STOICHIOMETRY

The stoichiometry of the reactions between ketones under study and quinquevalent vanadium in all absence and in presence of SLS was determined as follows.

The experiments were performed employing in each case on excess of vanadium in order to oxidize the substrate completely. The calculated volume of \( V \) (\( V \)) and sulphuric acid was taken in a conical flask. The requisite volume of ketones was taken in another flask and both were kept in a thermostat on experimental temperature. After attaining the temperature, the two solutions were mixed and the initial concentration of oxidant was estimated at zero time volumetrically procedure given earlier. The concentration of oxidant was determined every day till the constant titre volume was obtained. This shows that the ketones were completely consumed. The procedure was adopted separately for each ketones. The total amount of consumed vanadium (\( V \)) used in oxidation of ketones was calculated and from it the equivalent of \( V \) (\( V \)) consumed per mole ketones was evaluated. The stoichiometric results in absence and presence of surfactant are summarized in (Table-8.1).
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Ketones</th>
<th>[Ketones]</th>
<th>Initial [V(V)] M</th>
<th>Final [V(V)] M</th>
<th>Consumed [V(V)] M</th>
<th>[V(V)] Ketones</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Acetone in absence of SLS</td>
<td>1.0</td>
<td>10.0</td>
<td>8.05</td>
<td>1.95</td>
<td>1.95</td>
</tr>
<tr>
<td>2.</td>
<td>Acetone in presence of SLS</td>
<td>0.5</td>
<td>5.0</td>
<td>4.03</td>
<td>0.97</td>
<td>1.94</td>
</tr>
<tr>
<td>3.</td>
<td>Cyclohexanone in absence of SLS</td>
<td>1.0</td>
<td>10.0</td>
<td>8.11</td>
<td>1.89</td>
<td>1.89</td>
</tr>
<tr>
<td>4.</td>
<td>Cyclohexanone in presence of SLS</td>
<td>0.5</td>
<td>5.0</td>
<td>3.92</td>
<td>1.08</td>
<td>2.16</td>
</tr>
<tr>
<td>5.</td>
<td>Acetophenone in absence of SLS</td>
<td>1.0</td>
<td>10.0</td>
<td>8.08</td>
<td>1.92</td>
<td>1.92</td>
</tr>
<tr>
<td>6.</td>
<td>Acetophenone in presence of SLS</td>
<td>0.5</td>
<td>5.0</td>
<td>3.82</td>
<td>1.18</td>
<td>2.36</td>
</tr>
<tr>
<td>7.</td>
<td>Benzophenone in absence of SLS</td>
<td>1.0</td>
<td>10.0</td>
<td>7.99</td>
<td>2.01</td>
<td>2.01</td>
</tr>
<tr>
<td>8.</td>
<td>Benzophenone in presence of SLS</td>
<td>0.5</td>
<td>5.0</td>
<td>4.11</td>
<td>0.89</td>
<td>1.78</td>
</tr>
<tr>
<td>9.</td>
<td>Ethylmethyl ketone in absence of SLS</td>
<td>1.0</td>
<td>10.0</td>
<td>8.00</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>10.</td>
<td>Ethylmethyl ketone in presence of SLS</td>
<td>0.5</td>
<td>5.0</td>
<td>3.99</td>
<td>1.01</td>
<td>2.02</td>
</tr>
</tbody>
</table>
PRODUCT ANALYSIS

The equivalent concentrations of the reactants were taken in a reaction vessel and the reaction was allowed to completion. The final products of oxidation of ketones by vanadium (V) in aqueous and micellar media formed were identified by the following technique.

CHROMATOGRAPHY

Chromatography is a relatively modern technique for the separation of substances into individual components. It is an extremely valuable method for the separation, isolation, purification and identification of the constituents of a mixture [207]. The mixture is dissolved in the moving phase and passed over a stationary phase which may be a column or a paper strip. The moving phase may be a liquid or a gas [208]. Thin layer chromatography is described as a method for chromatography analysis on thin layer of adsorbents. The technique is rapid and helps in the separation of micrograms of the substances.

In the present study it was found that thin layer chromatography (TLC) was better suited than other form of chromatography. Hence throughout the present work this technique was employed for the separation of various oxidation products of ketones.

Preparation of chromatoplates and choice of adsorbents

The plates were prepared by spreading the slurry of silicagel-G in water by stahl type applicator was maintained at 0.5mm for analytical purposes and 1mm for preparative TLC. The coated plates were activated by keeping them three hours at
50°C. As the activity of the adsorbent is markedly affected by the moisture present, the plates were used after heating at 100°C for few minutes. The *R*<sub>f</sub> value of a substance depends up on the uniformity of the layer, thickness of the layer activation of the plates, solvents mixture used as the developer and size of the chamber in which the chromatogram is developed. Therefore, care was taken to keep the above conditions uniformity the same throughout the course of the study [209].

