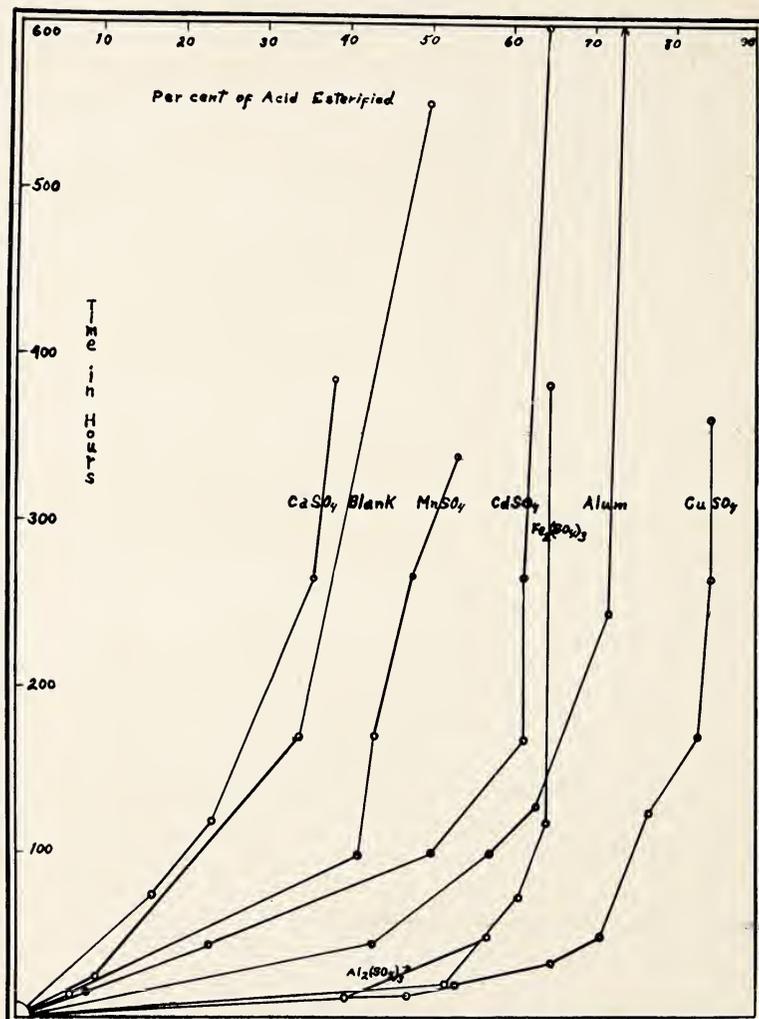


Fig. 1—Graphic presentation of results shown in Table II.

TABLE III. Esterification of Different Alcohols and Acetic Acid, with Copper Sulphate as Catalyst.

(Time 360 hours, Temperature 45°C.)

Alcohol	Yield (Per cent of Theory)
Ethyl.....	84.108
n-Butyl.....	61.800
iso-Butyl.....	60.560
Secondary Butyl.....	50.310
Tertiary Butyl.....	9.630

TABLE IV. Esterification of Different Acids and Ethyl Alcohol

(Time 360 hours, Temperature 45°C.)

Acid	Yield Per cent of Theory
Acetic.....	84.10
iso-valeric.....	82.48
n-valeric.....	81.62
Mono-chloro acetic.....	75.11
Propionic.....	49.71
iso-Butyric.....	48.33
n-Butyric.....	47.40
Di-chloro acetic.....	32.73

TABLE V. Temperatures of Dehydration of Salts and the Corresponding Effect on the Rate of Esterification of Ethyl Alcohol by Acetic Acid

(Time 4 hours, Temperature 100°C.)

Salt	Temperature of Dehydration	Acid Esterified
CuSO ₄	Hydrated	23.74%
CuSO ₄	130°C.	65.68%
CuSO ₄	240	71.68%
CuSO ₄	260	69.30%
CuSO ₄	340	69.43%
MgSO ₄	Hydrated	23.74%
MgSO ₄	160	42.73%
MgSO ₄	210	51.27%
MgSO ₄	260	31.70%

TABLE VI. Esterification of Ethyl Alcohol by Acetic Acid in the Vapor Phase over Anhydrous Salts.

Temperature: Vaporizing Chamber . . . 130°C.

Temperature: Reaction Chamber 230°C.

Salt	Acid Esterified
Blank	1.26%
$K_2SO_4 \cdot Al_2(SO_4)_3$	20.92%
$Al_2(SO_4)_3$	39.37%
$CdSO_4$	0.55%
$MnSO_4$	2.36%
$MgSO_4$	0.00%

CONCLUSIONS

The action of anhydrous salts in promoting esterification cannot be assigned to one cause. It is in part due to the dehydrating action or water-withdrawing action of the anhydrous salt, an action which shifts the equilibrium towards the formation of ester. This cannot be the sole factor, however, for plaster of Paris is a retardant, and anhydrous sodium sulphate has no effect. Neither is there any relation between the number of molecules of water with which the salt will combine and its efficiency in catalysing the reaction. There seems to be no relation between the catalytic action of the salts and their commonly accepted efficiencies in dessication and dehydration. There is, however, a marked increase in the accelerating effect of the catalyst, when it is dehydrated at temperatures which are calculated to remove all rather than a part of the water of crystallization; and this accelerating effect is reduced when the salt has been heated to a high temperature. The latter effect approximates the condition of "dead burning" in the case of quicklime, which becomes unreactive towards water after it has been heated for some time at high temperatures. That there are other factors that must be considered in addition to the removal of water by the catalyst, is shown by the fact that copper sulphate and magnesium sulphate, not dehydrated, produce many times as much ester as can be produced in their absence. Salts also accelerate ester formation at temperatures above those at which they are able to combine with water.