TRANSESTERIFICATION OF ETHYL ACETATE AND BUTYL BUTYRATE IN THE PRESENCE OF SULFURIC ACID

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A large number of papers has been devoted to a study of the reaction mechanism of esters [1]. At the same time, kinetic data on the transesterification of the low-molecular esters are absent in the literature, with the exception of [2, 3]. In the present paper we studied the transesterification rate of ethyl acetate (EA) and butyl butyrate (BB) in the presence of H₂SO₄. Based on the chromatographic analysis data, equal amounts of ethyl butyrate (EB) and butyl acetate (BA) were formed in all of the experiments. As a result, the general equation of the reaction has the form:

\[
\text{CH}_3\text{COOC}_2\text{H}_5 + \text{C}_4\text{H}_9\text{COOC}_2\text{H}_5 \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3\text{COOC}_4\text{H}_9 + \text{C}_2\text{H}_5\text{COOC}_2\text{H}_5
\]

Typical kinetic curves are given in Fig. 1. The reaction proceeds without an induction period and without autocatalysis. The kinetic curves are described by the first order equation

\[
-\frac{dx}{dt} = k (x_0 - 2x)
\]

where \(x_0 = [\text{EA}]_0 = [\text{BB}]_0\), and \(x = [\text{EB}] = [\text{BA}]\). A linearization of the kinetic curve in coordinates, corresponding to Eq. (1), is shown in Fig. 2. As can be seen from Fig. 3, the initial rate increases linearly with increase in the acid concentration. The initial rates as functions of the EA and BB concentrations are shown in Fig. 4. The reaction rate increases linearly with increase in the BB concentration. Formally the rate decreases with increase in the EA concentration (see Fig. 4, 2). Since this function was obtained in bulk and the BB and EA concentrations were related to each other, it is natural to assume that the reaction rate is independent of the EA concentration.

The temperature dependence of the initial reaction rate is shown in Fig. 5. The activation energy, calculated from this data, is \(\sim 13\) kcal/mole. Employing the NMR method it was established that the H₂SO₄
concentration remains practically constant during the course of reaction. The prior holding of the H₂SO₄ with one of the esters leads to the same values of the rates as in the experiments with simultaneous addition. Experiments were also run in which water and CH₃COOH were added. These additions in amounts, commensurate with the H₂SO₄ concentration, failed to affect the reaction rate.

According to the modern concepts regarding the mechanism of the reaction for the hydrolysis and formation of esters [4], the latter when reacted with acids form equilibrium protonated forms, which were detected in [5] by the NMR method at low temperature in liquid SO₂

\[
\begin{align*}
\text{H₂SO₄} + \text{C₃H₇CO₂H} & \rightarrow \text{C₃H₇COHSO₄} \\
\text{H₂SO₄} + \text{C₄H₉CO₂H} & \rightarrow \text{C₄H₉COHSO₄}
\end{align*}
\]

However, the kinetic rules obtained by us cannot be explained by a simple bimolecular reaction of one ester with products of type (I) and (II), which are formed from the second ester, or with other ions, which are found in equilibrium with (I) and (II), since here the reaction rate proves to be proportional to the concentrations of both reactants. The first order in BB and the zero order in EA can be explained if the steady-state mechanism is postulated for the formation of the active centers, in which the limiting step is the decomposition of the protonated BB form (reaction (b))

\[
\begin{align*}
\text{C₃H₇CO₂H} + \text{H₂SO₄} & \rightarrow \text{C₃H₇COHSO₄} \\
\text{C₄H₉CO₂H} + \text{H₂SO₄} & \rightarrow \text{C₄H₉COHSO₄}
\end{align*}
\]

If the steady state in active centers is taken into account the initial reaction rate is equal to:

\[
W_0 = - \frac{d [\text{BB}]}{dt} = - \frac{d [\text{EA}]}{dt} = \frac{d [\text{EB}]}{dt} = \frac{d [\text{BA}]}{dt} = k_2 \text{ (III).}
\]