CHAPTER - III

EXPERIMENTAL

Oxidation of acetophenone:

Sodium meta vanadate has been used in acid solutions for the purpose of oxidation. It was of E. Merck quality. Acetophenone and p-chloro acetophenone of analar BDH variety were distilled before use. p-Methoxy and p-nitro acetophenones were recrystallised from absolute alcohol and used. The stock solutions of V(v) were prepared in different acid concentrations and were standardised against ferrous ammonium sulphate solution using N-phenyl anthranilic acid as indicator. Sulphuric acid was of analar BDH variety and perchloric acid was also of 60% analar grade. Analar BDH glacial acetic acid was used to prepare different solvent composition with conductivity water, for preparation of ketone solutions.

Rate measurements were done by mixing equal volumes of V(v) solution and ketone solution, both of known concentration, being brought to the temperature of the thermostat (± 0.1°C). The course of the reaction was followed by withdrawing 5 c.c. of the reaction mixture at definite intervals of time, chilling by ice to check the reaction and then estimating the amount of unchanged oxidant volumetrically by a standard ferrous ammonium sulphate solution, using N-phenyl anthranilic acid (5 drops, 0.066M) as indicator.

In most cases the ketone was kept in excess compared to the concentration of the oxidant. Therefore the
rate constants have been calculated, using the equation

\[ k_r = \frac{2.303}{t} \log \frac{a}{a-x} \]

The values of energy of activation and entropy of activation have been computed from Arrhenius equation (Eqn.1) and Eyring's equation (Eqn.2)

\[ k_r = A e^{-\frac{E}{RT}} \quad \ldots (1) \]

and

\[ k_r = \frac{k_r}{h} e^{-\frac{\Delta S^\ddagger}{R} \cdot \frac{\Delta H^\ddagger}{RT}} \quad \ldots (2) \]

where \( k_r \) = rate constant.

**Stoichiometry and analysis of the product:**

The product analysis was done under kinetic conditions, i.e., at lower [\( \overline{v(v)} \)]. After the reaction the green solution was diluted and extracted several times with benzene. The benzene extract was washed with water to free it from any acid impurity. This was found to contain a NaHCO₃ soluble part, which was characterised to be benzoic acid. The NaHCO₃ insoluble part was found to be unreacted acetophenone.

No stoichiometry could be determined since at lower acetophenone concentration no reaction took place even after a fortnight. So from analogy with Ce(IV) oxidation of acetophenone it has been concluded that two moles of V(v) are absorbed per mole of acetophenone.

**Phenacyl bromide:**

Vanadium(v) solution was prepared by dissolving
sodium meta vanadate in aqueous perchloric acid. Phenacyl bromide and its substituted ones were prepared by bromination of acetophenones. Phenacyl bromide was recrystallised twice from ethyl alcohol and the purity finally checked by m.p. (51°C) and t.l.c. on a silica gel plate. On chromic acid spray only one spot was obtained. The concentration of vanadium(v) was estimated as before.

Stoichiometry was determined as in case of oxidation of acetophenones.

Analysis of the product:

A solution containing excess phenacyl bromide (in glacial acetic acid) and V(v) (in 2.0 M HClO₄) were kept at 50°C for 3 days. The colour of the solution became blue. The solution was then diluted with excess of water, when a reddish brown oil settled down. The whole contents were extracted with benzene and ether repeatedly till the solvent did not extract any further material. To the ether-benzene layer (reddish brown colour), very dilute KOH solution was added. The alkali layer became coloured (reddish brown). So the organic layer was repeatedly extracted with alkali. Finally, it was washed several times with water, HCl and then water. It was then dried over anhydrous MgSO₄ and the ether layer was removed, whence a reddish brown oil was left behind. This oil was found to be a mixture of three components (t.l.c. on a silica gel plate 0.05 mm thickness, developed in benzene and sprayed with chromic acid) with
Rf values 0.5 (phenacyl bromide, bright spot), 0.6 (lower concentration) and a very faint spot at 0.29. The mixture could not be characterised.

The alkali soluble part was acidified with HCl and extracted with ether. On removal of ether, a semi-solid mass containing two different components (white+brown) was obtained. It was treated with hot water. The white component dissolved and reappeared on cooling. It gave effervescence with NaHCO₃ and liberated iodine from KI-KIO₃ solution. So the compound is supposed to be a carboxylic acid. It was found to be benzoic acid. This was found to be a major product (80%).

The brown component did not react with NaHCO₃. This compound gave two spots on a t.l.c. plate (with Rf 0.31 and 0.0).

The individual products have been characterised by I.R. spectra.

Chalkone:

The chalkones have been prepared by the condensation of appropriately substituted acetophenones and benzaldehydes in presence of requisite quantity of sodium hydroxide. Most of the chalkones have been subjected to NMR and IR study to test their purity. The chalkones used for the purpose are: unsubstituted [m.p. 57°C; NMR-complex 12H signal (aromatic); i.r.; 6.02/μ sh (C = O), 6.25μ sh (aromatic), 6.3μ sh (conjugated aromatic),
7.68 μ, sh (C = 0), 10.12 μ, (C = C), p-NO₂ chalkone
\[ \text{m.p. 164°C; NMR-complex 11 H signal (aromatic)} \]
o-chlorochalkone \[ \text{m.p. 52°C; NMR-complex 11 H signal (aromatic)} \]
p-chlorochalkone \[ \text{m.p. 114°C, NMR-complex 11 H signal (aromatic)} \]
p-methoxychalkone \[ \text{m.p. 72°C, NMR-complex 11 H signal (aromatic and olefinic, 3H singlet at 3.32 d (OCH₃)} \]
o-Methoxychalkone \[ \text{m.p. 68°C, NMR-complex 11 H signal (aromatic)} \]
p-N0₂ chalkone \[ \text{m.p. 125°C, p'-NO₂ chalkone (m.p. 150°C), p'-chlorochalkone (m.p. 100°C, NMR-complex 11 H signal in the aromatic region), p'-Methoxychalkone (m.p. 110°C, NMR-complex 11 H signal (aromatic), 3H centred round 3.32 d (OCH₃)} \]
m-NO₂ chalkone \[ \text{m.p. 145°C)} \]