**Purification of silicagel-G layers**

Silicagel - G contains iron as an impurity which causes a considerable distortion in the chromatograms. Therefore, it becomes essential to purify the adsorbents. Iron free layers have been obtained by giving the coated and air-dried plates. A preliminary development with methanol concentrated HCl (9:1v/v). The iron gets migrated with the solvent front to the upper edge of the plate. The plates are again dried and activated at 110°C. Generally, calcium sulphate originally present as binder dissolves out during the cleaning process. The silica gel purified by this method will be reused to obtain plates with any other suitable binder such as gypsum, starch or agar [210].

**Selection of solvents**

The developed solvent system employed must afford adequate separation of the components of the mixture of oxidation products. Therefore, many solvent systems were tried. The best solvent system thus found was butanol: acetic acid: water (4:1:5). The chambers were well saturated with the developer solvent so as to ensure the equilibrium of atmosphere of the chamber.

**Locating reagents**

Since many compounds which are separated by TLC are colorless, their positions are located with the help of locating reagents. The best locating reagents thus found was iodine. This forms coloured and loosened complexes with a number of compounds. Either iodine is sprayed over the plates after dissolving in an
organic solvent or by keeping in a tank containing iodine vapours. Exposure to iodine vapours is done in between 1-5 minutes.

**Analysis of the oxidation product of ketones**

For product analysis, an aqueous solutions of ketones in oxygen free double distilled water was prepared and to it 1000 ml. of 0.2 M V(V) solution was added of each ketone solutions. The contents were thoroughly mixed and heated on a water bath at 50-60°C. The reaction mixture gradually become dark reddish-green in colour and with time colour deepened. The reaction mixtures were heated for about 2 hours and then were allowed to cool to room temperature. After that, it was filtered of and the brownish black precipitated was washed several times with warm distilled water to ensure removal of vanadium (v) and ketones. Similar efforts were also made to analyze products by making use of surfactants Table-8.2.

**Table – 8.2 Chromatographic Analysis**

<table>
<thead>
<tr>
<th>Reactions Mixtures of Ketones</th>
<th>Layer of Thickness</th>
<th>Rate of Development</th>
<th>Colour of the spot</th>
<th>Relative amount</th>
<th>Standard R&lt;sub&gt;f&lt;/sub&gt; Value</th>
<th>Observed R&lt;sub&gt;f&lt;/sub&gt; Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>0.5mm</td>
<td>15.5cm./70 min.</td>
<td>yellow</td>
<td>Major</td>
<td>0.11</td>
<td>0.13</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>0.5mm</td>
<td>20.5cm./90 min.</td>
<td>white</td>
<td>Major</td>
<td>0.41</td>
<td>0.39</td>
</tr>
<tr>
<td>Acetophenone</td>
<td>0.5mm</td>
<td>15.5cm./60 min.</td>
<td>white</td>
<td>Major</td>
<td>0.92</td>
<td>0.90</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>0.5mm</td>
<td>15.5cm./60 min.</td>
<td>white</td>
<td>Major</td>
<td>0.92</td>
<td>0.90</td>
</tr>
<tr>
<td>Ethylmethyl ketone</td>
<td>0.5mm</td>
<td>25.5cm./50 min.</td>
<td>yellow</td>
<td>Major</td>
<td>0.44</td>
<td>0.43</td>
</tr>
</tbody>
</table>
Better identification was achieved when sodium lauryl sulphate (SLS) is mixed in the reaction mixture. It is notable that the same product was formed in two different media. The observed R<sub>f</sub> value was found to be very close to the standard.

**Test for free radicals:**

The formation of free radicals during the course of the reaction was tested by polymerization of acrylonitrile monomer. About 5 ml. of reaction mixture was taken in a test tube periodically under the experimental condition and 1-2 drops of acrylonitrile (monomer) was added. A white turbidity was observed. The test was repeated by addition of mercuric chloride solution, again the appearance of white turbidity confirms the presence of free radical in each reaction [211].

**Test for carboxylic acid:**

To 1ml. of neutral solution of the test solution, add 1ml. conc. AgNO<sub>3</sub> solution. A white ppt. turning grey on heating shows the positive test for aliphatic carboxylic acid.

To 1ml. of neutral solution of test solution 2-3 drops of FeCl<sub>3</sub> solution was added, a wine red colour showing the positive test for aliphatic carboxylic acid.

1.0 ml. of test solution was heated with 2gm. sodalime in a dry test tube. Benzene vapours evolved, vapours ignited, a smoky flame suggested aromatic carboxylic acid presence in test solution [212-213].

**Test for carbon dioxide:**

Two drops or the test solution was treated with 3 drops of 2 N H<sub>2</sub>SO<sub>4</sub> A drop of solution of sodium carbonate reddened with phenolphthalein drop was decolourised immediately showing the positive test for CO<sub>2</sub> [214].

