The kinetics of epoxidation of 2-methyl-2-pentene with cumene hydroperoxide catalyzed by MoO$_2$(acac)$_2$ has been studied in the temperature range of 35-65 °C. The observed kinetic behavior is consistent with the formation of a hydroperoxide-catalyst complex and a simple competitive inhibition step, involving the formation of an inactive epoxide-catalyst complex. The reaction parameters have been calculated.

Lower alkene oxides are raw materials and semi-finished products for the synthesis of many important products such as polyurethanes, polyethers, alkanolamines, surface-active agents and others [1, 2]. Epoxidation of 2-methyl-2-pentene creates interesting possibilities for the synthesis of a number of oxy derivatives and especially ethyl isopropyl ketone, which is a starting material for the production of β-damascenon and other fine chemicals [3].

EXPERIMENTAL

Chemicals: 2-Methyl-2-pentene (Aldrich, 98 mol% purity) was distilled under nitrogen before use. Cumene hydroperoxide, concentration >98%, was purified by precipitation of the sodium salt. Cumene (Petrochemical Works, Burgas), concentration >99% was used without further treatment. Dioxomolybdenum(VI) acetyl-
acetonate, MoO$_2$(acac)$_2$ and triphenylphosphine were purified according to [4].

Kinetic procedure: The kinetic runs were made in a thermostated glass batch reactor (75 ml) fitted with a reflux condenser, calibrated thermometer and a rubber septum. Cumene (50 mL) was used as solvent. The concentrations of 2-methyl-2-pentene were between 0.46 and 1.2 M, the hydroperoxide concentrations were between 0.04 and 0.1 M and the concentrations of MoO$_2$(acac)$_2$ were between $0.54 \times 10^{-3}$ and $2.3 \times 10^{-3}$ M. When the well-stirred solution of cumene, 2-methyl-2-pentene and the hydroperoxide was heated to the reaction temperature, the catalyst dissolved in a small amount of cumene was introduced with a syringe and needle through the septum. Temperature was constant to within better than 0.1 °C during a given kinetic run.

Analyses: Cumene hydroperoxide was determined by iodometric titration. Epoxide content in the reaction mixture was determined as follows. Samples of 2 mL were withdrawn with a syringe, the reaction was quenched by using 1.2 eq. Ph$_3$P/eq. of hydroperoxide and after being weighed, a known amount of cyclohexane was added as internal standard. Then 0.1 μL of the resulting mixture was analyzed gas chromatographically. Analyses were carried out on a Sigma 2000 instrument (Perkin-Elmer Corp. Norwalk, CT, USA).

RESULTS AND DISCUSSION

Kinetic studies of the reaction

\[
\begin{align*}
\text{Ph - C - OOH + Me - C = CHEt + Me - C - CHEt + Ph - C - OH} \\
\text{Me} & \quad \text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} & \quad \text{Me} \\
A & \quad Y & \quad B & \quad Z
\end{align*}
\]

were made over a temperature range of 35-65 °C. Because of the autoinhibitory nature of the reaction, all kinetic parameters were calculated from the initial rates (extrapolated values),