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References


Kinetics of Oxidation of Cyclanols by Thallium Triacetate — Failure of I-Strain Concept

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The reaction between the chain carrying species with acrylonitrile also induced acrylonitrile polymerisation and is catalysed by added Mn(II). The above observations are explained on the basis of a radical mechanism operating in the case of cyclohexanol and involves the formation of Tl(II).

In the title investigation, cyclopentanol, cyclohexanol, cycloheptanol and cyclooctanol were chosen to study the effect of ring size on the rate and stereochemical aspects of Tl(III) oxidation. The reaction between the chain carrying species with acrylonitrile also induced acrylonitrile polymerisation and is catalysed by added Mn(II). The above observations are explained on the basis of a radical mechanism operating in the case of cyclohexanol and involves the formation of Tl(II).

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and Mn(II) are possible. The difference in the overall rate of oxidation of the secondary alcohols would, in such a mechanism, have to be ascribed to the kinetic chain length of the process, in addition to the rates of propagating reactions of the substrate (reaction 2) and the substrate derived radical (reaction 3). Probably the one electron route Ti(III) $\rightarrow$ Ti(I) $\rightarrow$ Ti(I) is more available for the strain-free six-membered ring than for the other cyclanols with the consequent failure of $I$-strain concept.

The reactivity pattern for the oxidation of several secondary alcohols by chromium (VI) in the presence of oxalic acid is discussed.

**CHROMIUM(VI) oxide can oxidise organic substrates by a one-electron process or a two-electron process. These processes involve the intermediate valence states of chromium, viz., Cr(IV) and Cr(V). Reduction of Cr(VI) directly to Cr(III) by a single step three-electron transfer has been reported by Rock and Hasan in the co-oxidation of propan-2-ol and oxalic acid. The cooxidation is several times faster than the oxidation of individual substrates by Cr(VI).**

The isotope effect is markedly decreased when a phenyl group replaces a methyl in propan-2-ol. A comparison of the first and the second columns of Table 1 shows a decreased selectivity of Cr(VI) towards several structurally different secondary alcohols. For example, the variation in $k_{\text{Alcohol}}$ is ten-fold while that in $k_{\text{Experimental}}$ is only two-fold. These observations can be explained by Rock's mechanism for cooxidation. The mechanism (Scheme 1) involves the formation of a termolecular complex containing alcohol, oxalic acid and Cr(VI) and its subsequent decomposition in a slow step.

**Reactivity Patterns in Cooxidations — Cr(VI) Oxide-Oxalic Acid - Secondary Alcohols Systems**

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The reactivity pattern for the cooxidation of several secondary alcohols by chromium (VI) in the presence of oxalic acid is discussed.


**Table 1 — Comparison of Rates of Normal Oxidation and Cooxidation of Secondary Alcohols by Cr(VI)**

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>$k_{\text{Alcohol}}$</th>
<th>$10^4 k_{\text{Exp}}$</th>
<th>$10^4 k_{\text{Exp}}$</th>
<th>$\Sigma k$</th>
<th>$10^4 k_{\text{Exp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenylmethylicarbinol</td>
<td>0.400</td>
<td>0.578</td>
<td>4.00</td>
<td>6.92</td>
<td></td>
</tr>
<tr>
<td>Propan-2-ol</td>
<td>0.165</td>
<td>0.343</td>
<td>3.90</td>
<td>11.4</td>
<td></td>
</tr>
<tr>
<td>Cyclobexanol</td>
<td>0.279</td>
<td>0.457</td>
<td>6.14</td>
<td>13.4</td>
<td></td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>0.015</td>
<td>0.230</td>
<td>3.38</td>
<td>14.7</td>
<td></td>
</tr>
<tr>
<td>Cyclopentanol</td>
<td>0.529</td>
<td>0.707</td>
<td>7.77</td>
<td>11.0</td>
<td></td>
</tr>
<tr>
<td>Cycloheptan</td>
<td>1.35</td>
<td>1.53</td>
<td>9.08</td>
<td>5.94</td>
<td></td>
</tr>
<tr>
<td>Adamantan-2-ol</td>
<td>1.98</td>
<td>2.16</td>
<td>16.0</td>
<td>7.41</td>
<td></td>
</tr>
<tr>
<td>Dicyclohexylcarbinol</td>
<td>0.40</td>
<td>0.58</td>
<td>15.8</td>
<td>6.13</td>
<td></td>
</tr>
<tr>
<td>Fluoren-9-ol</td>
<td>4.23</td>
<td>4.41</td>
<td>12.9</td>
<td>2.93</td>
<td></td>
</tr>
<tr>
<td>Fluoren-9-ol $\alpha$-d</td>
<td>0.856</td>
<td>1.03</td>
<td>5.12</td>
<td>4.95</td>
<td></td>
</tr>
<tr>
<td>2-Nitrofluoren-9-ol</td>
<td>1.48</td>
<td>1.66</td>
<td>5.53</td>
<td>3.33</td>
<td></td>
</tr>
</tbody>
</table>

$\Sigma k = k_{\text{Alcohol}} + k_{\text{Oxalic acid}}$; $(10^4 k_{\text{Oxalic acid}} = 0.178)$

(i) The rate of oxidation of a mixture of alcohol and oxalic acid is always faster than the individual oxidations of either oxalic acid or alcohol by Cr(VI). This is also shown by $k_{\text{Exp}} \Sigma k$ being always greater than unity.

(ii) The rate gain depends on the reactivity of the alcohol employed for the oxidation. For reactive alcohols (benzhydrol) the ratio $k_{\text{Exp}} \Sigma k$ is less than that for a less reactive alcohol (propan-2-ol).

(iii) Even among reactive alcohols, if the reactivity is lowered by an alpha deuterium substitution, the rate benefit increases.

(iv) The ratio $k_{\text{Exp}} \Sigma k$ also depends on the structure of the alcohol. The introduction of a phenyl group for a methyl in propan-2-ol decreases the ratio which is further lowered when a second phenyl is introduced. Generally the rate gain is more for an aliphatic alcohol than for an aromatic one.

(v) The isotope effect is markedly decreased when the oxidation of the alcohol occurs in the presence of oxalic acid.

(vi) A comparison of the first and the second columns of Table 1 shows a decreased selectivity of Cr(VI) towards several structurally different secondary alcohols. For example, between benzhydrol and propan-2-ol, the variation in $k_{\text{Alcohol}}$ is ten-fold while that in $k_{\text{Exp}}$ is only two-fold. These observations can be explained by Rock's mechanism for cooxidation.