VAPOR PHASE ESTERIFICATION

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This paper presents the results of a study of the effects of anhydrous salts upon esterification in the vapor phase, a subject heretofore unstudied. In fact, there has been very little investigation of this reaction in the presence of any substances which may act catalytically. Edgar and Schuyler¹ found that the vapor phase of the equilibrium-mixture of acetic acid, ethyl alcohol, ethyl acetate, and water contains a noticeably higher percentage of ester than liquid mixtures. Milligan, Chappell, and Reid² studied the effect of silica gel upon vapor-phase esterification. They found that the maximum conversion of acid and alcohol to ester and water occurred at a temperature of $150^{\circ}-200^{\circ}$ C. in the presence of this substance. Their yields consistently approached 90 per cent conversion and showed conclusively that the percentage of esterification varies inversely as the rate of passage of the vaporized mixture through the reaction chamber.

EXPERIMENTAL

Materials. Pure acetic acid was prepared by fractional crystallization. The anhydrous salts were prepared by dehydrating the purest salts obtainable in an electric oven, the temperature of which was carefully controlled. The salts were finely powdered and stored out of contact with air until used. The standard sodium hydroxide solution which was used in titrating the unesterified acid was prepared with particular care to exclude carbon dioxide. Its normality was checked preceding each determination. A thorough review of the literature showed that all of the many processes which have been suggested for the production of absolute alcohol claim a product which is 100 per cent alcohol. Attempts to duplicate these processes in our laboratory showed that the most consistently pure product is obtained by the use of calcium oxide.

The action of calcium oxide upon 95 per cent alcohol was thoroughly investigated. It was found that the maximum dehydrating action of lime was obtained by refluxing one litre of 95 per cent alcohol with 300 grams of lime for six hours, distilling off the partially dehydrated alcohol, and refluxing again with 300 grams of lime for a period of three hours. The alcohol was finally distilled from the lime just before use. It was redistilled through a long fractionating column to prevent small particles of calcium oxide from coming over into the distillate. Particular precautions were also taken to carry out the distillations in a moisture-free atmosphere. The quick-lime was prepared by heating a good grade of hydrated chemical lime to dull redness in an electric muffle-furnace at 700°C.

¹ Edgar and Schuyler, J. Am. Chem. Soc., 46:64 (1924).

² Milligan, Chappell, and Reid, J. Phys. Chem., 28:872. (1924).

[&]quot;Proc. Ind. Acad. Sci., vol. 42, 1932 (1933)."

Aldehydes, the most common impurities in ethyl alcohol, were most completely removed by the addition of 2.5 grams of lead acetate with the second portion of lime. This method was found much more efficient than the use of silver nitrate. Amines and other basic substances were removed from the alcohol previous to any treatment with lime. For this purpose 5 ml. of pure sulphuric acid were added to a liter of 95 per cent alcohol, and the mixture was then distilled.

The progress of the dehydration and purification was followed by refractive index readings on a Pulfrich refractometer and by specific gravity determinations. The latter appeared to be the more trustworthy. A series of eight samples of absolute ethyl alcohol prepared by the treatments above described showed an average specific gravity of 0.78523 at $25^{\circ}/4^{\circ}$ C., and an average refractive index of $N_D^{20} = 1.359084$.

Apparatus. The esterification was carried out in an electrically heated quartz tube which was placed inside of an iron pipe (1¹/₄" in diameter). The pipe was covered with a layer of asbestos paper, upon which the heating element was wound. All this was covered with heavy asbestos for insulation. The quartz tube was 770 mm. long and its inside diameter was 23 mm. Its inner surface was glazed. About 70 mm. of the tube protuded from one end of the furnace for the attachment of the necessary condensation fixtures. The temperature of the furnace was varied by means of a resistance placed in series with the current supply. The temperature of the inside of the furnace was measured by a copper-constant in thermocouple. The hot junction was placed between the quartz tube and the iron pipe at a point exactly outside that point of the interior where the vapors first made contact with the anhydrous salt. This furnace was modelled after that used by Milligan, Chappell, and Reid.

Specific gravity was measured by means of an 27 ml. pycnometer. These measurements were made in a $(25^{\circ}C.)$ constant temperature bath and were calculated with reference to water as unity at $4^{\circ}C$.

