

THE DECOMPOSITION OF DIMETHYL OXALATE BY ACETIC ACID.

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THE difficulty attending the preparation of pure methyl acetate suggested the desirability of investigating the action of acetic acid under various conditions upon dimethyl oxalate, since the latter may be obtained in a state of purity starting from commercial methyl alcohol, even when this product contains ethyl alcohol, whilst methyl acetate cannot be prepared without a preliminary purification of the alcohol through dimethyl oxalate.

It was thought probable that slightly diluted acetic acid would react with dimethyl oxalate to give a sufficiently large yield of methyl acetate to render the method useful in the laboratory as a means of obtaining small quantities of methyl acetate such as are frequently required for physico-chemical work. In practice, the method is even better than was anticipated; with sixty-five to seventy-five per cent. acetic acid, dimethyl oxalate is very completely converted into methyl acetate.

The results of a few initial experiments are given below:

Percentage concentration of acetic acid.	Molecular proportions of water.	Percentage yield of methyl acetate.
100	0	0
95	1	6
80	4	40
77	5	70
70	7	83
65	9	76
58	12	64

Method: One molecular proportion of dimethyl oxalate heated under reflux with five molecular proportions of glacial acetic acid and the appropriate quantity of water for three hours; the products fractionated twice, and the methyl acetate formed analysed by the usual methods. (It

contained not more than eight per cent. of water and less than 0.25 per cent. of acetic acid).

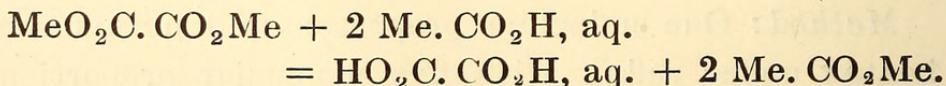
The above figures show that both glacial acetic acid and dilute acetic acid give less methyl acetate than acid of a moderate dilution.

Having established the fact that, with a large excess of acetic acid, dimethyl oxalate may be converted into methyl acetate, it was important to find to what extent a reduction of the excess could be carried. An experiment using one molecular proportion of dimethyl oxalate with two molecular proportions of acetic acid and two molecular proportions of water showed that an excess can be dispensed with entirely, since on this occasion over eighty per cent. of the desired conversion was effected.

It is thus evident that the investigation requires extending in order to determine, among other obvious factors:

- (1) The optimum concentration of acetic acid for the conversion.
- (2) The correlation between this concentration and the existence of definite hydrates of acetic acid.
- (3) The extent to which the method is capable of extension for the preparation of methyl esters generally.

At this stage, it is sufficient to point out that pure acetic acid is practically undissociated, and dilute acetic acid dissociated to a measurable degree, and that a definite hydrate, $\text{C}_2\text{H}_4\text{O}_2, \text{H}_2\text{O}$ is known and corresponds to the 77 per cent. acid giving the best yield of ester. It should further be pointed out that the formation of methyl acetate does not depend on its withdrawal from the system in which it is produced, but is the result of the equilibrium expressed by the equation:



It is therefore hoped that subsequent experiments may throw some light on the mechanism of ester formation generally.



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