Condensation of Acetone with Oxalic Ester

The results of these rate measurements are presented in tables, at the head of each of which are given the initial quantities of the reagents in milligramme-formula-weights, and the volume of the reacting mixture; in cubic centimeter under t the duration of the reaction in hours; under xthe amount of acetonoxalic ester formed in milligrammeformula-weights; and under x per liter the amount of acetonoxalic ester formed per liter expressed in the same units. The values of x were calculated as follows:

$x = \frac{\text{(color reading)} \times \text{(vol. after adding water)}}{\text{(vol. analyzed)} \times 5.4 \times 250}$

In Tables IV-IX to "vol. after adding water" was 40 cc.

The experiments show that the powers of the concentrations to which the rate of condensation is proportional depend upon the degree of dilution by alcohol. In Tables IV–IX (vol. 20 cc) the rate is proportional to the first power of the concentration of the acetone, and to about the 1.2 power of the concentrations of the oxalic ester and of the ethylate. On diluting the same amounts of the three reagents to a volume of 30 cc the powers become 1, 1.75, 1.75 respectively; and on further dilution to 40 cc (Tables X–XVI) and to 50 cc (Tables XVII–XX) while still proportional to the concentration of the acetone, the rate is found to vary with the square of the concentrations of the oxalic ester and of the ethylate respectively.

This difference between the behaviour of acetone on the one hand, and that of the other two reagents on the other, lends support to Claiser's free station of the condensation if it be supposed that the second product assumed by him is largely dissociated in all size solution. To account for the second powers of the concentrations met with at the higher dilutions, however, the addition product must be given twice the molecular weight assumed by Claisen.

Tables IV-IX give the experimental results without any attempt to represent them by a differential equation. For

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