

CLIII.—*The Inhibition of Esterification by Pyridine.*

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THE velocity of reaction of ethyl alcohol and acetic acid to form ethyl acetate and water is diminished by the addition of minute quantities of pyridine, the diminution being marked even with 3 parts (by volume) of pyridine per million parts of solution. Under the experimental conditions employed, an esterification of 3.1% in 6 hours, in the absence of any negative catalyst, was reduced to about 1.7% by addition of about 70 parts of pyridine per million; but further addition (up to 800 parts per million) only reduced esterification to 1.37%.

These results seem to indicate that the reaction takes place in two ways, probably (*a*) in the body of the liquid, and (*b*) on the surface of the containing vessel. If one assumes that the surface reaction is more likely to be inhibited by small traces of a negative catalyst—an assumption justified by the data given later—the results suggest that esterification takes place in manner (*a*) to the extent of about 1.7%, and in manner (*b*) to the extent of about 1.4%.

The effective surface was increased by the insertion of glass tubes, the total surface area of which was approximately the same as that of the vessel. Esterification, in the absence of pyridine, now reached 4.7%, the increase of 1.6% being ascribed to the increased surface. By addition of about 300 parts of pyridine per million the esterification was once more reduced to 1.7%, the addition of further pyridine having comparatively little effect.

The glass surface possesses, no doubt, a limited number of active points at which reaction takes place. These can be preoccupied by pyridine molecules, even when the concentration of pyridine in the body of the liquid is small. The effect of pyridine on the liquid reaction depends, however, on its absolute concentration, and is therefore small unless the concentration of pyridine is considerable. With increased surface, a greater amount of pyridine is necessary to saturate the active points, but the extent of liquid reaction, after the surface reaction has been eliminated, is approximately the same.

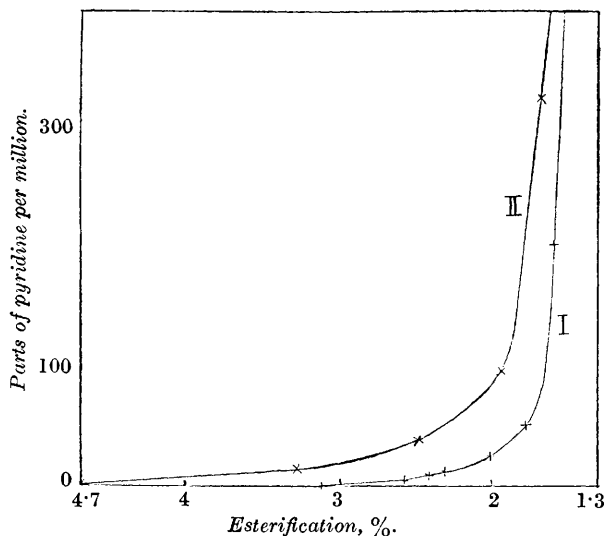
Experiments are being carried out with a view to elucidate the mechanism by which the surface reaction is inhibited by pyridine.

EXPERIMENTAL.

The physical constants of the reagents employed were as follows : Ethyl alcohol, *d* 0.794 (99%); acetic acid, redistilled, b. p. 116—118°; pyridine, dried with potassium hydroxide and distilled, b. p. 114°. Three mols. of ethyl alcohol were used to one mol. of acetic acid.

The duration of each experiment was six hours, during which the temperature could be accurately controlled, and the temperature coefficient was determined. The vessel employed (volume about 110 c.c.; surface area about 112 sq. cm.) was approximately spherical, with a ground glass stopper which fitted closely, but permitted the escape of vapour as the liquid expanded. The vessel was thus always completely, or almost completely, full of liquid. In the following tables the esterification is given as percentages of

acetic acid esterified, and the concentration of pyridine as parts per million parts of solution.



Change of velocity with temperature (no catalyst).

Temperature	31.9°	33.1°	39.6°	41.6°	44.1°	47.7°
Esterification, % ...	1.70	1.98	2.67	2.84	3.16	4.11

A curve was drawn, from which the results of subsequent experiments were corrected for small variations of temperature.

Effect of addition of pyridine (Curve I); temperature 43°.

Conc. of pyridine ...	Nil	3	8	11	24	50	200	800
Esterification, % ...	3.12	2.57	2.41	2.31	2.09	1.78	1.60	1.37

A second series of similar experiments, carried out with different specimens of alcohol and acid, gave a curve almost identical with Curve I, thus :

Conc. of pyridine	Nil	16	40	80	400
Esterification, %	3.12	1.72	1.57	1.57	1.33

Effect of increasing the glass surface (Curve II).

Eight small glass tubes (total surface area about 112 sq. cm.) were inserted, to double the effective surface area of the vessel.

Conc. of pyridine	Nil	13	38	96	320
Esterification, %	4.70	3.28	2.49	1.94	1.69

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