The rate of evaluation of carbon dioxide was studied under the same conditions as those for carboxylic acid formation.
Spectroscopic Analysis of Product

1. Analysis of the oxidation product of Acetone:

**UV and IR Studies:** The ethanolic solution of the compound was found to absorb at $\lambda_{\text{max}} \approx 200$ to 210 nm with no absorption maxima in visible region suggesting thereby the presence of carboxylic acid group in compound.

<table>
<thead>
<tr>
<th>$\lambda_{\text{max}}$</th>
<th>$\varepsilon_{\text{max}}$</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>204</td>
<td>41</td>
<td>$n \rightarrow \pi^*$</td>
</tr>
</tbody>
</table>

The infrared spectrum of the product indicated the presence of carboxylic acid group.

It may be instructive to remember that a compound which likes acetic acid shows strong absorption band around:[215].

1. 3400 cm$^{-1}$ to 2500 cm$^{-1}$ Broad absorption band with minor peaks characteristic of carboxylic acid dimers (O-H Stretching frequency).

2. 2650 cm$^{-1}$ (O-H Stretching)

3. 1710 cm$^{-1}$ (O=C Stretching frequency).

4. 1230 cm$^{-1}$ C=O stretching frequency.

5. 920 cm$^{-1}$ Broad band, O-H out-of-plane deformation in dimers.

2. Analysis of the oxidation product of cyclohexaone: The compound was found to absorb at below 210 nm (solvent ethanol) and there was no absorption maxima in visible region suggesting there the presence of dicarboxylic group present in compound[216].
1. Broad O-H stretching at 3300-2500 cm⁻¹.

2. C-H stretching at 2950, 2920, 2850 cm⁻¹ (Superimposed upon O-H Stretch.)

3. Normal dimeric carboxylic C = O Stretching at 1715 cm⁻¹

4. C – O - H in plane bending at 1408 cm⁻¹

5. C-O Stretching dimer at 1280 cm⁻¹

6. O-H out of plane bending at 930 cm⁻¹

Bands D and E involve C-O-H interaction

3. Analysis of the oxidation product of Acetophenone:

The compound was found the K-band at 230 nm and the B-band being still clearly visible at 273 nm which prove the presence of aromatic carboxylic group in the product. The various bands of IR spectrum of compound have been characterized in the following manner.

1. Broad O-H stretching at 3300-2500 cm⁻¹.

2. C-H stretching at 2950, 2920, 2850 cm⁻¹ (Superimposed upon O-H Stretch.)

3. Aromatic carboxylic C = O Stretching at 1685 cm⁻¹

4. C – O - H in plane bending at 1408 cm⁻¹

5. C-O Stretching dimer at 1280 cm⁻¹

6. O-H out of plane bending at 930 cm⁻¹
4. Analysis of the oxidation product of Benzophenone:
The compound was found the K-band at 230 nm the B-band being still clearly visible at 273 nm which prove the presence of aromatic carboxylic group in the product [217]. The various bands of IR spectrum of compound have been characterized in the following manner.

1. Broad O-H stretching at 3300-2500 cm⁻¹.
2. C-H stretching at 2950, 2920, 2850 cm⁻¹ (Superimposed upon O-H Stretch.)
3. Aromatic carboxylic C = O Stretching at 1685 cm⁻¹
4. C - O - H in plane bending at 1408 cm⁻¹
5. C-O Stretching dimmer at 1280 cm⁻¹
6. O-H out of plane bending at 930 cm⁻¹

5. Analysis of the oxidation product of Ethyl methyl ketone:

UV and IR Studies: The ethanolic solution of the compound was found to absorb at λmax ≈ 200 to 210 nm with no absorption maxima in visible region suggestion thereby the presence of carboxylic acid group in compound.

<table>
<thead>
<tr>
<th>λmax</th>
<th>εmax</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>204</td>
<td>41</td>
<td>n→π*</td>
</tr>
</tbody>
</table>

The infrared spectrum of the product indicated the presence of carboxylic acid group. It may be instructive to reamer that a compound which likes propionic acid show strong absorption band around:
1. 3400 cm\(^{-1}\) to 2500 cm\(^{-1}\) Broad absorption band with minor peaks characteristic of carboxylic acid dimers (O-H Stretching frequency).

2. 2650 cm\(^{-1}\) (O-H Stretching)

3. 1710 cm\(^{-1}\) (O=C Stretching frequency).

4. 1410 cm\(^{-1}\) CH\(_2\) scissoring frequency, adjacent to –COOH

5. 1230 cm\(^{-1}\) C-O stretching frequency

6. 920 cm\(^{-1}\) Broad band, O-H out-of-plane deformation in dimmers.
Fig.-8.1 I.R. Spectra of oxidation product of Acetone
Fig.-8.2 I.R. Spectra of oxidation product of Cyclohexanone
Fig. 8.3 I.R. Spectra of oxidation product of Acetophenone
Fig.-8.4 I.R. Spectra of oxidation product of Benzophenone
Fig.-8.5 I.R. Spectra of oxidation product of Ethylmethyl ketone