ACTIVITY OF DIFFERENT CATALYSTS FOR VAPOUR PHASE ESTERIFICATION.

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INTRODUCTION.

In the course of the work on the systematic investigations of vapour phase equilibria in organic reactions of industrial importance which is being carried on in our laboratory [*cf.* Jatkar and Watson (*This Journal*, 1926, **9A**, 71–109), Gajendragad, Jatkar and Watson (*Ibid.*, 1932, **15A**, 59–70), Gajendragad and Jatkar (*Jour. Ind. Chem. Soc.*, 1935, **12**, 486–93) and Jatkar and Gajendragad (*Jour. Amer. Chem. Soc.*, 1937, **59**, 798)] a very active catalyst was prepared from potassium alum for preparing ether, and was tried for esterification. About 1926, reports of high percentage of esterification obtained with silica gel catalyst in vapour phase, were current, and the alum catalyst was found to be much more active than silica gel. However the limit of esterification observed, was the same as in liquid phase. The fortuitous coincidence of this value with the esterification in the liquid phase has subsequently been proved to be due to the simultaneous establishment of ether equilibria, the preference of esterification being only limited in effect (Jatkar and Gajendragad, *loc. cit.*).

Although the percentage of esterification in the vapour phase at equilibrium is high, the reaction velocity even with alum as the catalyst, is very low. For this reason, it is not possible to employ the vapour phase esterification for commercial work. We have, therefore, studied the comparative activity of different catalysts for vapour phase esterification of acetic acid by ethyl alcohol at 150°, where the thermodynamical equilibrium is more favourable.

HISTORICAL.

Sabatier and Mailhe (*Compt. Rend.*, 1911, **152**, 358 and 494) using *titanium* and *thorium oxides*, showed that the limit of esterification at 280–300° was about 70 per cent. and the reverse reaction also went up to 30 per cent. Mailhe and Godon [*Bull. Soc. Chim.*, 1921, **29**, (4), 101] using *zirconium oxide* as the catalyst, obtained a maximum conversion of 69.5 per cent.

Partrick's *silica gel* has a surface of 2.5×10^8 cm.^{2}/gram. Although it is an excellent adsorbent it possesses no marked catalytic activity. Bancroft suggested that it would be interesting to try this substance with mixed vapours of ethyl alcohol and acetic acid because the esterification takes place to an appreciable extent in the absence of any catalytic agent. Milligan, Chappell and Reid (*Jour. Phys. Chem.*, 1924, **28**, 872) used the above suggestion and obtained 89.4, 84 and 77.5 per cent. conversions at 150°, 200° and 250° respectively.

Frolich, Carpenter and Knox (*Jour. Amer. Chem. Soc.*, 1930, **52**, 1565–70) studied the vapour phase esterification of acetic acid by ethyl alcohol in the presence of *zirconium oxide* catalyst over a temperature range of 250–300°. At 250° the reaction proceeded too slowly for equilibrium to be reached in the flow system employed. Above 300°, there was a tendency for simultaneous dehydration of the alcohol into ethylene. Esterification experiments with equimolecular concentrations of ethyl alcohol and acetic acid gave 87.5 per cent. conversion at 280°, and 88.8 per cent. at 300°.

Tidwell and Reid (*Jour. Amer. Chem. Soc.*, 1931, **53**, 4352–58) studied the vapour phase esterification of ethyl alcohol and acetic acid in the presence of *silica gel*, and obtained 85 per cent. conversion at 150° and 75 per cent. at 300°.

Essex and Clark (*Ibid.*, 1932, **54**, 1290–306) studied the equilibrium constant Ka for the equation Ka = $(a_{\text{ester}} \times a_{\text{water}})$ $(a_{\text{acid}} \times a_{\text{alc.}})$, in which the a's are the activities of the respective compounds in the equilibrium mixture, by approaching equilibrium from both sides in the presence of *silica gel* as a catalyst. The average values of Ka for the temperatures, 150°, 165° and 200° are 33.62, 26.38 and 16.07 respectively.