Vanadium solution and chalkone solutions were prepared in similar manner as described in oxidation of acetophenones. The salts, ammonium sulphate and sodium perchlorate were used to maintain ionic strength of the solutions in sulphuric and perchloric acid media respectively. The effect of cations on reactivity has been observed, using anaalR samples of the various salts.

Kinetic measurements were done as described in case of acetophenone oxidation.

**Stoichiometry and product analysis:**

A solution of chalkone (25 c.c. of 0.02 M) was mixed with V(v) (25 c.c. of 0.1 M solution in 6 N HClO₄) solution at room temperature. 5 c.c. of the reaction mixture was pipetted out everyday and estimated for residual oxidant.
After about three days, the rate of consumption of V(v) became negligible. The results indicate that 2 moles of the oxidant are consumed per mole of chalkone. The products are found to be phenylacetaldehyde (characterised by its 2,4 dinitrophenyl hydrazone, m.p. 138\(^\circ\)C against the literature value of 189-90\(^\circ\)C) and benzoic acid. Therefore the overall reaction for V(v) oxidation of chalkone may be written as:

\[
\text{C}_6\text{H}_5\text{COCH} = \text{CHC}_6\text{H}_5 + 2\text{V}(v) + 2\text{H}_2\text{O} = \text{C}_6\text{H}_5\text{CH}_2\text{CHO} + \text{C}_6\text{H}_5\text{COOH} + 2\text{V}(v) + 2\text{H}^+ 
\]

Acetonaphthones:

Ammonium vanadate has been used in acid solutions for the purpose of oxidation. The acetonaphthones were obtained and the purity was checked on a silica gel t.l.c. plate. The stock solutions of V(v) were prepared in different acid concentrations and were standardised against ferrous ammonium sulphate solution using N-phenyl anthranilic acid as indicator (loc cit). AnalaR BDH sulphuric acid was used. AnalaR BDH glacial acetic acid was used for preparation of ketone solutions.

Rate measurements were done according to procedure given by Rout et al\(^{27}\).

Stoichiometric experiments were carried out by determining the excess of V(v), till there was no change in concentration.
Analysis of the product:

The reaction mixture of an excess of beta-acetonaphthone and V(v) solutions was kept at 50°C for about 48 hours. This was then extracted several times with ether. The ether layer was repeatedly treated with dilute sodium hydroxide solution and finally washed several times with water, dil. HCl and water. This was dried over anhydrous MgSO₄ and on removal of ether, a solid with m.p. 48-50°C was obtained. This was subjected to t.l.c. on a silica gel plate developed with benzene and on finally spraying with chromic acid gave only one spot with R_f 0.37, same as that for beta-acetonaphthone under similar experimental conditions. Hence the ether soluble part was unreacted ketone.

The alkali layer was acidified with dilute HCl and extracted with ether. On removal of ether, a solid of m.p. 153°C was obtained. This responded to the characteristic phenol tests like FeCl₃ and back azo dye test. Hence the compound was characterised as a phenol. A portion of the compound was found to be soluble in NaHCO₃ solution, which was reprecipitated from HCl. The white substance was found to be soluble in hot water and had a melting point 183°C. It was characterised to be β-naphthoic acid. The NaHCO₃ in soluble substance was found to be a keto-phenol and had a melting point 170°C. It was characterised to be 3-acetyl-1-naphthol. Similarly by working out as above the products isolated from α-naphthol were α-naphthoic acid and 4-acetyl-1-naphthol.
Indane 1:3-dione:

Indane 1:3-dione was prepared by the condensation of diethyl phthalate and ethyl acetate in presence of sodium followed by hydrolysis with dilute sulphuric acid. The compound was recrystallised thrice from absolute alcohol (m.p. 130°C).

Preparation of V(v) solution, ketone solution and rate measurement etc. have been given in detail in case of acetophenone.

Mixtures containing different quantities of indane 1:3-dione and excess of V(v) were left overnight and then residual V(v) estimated. The results indicate that 5 mole V(v) are consumed per mole of the diketone.

The products formed from the oxidation of indane 1:3-dione are phthalic acid (indicated by its fluorescein test and characterised by taking the mixed m.p. with an authentic sample), formaldehyde (known by its 2:4 dinitrophenyl hydrazone, m.p. 154°C) and evolution of carbon dioxide.

Deoxybenzoin:

The kinetics of the oxidation have been followed as before. The stoichiometry has been determined with excess (1:5) of V(v). The product analysis has been conducted at two different conditions: one with excess (1:2.5) of V(v) and another with excess of deoxybenzoin (1:0.25). After the reaction was over the solution changed to green. Excess acetic acid and perchloric acid was neutralised with NaHCO₃.
Then it was extracted several times with benzene. The aqueous layer was concentrated and was neutralised. On chilling benzoic acid was isolated. Benzene was removed from the benzene layer. One with excess of V(v) on t.l.c. gave two spots corresponding to dibenzyl and benzil and the other with less of V(v) also gave two spots corresponding to dibenzyl and benzoin.