MECHANISM OF THE CARBONYLATION OF METHANOL TO METHYL FORMATE O. A. Tagaev, M. D. Gashchuk, UDC 541.124:541.127:542.91:547.261:546.262.3-31 Yu. A. Pazderskii, and I. I. Moiseev

We studied the kinetics of the formation of methyl formate (MF) in the carbonylation of methanol in the presence of strong bases in order to clarify the mechanism of this reaction. The reaction rate satisfies the following equation at $60-110^{\circ}$ C and 10-40 atm in 0.1-0.4 M CH₃ONa:

$W = \vec{k}$ [CH₃ONa][CO][CH₃OH] $-\vec{k}$ [CH₃ONa][HCOOCH₃]

The fact that the rate of formation of MF is proportional to the methanol concentration indicates that CH_3OH takes part in the nucleophilic attack of CH_3O^- on CO. However, when CH_3OD is substituted for CH_3OH (98% enrichment by D) the reaction rate is unchanged within the limits of experimental error, indicating that the O-H bond of the methanol is not broken in the transition state. Apparently, the methanol molecule that takes part in the slow step of the reaction solvates only the carbanion that is formed, by an H-bond with the unshared sp² orbital pair that appears, stabilizing the carbanion and lowering the energy of the reaction's transition state:

$$CH_{3}O^{-} + CO \xrightarrow{CH_{3}OH} \begin{bmatrix} O \\ CH_{3}O^{\delta} - \dots C^{\delta} - \dots H - OCH_{3} \end{bmatrix}^{\#} \xrightarrow{O} CH_{3}O - C^{-} \dots H - OCH_{3}$$

In the transition state, the negative charge on the C atom of CO may not be high enough for the carbanion to accept the H^+ and the H^+ is transferred at the next step:

$$\begin{array}{c} O \\ CH_8O - C^- \cdots H - OCH_3 \xrightarrow{fast} CH_3O - C^- H + OCH_3 \end{array}$$

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