Dolian and Briscoe (*Proc. Indiana Acad. Sci.*, 1933, **42**, 101–7) found that aluminium sulphate and potassium alum had little effect on the yield of esters in vapour phase esterification equilibria. Jatkar and Gajendragad (*loc. cit.*) showed that the optimum temperature for *silica gel* catalyst is 260°. Below this temperature the reaction is too slow to attain equilibrium and above this temperature side reactions occurred. They also pointed out that potassium alum was far more active than silica gel, but the conversion did not rise above 66%, although the equilibrium value was 77%.

A study of the papers on this subject shows that the esterification equilibria in vapour phase is very much higher than that in the liquid phase, and that the equilibrium conversion is more favourable at lower temperatures, where the activity of silica gel catalyst is very poor. Essex and Clark (*loc. cit.*) got over the low activity of this catalyst, by using 1100 grams of catalyst in a tube 9.5 metres long. Apart from the difficulty of keeping such a large tube at uniform temperature, there is the vexed question of possible shift of the equilibrium by the large mass of the highly absorbent silica, by the slightest change of rate or temperature. Silica gel is thus unsuitable as a catalyst for equilibrium studies at lower temperatures.

As most of the researches given above, deal mainly with the equilibrium studies, it was thought worth while to study the activity of different catalysts for esterification from a technical point of view. In the present paper we have made a comparative study of the activity of different catalysts at 150°, and we have discovered some catalysts which are far more active than silica gel. But it was found that the limiting conversion in most of the experiments, was lower than the theoretical equilibrium value, which was attained only at inconveniently low rates. This peculiar result has been explained by assuming that the catalyst gets saturated with products of reaction, so that it is 'poisoned' when the reaction proceeds to some specific value for each one of the catalyst, indicating the necessity of working at higher temperatures.

EXPERIMENTAL.

The apparatus consisted of a long copper cylinder with a round bottom which served as the container for the thermostatic liquid. Heavy mineral oil was used as the liquid for the bath, in the earlier experiments. As this oil began to form a thick viscous sediment with use, and fumed appreciably at 200°, it was replaced by a mixture of ten parts of cottonseed oil and one part of bees-wax. The liquid in the bath was heated by a coil wound round the cylinder and supplemented by an additional heater dipping in the oil at the bottom. The bath was stirred with a long stirrer and the temperature was maintained ± 1° with the help of a spiral thermo-regulator introduced in the bath.

The catalyst tube was made of pyrex glass 1 cm. diameter and 100 cm. long bent into the form of U. The reaction products were condensed in a tube surrounded by a mixture of ice and salt in a Dewar's flask.

The mixture to be passed over the catalyst, was dropped in, through a dropper connected to a burette with a side tube attached near the top. The level in this burette was kept constant by maintaining the flow of mixture from another burette fitted above this, slightly faster than the rate of the dropper, the excess of the mixture being collected separately.

PREPARATION OF CATALYSTS.

Ferric alum was dried in an oven at 110°. *Sodium-hydrogen-sulphate* was dehydrated at 150° under reduced pressure. *Zirconium-oxide* was prepared by precipitation from zirconium nitrate containing free nitric acid, by sodium silicate solution. The catalyst contained 10% zirconium oxide. *Potassium hydrogen sulphate* was dehydrated at 150° under reduced pressure. *Silica gel*: A sample from the "Silica Gel Corporation" was used first, and gave unsatisfactory results. Hence an active variety of the silica gel was prepared according to the method described by Holmes and Anderson (*Ind. Eng. Chem.*, 1925, 17, 280). 500 c.c. of sodium silicate solution of density 1.375 diluted to 10 litres were treated with 1440 c.c. of 2 N. ferric chloride solution with vigorous stirring. The mixture was allowed to stand for 2 days, and filtered. The wet mass on the filter paper was spread out and dried in air. These were treated with warm hydrochloric acid in order to remove the iron-oxide in the dried gel. The ferric chloride formed was washed out, leaving a hard white gel of hydrated silica which was dried in a current of dry air at 150° for twelve hours.

