

CCCCXXXV.—*The Inhibition of Chemical Reactions.*  
*Part II. The Mechanism of the Inhibition of*  
*Esterification by Alkaline Substances.*

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THE author has recently demonstrated (this vol., p. 1204) that the reaction of ethyl alcohol and acetic acid takes place in two ways, (*a*) in the body of the liquid, and (*b*) on the surface of the containing glass vessel, and that the reaction of type (*b*) is inhibited by the presence of a trace of pyridine (one part or less per 10,000 parts), whilst the reaction of type (*a*) is only slightly affected, even by the addition of much larger quantities of pyridine.

The following mechanism is suggested. The surface of the vessel contains a number of active areas, at which pyridine molecules are adsorbed. Molecules of alcohol and acid, possessing sufficient energy to react, come into contact on an active area, forming a complex. In the absence of an inhibitor, this complex undergoes re-arrangement and breaks up into water and ethyl acetate. If a molecule of pyridine is present on the glass surface immediately beside the alcohol-acid complex, it attracts the acetic acid, withdraws it from the complex, and returns with it into the solution as pyridine acetate which dissociates, regenerating pyridine and acetic acid.

If we assume that a considerable proportion of the added pyridine is adsorbed on the surface, alcohol-acid complexes which form in the body of the liquid, with sufficient energy to react, are unlikely to meet a pyridine molecule when this base is present in small concentration, and reaction of type (*a*) is therefore scarcely affected.

This hypothesis, according to which the function of pyridine as an inhibitor depends on its nature as a weak base, has been tested by

experiments on the effect of quinoline, piperidine, ammonia, sodium hydroxide, benzyl chloride, *m*-cresol, benzene, chloroform, and hydrogen chloride on the reaction of ethyl alcohol and acetic acid.

Hydrogen chloride acted, of course, as a powerful positive catalyst, and was included as a control. Benzyl chloride, *m*-cresol, benzene, and chloroform either encouraged the reaction slightly or had no pronounced effect. Quinoline, piperidine, ammonia, and sodium hydroxide gave curves of exactly the same type as pyridine. The inhibiting action became more marked with increase of basic strength in passing from quinoline to pyridine and thence to piperidine, which almost completely inhibited reaction of type (b) in a concentration of about 1 in 30,000. The action of ammonia was rather less marked, and that of sodium hydroxide still less marked. This was no doubt due to the fact that these inorganic bases existed in solution as acetates to a greater extent than the organic bases.

The present interpretation, if correct, indicates that sodium and ammonium acetates, present in low concentration in alcoholic acetic acid solution, are highly dissociated on the glass surface, the basic constituent being adsorbed. Dissociation by adsorption has been observed by Bartell and Miller (*J. Amer. Chem. Soc.*, 1923, 45, 1106), Miller (*ibid.*, 1924, 46, 1150) and others.

#### EXPERIMENTAL.

The reaction mixture, which consisted of 9.275 mols. of ethyl alcohol per mol. of acetic acid, was placed in a specific gravity bottle of 25 c.c. capacity, closed by a ground-glass stopper with capillary aperture. This was completely filled and inverted in a wide test-tube containing solution of the same composition. The test-tube was closed by a loosely-fitting cork stopper and placed in an incubator at 43°. Five bottles of similar type were used, and as it had been shown by preliminary experiments that they gave almost identical esterification velocities, it was assumed that they possessed surfaces of equal activity.

Four or five mixtures, of which one was a control and the others contained varying amounts of inhibitor, were placed in the incubator simultaneously, so that slight variations of temperature affected equally all solutions of a series. At the close of an experiment the solutions were removed simultaneously, poured into cold water, and analysed as rapidly as possible.

In the table, esterification during 20 hours at 43° in absence of a catalyst is taken as standard (100), and other results are expressed in terms of this.

Conc. of added substance (mols.  
per 100,000 mols. of reaction  
mixture).....

	Nil.	3·34	8·34	83·4
		Esterification.		
Added substance.				
Quinoline .....	100	68·5	50·5	22·8
Pyridine .....	100	57·0	38·8	20·4
Piperidine .....	100	25·0	19·0	14·0
Ammonia .....	100	28·8	23·3	20·0
Sodium hydroxide .....	100	43·1	27·0	20·2
Hydrogen chloride .....	100	199	326	749
Benzyl chloride .....	100	107·9	115	137·5
<i>m</i> -Cresol .....	100	97·4	104·1	114·2
Benzene .....	100	101·5	102·3	105·4
Chloroform .....	100	92·4	99·6	111·5

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