Experimental Procedure. A mixture of equivalent amounts of acetic acid and ethyl alcohol was admitted to the furnace through a small capillary sealed to the end of a section of a burette. The rate of flow was regulated by reducing or increasing the pressure on the surface of the liquid in the burette.

The issuing vapors were condensed and collected in a small Erlenmyer flask. A 2 ml. portion was withdrawn and titrated immediately with standard sodium hydroxide solution. Phenolphthalein was used as the indicator. The result of the titration was subtracted from the result of a similar titration on a 2 ml. portion of the starting mixture. This difference, divided by the number of milliliters of the base necessary to neutralize 2 ml. of the starting mixture, gave directly the percentage of acid converted into ethyl acetate. Fifteen grams of the anhydrous salt, an amount well above that theoretically required to combine with all the water formed in the reaction, occupied 250 mm. at the exit end of the furnace.

RESULTS

Preliminary experiments were performed to determine whether or not the empty furnace possessed any promoting activity. Different temperatures and different rates of passing the vapors through the furnace were investigated. The results showed definitely that esterification occurs only at a high temperature and only when the vapors are passed very slowly. The maximum yields of ester were about 3 to 4 per cent. The products of these blank runs gave positive tests with fuchsinsulphurous acid solution and, therefore, indicated that some oxidation occurred under the conditions employed.

Hydrated aluminum sulphate, containing 18 molecules of water per molecule of the salt, was dehydrated at 200°C. Its promoting activity was then investigated in the manner already described. The results are shown in Table 1. These indicate that the high temperatures and lower rates are more favorable for esterification. The presence of a large excess of salt did not increase the yield significantly.

TABLE 1.

ALUMINUM SULPHATE

		\mathbf{Rate}	
No.	Temperature	cc. vapors per min.	Acid esterified
1	175°C.	386	3.92%
2	175	193	2.74
3	175	73	1.57
4	250	386	30.13
5	250	193	42.35
6	250	84	40.13
7^{*}	250	193	44.38
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* 35g. anhydrous salt used.

Potassium aluminum sulphate (potash-alum), containing 24 molecules of water per molecule of salt, was also dehydrated at 200°C. As shown in Table 2, the presence of potassium sulphate has little effect upon the extent of esterification, since these results are only slightly higher than those for aluminum sulphate. The slightly greater yields in this case may be due to the ability of the molecules of the double salt to combine with the greater number of molecules of water.

TABLE 2.

POTASSIUM ALUMINUM SULPHATE

Rate

No.	Temperature	cc. vapors per min.	Acid esterified
1	175° C.	386	5.29%
2	175	193	7.51
3	175	193	7.07
4	175	93	13.33
5	250	386	30.70
6	250	386	27.01
7	250	193	43.90
8	250	89	47.07

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The difference in the effects of chromium sulphate and potassium chromium sulphate, however, is much more pronounced. The best result obtained with the former was only 6.34 per cent of ester. With the latter, yields of 50-60 per cent of ester resulted. (See Tables 3 and 4). These salts, in their hydrated states, contain the same relative amounts of water as the pair, aluminum sulphate and potassium aluminum sulphate. Hence, in this case, we are forced to the conclusion that the presence of potassium sulphate in the molecule increases the promoting activity of the salt.

TABLE 3.

CHROMIUM SULFATE

	Rate				
No.	Temperature	cc. vapors per min.	Acid esterified		
1	175° C.	87	0.49%		
2	250	87	6.34		

TABLE 4.

POTASSIUM CHROMIUM SULPHATE

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No.	Temperature	cc. vapors per min.	Acid esterified
1	$175^{\circ}\mathrm{C}.$	87	6.21%
2	175	87	7.64
3	200	87	16.19
4	250	87	53.82
5	250	87	55.72
6	300	87	48.63
7	350	87	27.52

TABLE 5.