Active charcoal: A sample from "Sutton and Sutcliffe" was used, after heating in a current of dry air at 200°.

The results obtained with the various catalysts are summarised in the following table and shown in Fig. 1.

Activity of different catalysts.

Temperature 150°

Catalyst	% Conversion at rate c.c./hr.					
	3	5	10	15	20	25
Silica gel .. .	86	79	26	..	..	..
$KHSO_4$	85	80	80	79	78	75
Charcoal	76	76	75	75	73	65
Phosphoric acid ..	75	74	71	73	73	72
Zirconium oxide ..	..	73	54	33	12	..
$NaHSO_4$	43	43	42	40	34	20
Ferric Alum ..	8	8	6	0	..	..

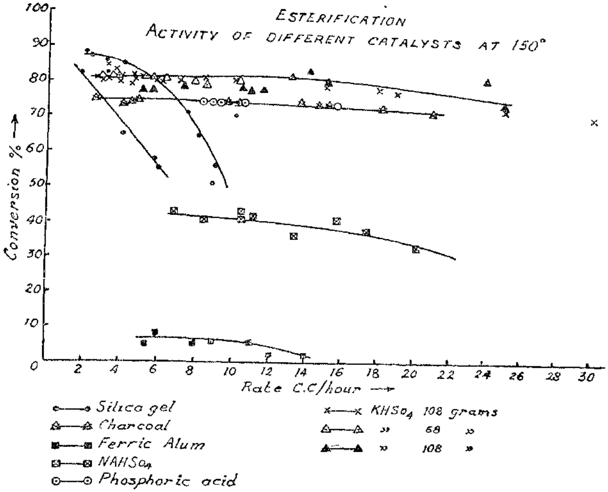

Fig. 1.

DISCUSSION.

With equal rates of flow ferric alum, 10% zirconium oxide, sodium hydrosulphate, silica gel, phosphoric acid, activated carbon and potassium hydrosulphate gave at 150°, 5, 38, 40, 50, 75 and 80% conversions respectively. The conversion with potassium hydrosulphate and activated carbon catalysts did not increase with reduction of rate, beyond 80 and 75%, although the equilibrium conversion is 85% at this temperature. Potassium hydrosulphate is the most active catalyst. The failure of this catalyst as also of activated carbon, in attaining equilibrium even at low rates may be due to the fact that the optimum temperature is higher than 150°. The equilibrium conversion at higher temperatures is, however, less favourable for esterification. Results of the experiments conducted at higher temperatures will be reported in a subsequent communication. At 150°, the reaction does not proceed above 90% of the equilibrium value, owing to the high adsorptive power of the activated carbon. The results with other catalysts can similarly be explained on the assumption of temporary poisoning of the catalyst mass by water vapour formed in the reaction, so that the reaction proceeds until the partial vapour pressure of water formed, is equal to the vapour pressure of complex hydrates of the catalyst mass. Thus, only a portion of the catalyst in initial portions of the tube is effective. This is proved by the fact that in the case of potassium hydrosulphate, similar results were obtained even when the length of the catalyst employed was doubled by joining one more U-tube in series. A quadruple mixture of ethyl acetate, water, ethyl alcohol and water, corresponding to 80% conversion, was also received unchanged, although the equilibrium conversion is higher.

SUMMARY.

Comparative activities of different catalysts for vapour phase esterification equilibria of acetic acid by ethyl alcohol, have been studied at 150°. Potassium hydrosulphate and activated carbon have been tound to be the best.

In the case of both the catalysts, the maximum conversion observed is 94% and 89% of the equilibrium conversion at high space velocities, owing to the temporary poisoning of the catalyst mass by water vapour. Silica gel is the most unsuitable catalyst for esterification in vapour phase at 150°.

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