From the expression for the rate of induced decomposition it follows that \( W \approx W_1 k_2/k_6 \) with the activation energy for decomposition given by \( E = E_1 + E_2 - E_6 \). Drawing on the reported [6] value of the \( E_2 - E_6 \) difference, namely 5 kcal/mole (22 kJ/mole), one finds that \( E = E_1 + 22 \text{ kJ/mole} \). On this basis, the difference in the activation energies for decomposition and radical formation would be \( E - E_1 \approx 18.45 \text{ kJ/mole} \), which is close to 22 kJ/mole. The conclusion then is that the CrSt\(_3\)-catalyzed decomposition of TBHP follows an induced free-radical chain mechanism. It would be natural to assume that radical formation proceeds through a Haber-Weiss mechanism, though further work will be needed to determine the valence state of the chromium involved in the decomposition process.

CONCLUSIONS

1. Under the action of chromium stearate, free radicals of tert-butyl hydroperoxide are formed through a bimolecular reaction in chlorobenzene solution.

2. Although the overall breakdown of the hydroperoxide can be described by a second-order equation, the reaction is a complex radical-initiated chain process.

LITERATURE CITED


THE OXIDATION OF AMINES BY MOLECULAR OXYGEN.

9. THE LIQUID-PHASE OXIDATION OF DIMETHYLANILINE

G. Sh. Bakhturidze, A. L. Aleksandrov, and I. L. Edilashvili

The ability of inhibitor (InH) molecules to repeatedly break amine oxidation chains is due to the fact that the \( \alpha \)-aminoperoxide radical (ROO\(^{\cdot} \)) not only oxidizes InH to In\(^{\cdot} \) but also reduces In\(^{\cdot} \) to InH in the chain rupture process [1,2]

\[
\text{ROO}^{\cdot} + \text{InH} \rightarrow \text{ROOH} + \text{In}^{\cdot}
\]

\[
\begin{align*}
\text{CH} &- \text{CH(OO')}\text{N} + \text{In}^{\cdot} \rightarrow \text{InH} + \text{C} = \text{CHN} + \text{O}_2 \\
\text{(a)}
\end{align*}
\]

\[
\begin{align*}
\text{C(OO')}\text{NH} + \text{In}^{\cdot} \rightarrow \text{InH} + \text{C} = \text{N} + \text{O}_2 \\
\text{(b)}
\end{align*}
\]

It has been suggested that ROO\(^{\cdot} \) radical reducing activity is limited to radicals with \( \beta \)-CH [1] or NH [2] bonding [reactions (a) and (b)]. We have tested this point by studying the oxidation of dimethylaniline (DMA), a compound whose molecule shows neither of these bonding types.

EXPERIMENTAL

The DMA used here had been purified by the method of [3] and stored in Ar. It was passed through freshly activated Al\(_2\)O\(_3\) prior to use. The rate of oxidation was obtained from manometric measurements of the \( \text{O}_2 \) uptake and from iodometric determination of the build-up of peroxides in the system. Azoisobutyronitrile (AIBN) served as the initiator. Determined by the use of catalase [3,4], the \( \text{H}_2\text{O}_2 \) content of the oxidate proved to be 24 ± 2%.
DISCUSSION OF RESULTS

The initiated oxidation of DMA proceeded readily, even at 30°C, the length of the oxidation chain, ν, being something in excess of 100. Over the range of oxygen pressures (P0₂) from 0.21 to 1.0 atm, the rate of oxidation of the freshly purified amine was almost independent of the O₂ pressure: Wair/W0₂ ≥ 0.9. Up to 0.2% oxidation, the amount of O₂ consumed was equivalent to the amount of titrated peroxides, with W₀ ∝ [DMA][AIBN]₁/₂ (Fig. 1). Auto-inhibition through the buildup of inhibiting products was observed at higher degrees of oxidation. In its initial stages where this effect could be neglected, the oxidation of the amine was described by the classical reaction scheme [6]

\[
\begin{align*}
\text{ABN} & \rightarrow \text{R}^*\{\text{C}_6\text{H}_5\text{N(CH₃)CH₂}\} & \text{(1)} \\
\text{R}^* + \text{O}_2 & \rightarrow \text{ROO}^* & \text{(1)} \\
\text{ROO}^* + \text{RH} & \rightarrow \text{ROOH} + \text{R}^* & \text{(2)} \\
2\text{ROO}^* & \rightarrow \text{Molecular products} & \text{(6)} \\
\end{align*}
\]

At P0₂ = 1 atm, \( W_i = k_i[AIBN] \approx k_6[\text{ROO}^*]^2 \) and

\[
W_0 = k_3k_6[\text{RH}][\text{ABN}] \frac{[\text{ROO}^*]^2}{k_1[\text{O}_2]} \quad (I)
\]

Measured under standard conditions, the oxidation rate was 20-30% lower and closely dependent on P0₂, in stored DMA, the aminoalkyl radicals, rather than the peroxide radicals, being preferentially destroyed on the inhibiting products. It is not clear as to which of the system components it is that functions as the alkyl radical acceptor. The peroxide radicals can interact with the N-methylaniline formed in the DMA oxidation (see below). The effect of the inhibiting products could be explained through the following hypothetical reaction scheme:

\[
\begin{align*}
\text{ROOH} & \rightarrow X(XH) & \text{(3)} \\
\text{R}^* + X & \rightarrow \text{RX}^* & \text{(RROO , R) \text{ Linear chain rupture}} \\
\text{ROO}^* + \text{HX} & \rightarrow X^* & \text{(4)}
\end{align*}
\]

For reaction according to this scheme one has (\( ν > 10^2, [R^*] = k_2[\text{RH}][\text{ROO}^*]/k_1[\text{O}_2] \))

\[
W_i = \left(2k_3[X]k_4[\text{RH}]k_3\gamma P_{0₂} + 2k_4[\text{HX}]\right)[\text{ROO}^*] + k_4[\text{ROO}^*]^P
\]

\[
\frac{1}{W} - \frac{1}{W_0} = \frac{2k_4[\text{HX}]}{k_2[\text{RH}]W_i} + \frac{2k_3[X]}{k_1\gamma W_i} \cdot \frac{1}{P_{0₂}} \quad (II)
\]

The oxidation products were analyzed in a Khrom-4 system (3 m × 3 mm column, 3% KOH and 20% PEG-4000 on Chromosorb W, 25-35 mesh). The value of t, the mean lifetime of the ROO' radical, was determined by intermittent illumination, following the method of [5].