MAGNESIUM SULFATE

No.	Temperature	Rate cc. vapors per min.	Acid esterified
1	175° C.	87	6.31%
2	200	87	9.54
3	225	87	19.07
4	250	87	33.60
5	275	87	47.55
6	300	87	47.80
7	325	87	40.37
8	350	87	33.10

The heptahydrate of magnesium sulphate (Epsom salts) was dehydrated at 200°C. The effect of temperature upon the promoting activity of this anhydrous salt was thoroughly studied. The results are shown in Table 5. The relation between temperature and the extent of esterification is shown in Fig. 1. This curve shows a very decided maximum of approximately 50 per cent of esterification at a temperature near 285°C. This temperature is far above the temperature

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at which the molecule loses all of its water of hydration. The heptahydrate loses six molecules of water at 150° C., and the seventh molecule is removed at 200°C. We should expect the dissociation pressure of the hydrated salt to exceed the partial pressure of water vapor in the furnace at a temperature of 285°C. The results indicate that the action of anhydrous salts in promoting esterification is not entirely due to the withdrawal of water.



Fig. 1.

The effect of anhydrous, fused calcium chloride was also studied very thoroughly with regard to the effect of temperature upon the extent of esterification in its presence. The temperature-esterification curve for this salt shows a minimum as contrasted with the maxima for magnesium sulphate and potassium chormium sulphate. (See Fig. 1). This minimum occurs at 275° C., at which temperature 45 per cent of the acid is converted into ester (Table 6). This result is difficult to interpret after the results with magnesium sulphate and potassium chromium sulphate. The great affinity which fused calcium chloride exhibits for water vapor, however, might serve as a basis for an explanation of its effect upon vapor-phase esterification. Because of its pronounced hygroscopy, this salt gives a very good yield of ester at relatively low temperatures (up to 175°C.). Above 175°C., however, the combining capacity of the salt toward water vapor is naturally decreased, since at these higher temperatures the dissociation pressure of the hydrated salt exceeds the partial pressures of water vapor in the furnace. At approximately 275° C., which marks the minimum on the curve, the purely catalytic activity of the salt begins to manifest itself.

Since this activity increases up to a certain limit with increasing temperature, the amount of acid esterified increases. It is probable that the curve reaches a maximum somewhere near 425° C., and then falls normally as in the case of magnesium sulphate.

Other anhydrous salts were investigated, but limited time prevented a complete survey of all the possibilities in connection with this

TABLE 6.

CALCIUM CHLORIDE

		1000	
No.	Temperature	cc. vapors per min.	Acid esterified
1	$175^{\circ}C.$	386	48.31%
2	175	193	52.81
3	175	97	54.31
4	200	87	54.52
5	225	87	48.12
6	250	193	36.33
7	250	386	32.60
8	250	63	48.58
9*	250	193	49.44
10	275	87	42.87
11	275	87	45.65
12	275	87	45.29
13	300	87	47.98
14	325	87	50.00
15	400	87	58.03
16	425	87	60.02

* 35g. anhydrous salt used.

TABLE 7.

Esterification of Acetic Acid by Different Alcohols with Potassium Chromium Sulfate at $250\,^\circ$ C.

	Rate		
Alcohol	cc. vapors per min.	Acid esterified	
methyl	87	35.84%	
ethyl	87	55.72	
n-butyl	87	6.01	

TABLE 8.

OTHER ANHYDROUS SALTS.

		Rate	
Salt	Temperature	cc. vapors per min.	Acid esterified
Na_2SO_4	$250^{\circ}\mathrm{C}.$	386	1.11%
CH ₃ .COONa	250	386	1.39
$NaPO_3$	250	87	2.19
CdSO_4	250	85	10.78
$ZnSO_4$	250	87	11.24
MnSO ₄	250	87	11.95
${ m ZnCl}_2$	250	87	39.22
$NiSO_4$	250	87	46.12

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reaction. Table 8 shows the highest yields obtained with each of these salts and the conditions under which the yields were obtained. Of these salts nickel sulphate showed the most interesting possibilities and should be further investigated.

Table 7 shows the results of the vapor-phase esterification of acetic acid by three alcohols. These results were obtained at a temperature of 250° C., and in the presence of anhydrous potassium chromium sulphate.

Conclusion

The effects of several anhydrous salts upon the vapor-phase esterification of ethyl alcohol and acetic acid have been studied. It appears that these effects are not due, in every case at least, to the combination of the salt with the water produced by the reaction. No attempt has been made to determine the extent to which esterification might be carried under optimum conditions of temperature, velocity of the vapors, physical state of the salts, etc. The reaction has been studied under conditions which were comparable for each series of experiments attempted.

