The oxidation of α-terpinene by molecular oxygen is shown to occur by a radical chain mechanism involving hydroperoxy radicals. The principal molecular reaction products are \( \text{H}_2\text{O}_2 \) and 1-methyl-4-isopropylbenzene.

The rate constants for chain propagation and chain breaking measured at 35-70°C are (liter/mol-s) \( \lg k_3 = 7.10 - \frac{(6700 \pm 400)}{4.57T} \) and \( \lg k_5 = 9.80 - \frac{(2700 \pm 300)}{4.57T} \) respectively.

Terpinenes are unique among the components of volatile oils which are solvents for paints and lacquers [1]. To establish the mechanism of antioxidant stabilization of paints and resins and the role of terpinenes it is very important to know the composition of the molecular products, the mechanism and elementary steps in the oxidation of terpinenes [2, 3].

In the present work we have for the first time investigated the mechanism of the oxidation of α-terpinene (RH) by molecular oxygen at 35-70°C.

The rate of oxidation of RH was measured by the absorption of oxygen volumetrically [3] and independently by the accumulation of peroxides, measured iodometrically [3]. Azo-bis-isobutyronitrile was used as initiator for the oxidation of RH [2]. The substrate was purified from possible inhibitors and peroxides by passing three times through a column of activated alumina in an atmosphere of argon [4] with subsequent vacuum distillation (50°C). The molecular oxidation products, \( \text{H}_2\text{O}_2 \) and 1-methyl-4-isopropylbenzene, were determined by selective decomposition of the reaction mixture with \( \text{Penicillium vitale} \) catalase [5] coupled with iodometric analysis and GLC [2] respectively.

The rate of initiation of RH oxidation (\( W \)) at \( P_{\text{O}_2} = 0.19-0.98 \) MPa (Fig. 1, 2) is defined by the empirical equation

\[
W = \text{const}[\text{O}_2]^n[\text{RH}]^{1/2},
\]

where \( W_i \) is the rate of chain initiation for the oxidation of RH. Accumulation of peroxides in the autooxidation regime is described by kinetic curves which are typical for autocatalytic reactions (Fig. 2). Consequently the results observed indicate that RH is oxidized by a radical chain mechanism with biradical chain breaking [2]. The basic products from RH oxidation at a conversion of \( \leq 0.1 \) mol/liter are \( \text{H}_2\text{O}_2 \) and 1-methyl-4-isopropylbenzene. For example, \((2.1 \pm 0.1) \times 10^{-2} \) mol/liter \( \text{O}_2 \) reacted at 45°C in 40 min with \( W_i = 6.4 \times 10^{-8} \) mol/liter-s and \((1.8 \pm 0.1) \times 10^{-2} \) mol/liter\(^3 \) \( \text{H}_2\text{O}_2 \) and \((1.7 \pm 0.1) \times 10^{-2} \) mol/liter 1-methyl-4-isopropylbenzene were formed. The formation of unidentified oxidation products (\( \sim 3 \times 10^{-3} \) mol/liter), e.g., epoxides and polyperoxides of α-terpinene [2], is not excluded.

Consequently the hydroperoxy radical HOO\(^*\) is responsible for chain prolongation and chain rupture. This is demonstrated unambiguously by formation at 50°C of the recombination product 2,6-di-tertbutyl-4-methyl-4-hydroperoxycyclohexadien-2,5-one in reaction (2) which is normally used as an indicator for the participation of HOO\(^*\) radicals in oxidations inhibited by 2,6-di-tertbutyl-4-methylphenol [6]:
These results indicate that chain prolongation and chain rupture in α-terpinene oxidation occur according to the following scheme:

\[
\begin{align*}
(\text{CH}_3)_2\text{CH} & \quad \text{CH}_3 + \text{HOO}' \quad \rightarrow \quad (\text{CH}_3)_2\text{CH} & \quad \text{CH}_3 + \text{H}_2\text{O}_2 & \quad (3) \\
(\text{CH}_3)_2\text{CH} & \quad \text{CH}_3 + 2\text{O}_2 \quad \rightarrow \quad (\text{CH}_3)_2\text{CH} & \quad \text{CH}_3 + 2\text{HOO}' & \quad (4) \\
\text{HOO}' + \text{HOO}' & \quad \rightarrow \quad \text{H}_2\text{O}_2 + \text{O}_2
\end{align*}
\]

The kinetic equation (6), which was obtained taking equations (3) to (5) into account, agrees with the empirical equation (1):

\[
W = \left(\frac{k_3}{k_5^{1/2}}\right)[\text{RH}]W_i^{1/2}.
\]

The ratio \(k_3/k_5^{1/2}\) was obtained from the dependence of \(W\) on \(W_i^{1/2}\) (Table 1).

The rate constant for chain rupture \(k_5\) was obtained from the oxidation of RH inhibited by 2,4,6-tritertbutylphenol according to [7] (Table 1).

The values of \(k_5\) obey the Arrhenius equation over the temperature range studied:

\[
\log k_5 = 9.80 - \frac{2700 \pm 300}{4.57T}.
\]

The value of \(k_5\) at 50°C is similar to those we have obtained for the oxidation of 1,3-dihydrobenzene \((k_5 = 1.0 \pm 0.2) \times 10^5\) and 9,10-dihydroanthracene \((k_5 = 0.8 \pm 0.1) \times 10^8\) liter/mol·s, in both of which the oxidation chain carrier is also the hydroperoxy radical [3].

The value of \(k_3\) was obtained from the values of \(k_3/k_5^{1/2}\) and \(k_5\). This rate constant obeys the normal Arrhenius equation:

\[
\log k_3 = 7.10 - \frac{6700 \pm 400}{4.57T}.
\]