

composed by alcohol; if sodium is present, the alcohol formed by the reaction is at once decomposed, otherwise it accumulates and spoils the yield.

In defending his theory, Claisen thus perhaps unconsciously appeals to the principles of chemical kinetics and equilibrium; but his main argument is based on the analogy between the acetacetic ester synthesis and the condensations discovered by himself and Wislicenus. One explanation must do for all, he says; and that must be the ethylate explanation, for many of these condensations may be carried out successfully in dilute alcoholic solutions of that substance.

The methods of physical chemistry for attacking problems such as this, which deal with the mechanism of reactions, have all grown up since Claisen's first paper was published, and have not hitherto been applied to the elucidation of this particular question. It seemed, therefore, desirable to test the validity of Claisen's assumption that the condensation of esters with esters is identical with that of ketones with esters; and to see whether the results of kinetic measurements can be brought into line with his theory of the synthesis.

The reaction between ethyl oxalate and ethyl acetate was selected as typical of one group, and that between ethyl oxalate and acetone of the other. The present paper contains the results of my measurements on the rate of the latter, while Mr. H. C. Cooke is engaged with a study of the former reaction; the condensation of acetophenone with acetic ester is also being studied in this laboratory. It is proposed to publish the results of these investigations as they are obtained, and to postpone theoretical discussion until the material has been collected.

In investigations of this kind it is necessary to be provided with some means of stopping the reaction at will, and of determining the amount of change that has taken place. In the present case, the first end was attained by neutralizing the sodium ethylate, and the second by determining the depth of color produced by the addition of a solution of ferric chloride.