METHYL RADICAL ADDITION TO METHYL ETHYL KETONE

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

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 temperatures, 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 competing decomposition paths. Then from analytical results on the radical displacement...
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products R1 COR2 or R1 COR3, 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:

\[
\begin{align*}
\cdot CH_3 + CH_3 COCH_2 CH_3 & \rightarrow CH_3 \cdot + CH_2 CH_3 \rightarrow CH_3 COCH_3 + \cdot C_2 H_5 \quad (1)
\end{align*}
\]

From the paper of Batt et al. /4/, and earlier experimental evidence, it follows that the tert-amylloxy 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-amylloxy 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.

\[
\begin{align*}
\cdot CH_3 + CH_3 COCH_2 CH_3 & \rightarrow CH_4 + \cdot C_4 H_7 O \quad (2)
\end{align*}
\]

\[
\begin{align*}
\cdot CH_3 + CH_3 NNCH_3 & \rightarrow CH_4 + \cdot CH_2 NNCH_3 \quad (3)
\end{align*}
\]

It follows that

\[
\frac{[CH_4]}{[A]} = \frac{r_{CH_4}}{r_A} = \frac{k_2}{k_1} + \frac{k_3}{k_1} \frac{[AM]}{[MEK]} \quad (4)
\]

for low degrees of conversion.

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