AMINE OXIDATION BY MOLECULAR OXYGEN
5. LIQUID-PHASE OXIDATION OF BENZYLAMINE

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Inhibitors (InH) for aliphatic amine oxidation are regenerated in the course of the oxidation process [1-4], thus becoming available for repeated chain-rupture attack. Regeneration in the primary and secondary amines is assured by participation of the NH peroxide radical bonds in the chain-rupture process [1-3],

\[
\text{C(OO')NH} + \text{In}' \rightarrow \text{InH} \rightarrow \text{C=N} + O_2
\]

The tertiary amines contain no NH bonds, InH regeneration there being through \(\beta\)-CH bond chain rupture of RO₂⁺ [4]

\[
\text{CH} - \text{CH(OO')N} + \text{In}' \rightarrow \text{InH} \rightarrow \text{C=CHN} + O_2
\]

It is not clear whether NH bonds are actually necessary for InH regeneration since the primary and secondary amines which have been studied so far contained not only these but \(\beta\)-CH bonds as well.

By studying the oxidation of benzylamine (BA), a compound whose molecules are free of \(\beta\)-CH bonds, the present work aimed at elucidating the role of NH bonds in antioxidant regeneration.

EXPERIMENTAL

Benzylamine prepared according to the methods of [1] was further purified by passage through activated Al₂O₃ with subsequent vacuum distillation at 60°C. The rate of oxidation was determined either by volumetric measurement of the O₂ uptake, or by iodometric titration of the hydroperoxide in the system. Flash photolysis by the method of [5] was used to determine the mean lifetime of the RO₂⁺ amine peroxide radicals. The Mn(III) concentration was determined by spectrophotometric measurements at 400 nm. At concentrations in the interval from \(1 \cdot 10^{-4}\) to \(30 \cdot 10^{-4}\) mole/liter, the 300-600 nm region of the spectrum of Mn(CH₃COO)₃ in BA solution proved to be identical with the spectrum of a solution of Mn(CH₃COO)₃ in BA which had been oxidized by BA peroxide radicals, the indication being that the ligand environment had essentially no affect on the extinction coefficient. This made it possible to measure the Mn(III) concentration at fixed wavelength. The consumption of \(\alpha\)-naphthol was determined colorimetrically, using p-sulfophenylazobenzene ions to nitrogen-bond the compound in alkaline solution. ESR methods were used to determine the rate of consumption of the stable nitroxyl radicals \((\tilde{N}O)\). The rate constant for azodilisobutyronitrile (AIBN) initiation in BA \((k_i)\) was determined from the rate of
TABLE 1. Temperature Variation of $k_2/k_6^{1/2}$ and $k_i$ in Benzylamine

<table>
<thead>
<tr>
<th>$T$, °C</th>
<th>$k_2/k_6^{1/2}$, liter/mol·sec</th>
<th>$k_i$, 10^4, sec^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>4.6</td>
<td>2.4</td>
</tr>
<tr>
<td>65</td>
<td>3.8</td>
<td>18.0</td>
</tr>
<tr>
<td>70</td>
<td>4.5</td>
<td>42.6</td>
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<td>75</td>
<td>5.4</td>
<td>84.1</td>
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<tr>
<td>80</td>
<td>7.0</td>
<td>173</td>
</tr>
<tr>
<td>85</td>
<td></td>
<td>316</td>
</tr>
</tbody>
</table>

Fig. 1. Kinetics of 2,2,6,6-tetramethyl-4-oxypiperidine-1-oxyl (1) consumption (1), and buildup from the corresponding hydroxylamine (2), in the oxidation of benzylamine at $pO_2 = 0.21$ (a), and 1.0 atm (b). The consumption of $\geq NO^-$ at $pO_2 = 0$ atm (3); $65^\circ C$, $W_i = 8.3 \cdot 10^{-7}$ mole/liter·sec.

Fig. 2. Variation of the rate of benzylamine oxidation with $W_i^{1/2}$ (1), and $[BA]$ (2), in chlorobenzene at 70°C.

consumption of 2,2,6,6-tetramethyl-4-oxo(II-4-oxo)piperidine-1-oxyl, working in an Ar atmosphere and at conditions such that the steric inhibition coefficient $f$ was equal to unity (Fig. 1, curve 3). The value of $k_i$ was not affected by changes in either $[\geq NO^-]$ or $[AIBN]_0$, satisfying the equation

$$\log k_i (c^{-1}) = (16.9 \pm 0.9) - (33.400 \pm 1300) / 4.57 T$$

over the temperature interval from 50 to 85°C (Table 1). The activation energy, ~2.6 kcal/mole, was determined from the temperature variation of the probability of radical passage into volume $\beta = k_i/2k$, $k$ being the rate constant for AIBN breakdown [6]. Values of $f$ for InH and $\geq NO^-$ in BA oxidation were determined by the methods of [1, 3].

DISCUSSION OF RESULTS

Rate Constants for Chain Propagation and Rupture. Calculated from the expression $W_0 \sim [RH]W_i^{1/2}$ (Fig. 2), the rate of initiation of amine oxidation by AIBN proved to be constant under variation of $pO_2$ from 0.2 to 1.0 atm. Working at 80°C with the degree of BA conversion < 0.1%, the $O_2$ uptake was quantitatively equivalent to the hydroperoxide content of the system as determined by titration. The kinetic data indicated that the general scheme of primary and secondary aliphatic amine oxidation [1, 5] must apply in the initial stages of BA oxidation with $[RO_2^-] >> [R^+]$. 