From relative rates of acetone formation in the azomethane sensitized decom-
position of methyl ethyl ketone at 290 °C, log_{10} (k/cm^3mol^{-1}s^{-1}) = 5.3 ± 0.4
for the methyl radical addition to methyl ethyl ketone has been determined.

Из относительных скоростей образования ацетона при разложении метилицетилкетона
при 290 °C, сенсибилизированным азометаном, была определена константа ско-
рости присоединения метиленового радикала к метилицетилкетону.
lg_{10} k (cm^3 моль^{-1} сек^{-1}) = 5,3 ± 0,4.

INTRODUCTION

Contrary to addition to C-C double bonds, kinetic data on addition to C-O double
bonds are almost nonexistent. Because of the lower reactivity of the C-O double
bond in ketones, such reactions occur to a measurable extent, only at higher tem-
peratures, where the alkoxy radicals formed decompose immediately:

\[ {\cdot R_1 + R_2 \text{COR} \rightarrow R_1 \text{COR} + \cdot R_2} \]

In some cases it is possible to estimate the ratio of rate constants of the three com-
peting decomposition paths. Then from analytical results on the radical displacement
products \( R_1\text{COR}_2 \) or \( R_1\text{COR}_3 \), kinetic data on the addition step can be derived. In this manner Arrhenius parameters for the methyl radical addition to biacetyl and acetone have been determined /1, 2/.

Data on alkyl radical addition to carbonyl compounds are of interest in connection with photochemical smog modelling /3/.

We have extended our investigations to the addition of methyl radicals to methyl ethyl ketone (MEK) with the thermal decomposition of azomethane (AM) as a methyl radical source:

\[
\begin{align*}
\cdot \text{CH}_3 + \text{CH}_3\text{COCH}_2\text{CH}_3 & \rightarrow \text{CH}_3\cdot - \text{CH}_2\text{CH}_3 + \text{CH}_3\text{COCH}_3 + \cdot \text{C}_2\text{H}_5 \quad (1)
\end{align*}
\]

From the paper of Batt et al. /4/, and earlier experimental evidence, it follows that the tert-amyloxy radical almost exclusively decomposes according to reaction (1') at 150 °C. Also, taking into account the activation energy difference \( E_1 - E_1' \) reported /4/, reaction (-1) contributes only about 5% to the decomposition of the tert-amyloxy radical around 300 °C. Kinetic data on acetone (A) formation in the sequence (1, 1') should therefore be a good approximation for addition step (1).

As a reference reaction, methane formation was used, which occurs in two elementary reactions at the initial stages of the experiments.

\[
\begin{align*}
\cdot \text{CH}_3 + \text{CH}_3\text{COCH}_2\text{CH}_3 & \rightarrow \text{CH}_4 + \cdot \text{C}_4\text{H}_7\text{O} \quad (2)
\end{align*}
\]

\[
\begin{align*}
\cdot \text{CH}_3 + \text{CH}_3\text{NNCH}_3 & \rightarrow \text{CH}_4 + \cdot \text{CH}_2\text{NNCH}_3 \quad (3)
\end{align*}
\]

It follows that

\[
\frac{[\text{CH}_4]}{[A]} = r_{\text{CH}_4}/r_A = k_2/k_1 + (k_3/k_1)[\text{AM}]/[\text{MEK}] \quad (4)
\]

for low degrees of conversion.