

Since experiment (b) on page 1805 showed that an oxalic ester is not converted to a different ester by treatment with another alcohol, the change must take place under the influence of the alcoholic solution of potassium hydroxide or, possibly, the potassium alkyl salt first formed acts as a catalyzer for the reaction.

Potassium ethyl oxalate was added to ethyl oxalate dissolved in methyl alcohol and, after a few hours, the dialkyl ester was found to be unchanged diethyl oxalate.

In a solution of potassium hydroxide in methyl alcohol it may be considered that potassium hydroxide and potassium methylate are in equilibrium. Addition of water to this solution would disturb this equilibrium forming more potassium hydroxide. Hence, the addition of water to the potassium hydroxide solution would hasten or retard the formation of dimethyl oxalate depending on whether the potassium hydroxide or the potassium methylate is the determining influence in the reaction.

Table III contains the results of experiments in which the solutions of potassium hydroxide in methyl alcohol contain varying amounts of water. These solutions were made up by adding the necessary weight of water to the methyl alcohol solution of the potassium hydroxide and the methyl alcohol used for dissolving the diethyl oxalate was also diluted with water.

TABLE III.
Diethyl Oxalate 4 cc. and Methyl Alcohol of Varying Strength.

10.9 cc. CH ₃ OH (90%).		11.7 cc. CH ₃ OH (80%).		12.9 cc. CH ₃ OH (70%).		17.5 cc. CH ₃ OH (50%).		11.1 cc. 90% CH ₃ OH; 10% CH ₃ COCH ₃ .	
KOH sol. Me. alc. (90%).	Di- methyl oxalate. %	KOH sol. Me. alc. (80%).	Di- methyl oxalate. %	KOH sol. Me. alc. (70%).	Di- methyl oxalate. %	KOH sol. Me. alc. (50%).	Di- methyl oxalate. %	KOH sol. Me. alc. (90%). Acetone (10%).	Di- methyl oxalate. %
5.2	0.0	10.4	0.0	26.0	0.0	57.2	0.0	5.2	4.0
10.4	0.0	15.6	0.0	31.2	0.0	62.4	3.9	10.4	12.9
15.6	6.5	20.8	6.0	36.4	6.0	67.8	8.75	15.6	22.0
20.8	11.5	26.0	10.9	41.6	11.5	72.8	14.0	20.8	31.1
26.0	17.9	31.2	16.9	46.8	17.0	78.0	20.0	26.0	39.9
31.2	23.5	36.4	22.6	57.2	28.0
..	67.6	38.5

Table III shows that under the influence of a given amount of potassium hydroxide dissolved in methyl alcohol much less dimethyl oxalate is formed when water is present and that the more water is present the less dimethyl oxalate is formed. It must be considered that the potassium methylate rather than the potassium hydroxide is the influence causing the reaction.

The last two columns which record experiments in which the alcohol was diluted with acetone instead of water shows a smaller production of dimethyl oxalate than when pure methyl alcohol was used but a much greater production than when the alcohol was diluted with the corresponding amount of water.