

CHAPTER III

EXPERIMENTS

3.1. The oxidation behaviour of certain oxidants

Since lead (IV) acetate is an oxidant that is widely used in organic systems, the procedure was first developed for this oxidant and was given below for the system of 2, 3-butanediol and ethylene glycol. Similarly other oxidants of interest were tested for their oxidation behaviours. All the experiments reported in this thesis were performed in triplicates. A typical experiment is as follows:

A solution of 15 ml of $4.102 \times 10^{-2} \text{F}$ lead (IV) acetate was pipetted into a 100 ml round bottom flask, 0.56 ml containing 6.0×10^{-3} mole of 2, 3-butanediol was then added. The flask was fitted to a water condenser which was connected to an ether condenser reservoir containing salt-ice mixture. The temperature of the system was controlled at $15 - 20^\circ\text{C}$ and the content was stirred by means of the electrical magnetic stirrer for twenty hours. After the reaction was completed, the saturated solution of 2, 4-dinitrophenylhydrazine was added in excess and the system was refluxed at 50°C for one hour. The whole content was transferred quantitatively into a 250 ml volumetric flask, dissolved and made to volume with carbonyl free ethyl

alcohol. A 10 ml aliquot was pipetted into a 250 ml rotator and distilled under diminished pressure to expel most of the acid. The residue was then dissolved with carbonyl free ethyl alcohol in a 100 ml volumetric flask. The volume was adjusted to the mark and a 5-ml aliquot was pipetted into a 100 ml beaker. This solution was found to be slightly acid, therefore a few drops of 4% sodium bicarbonate solution were added until it was neutral to litmus. In order to decrease the solubility of the product in the aqueous alcohol phase, 10 ml of carbonyl free methyl alcohol was pipetted into this neutral solution, after which it was transferred quantitatively to a separatory funnel and was extracted with 10 ml of n-hexane.

The hexane layer was collected and the reextraction of the aqueous alcohol phase was carried out until the hexane layer became colourless. The combined extracts (n-hexane layer) were dehydrated using anhydrous sodium sulphate. The dried extract was transferred to a 100 ml volumetric flask and diluted to the mark with n-hexane. The maximum absorbance of this solution occurred at 335 nm (Figure I) using a 1 cm quartz cell having n-hexane as reference. Throughout this work the Perkin-Elmer double beam grating spectrophotometer model 124 was used for the determination of the concentrations of the aldehyde 2,4-dinitrophenylhydrazones. The calibration curve was first constructed for standard solutions of formaldehyde-2,4-dinitrophenylhydrazone (F-2,4-DNPH) and acetaldehyde-2,4-dinitrophenylhydrazone (A-2,4-DNPH) as shown in Appendix I and II,

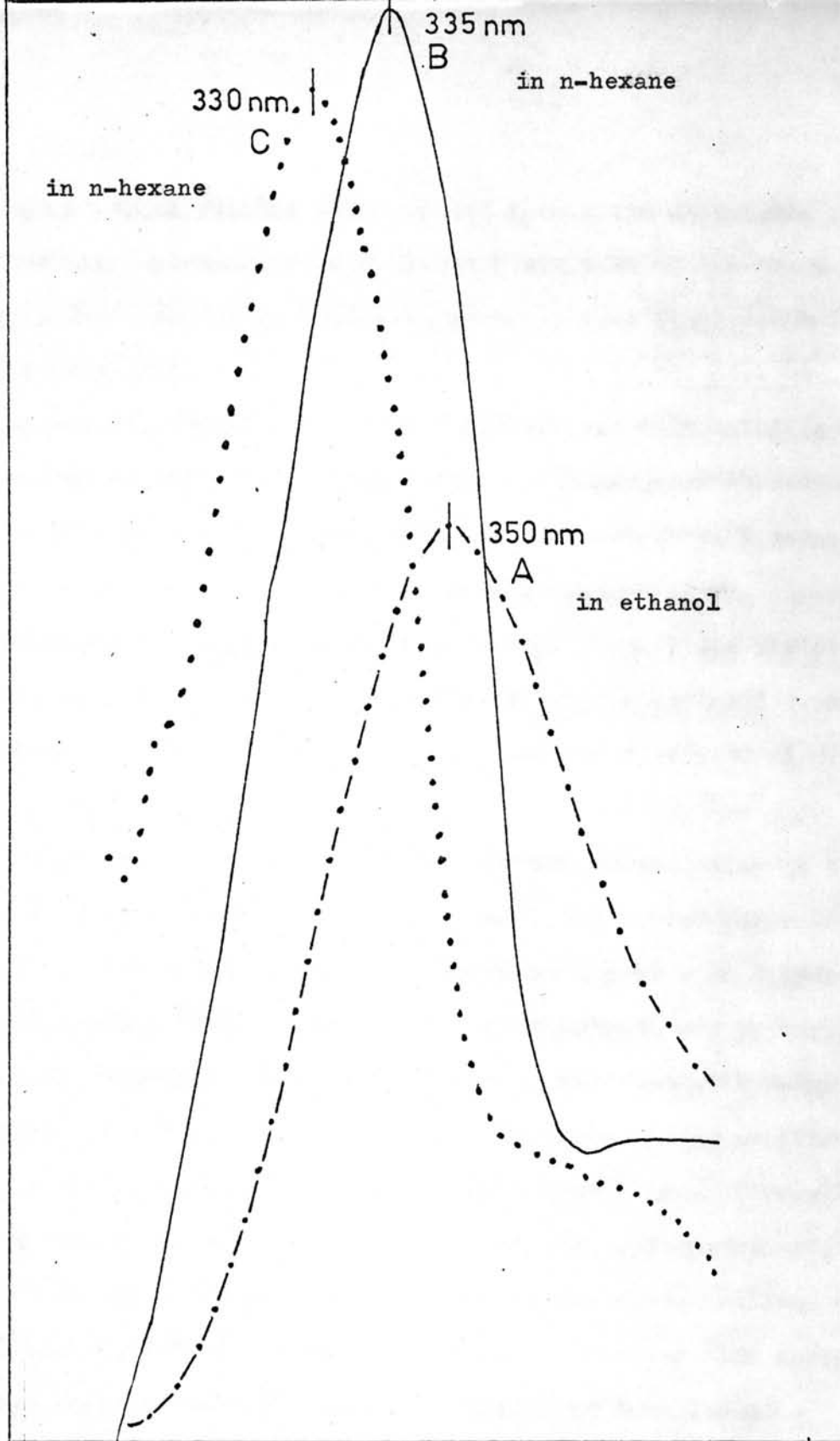


FIG. I · ABSORPTION SPECTRA OF 2,4-DNP (CURVE A)
A-2,4-DNPH (CURVE B) AND F-2,4-DNPH
(CURVE C)



Figures IV and V from which the concentrations of the phenyl-hydrazone products of the systems under investigation were then read out.

When ethylene glycol was oxidized the product obtained is formaldehyde whose boiling point is -21°C . This necessitates the use of dry ice-acetone mixture (-70°C) in the ether condenser reservoir instead of ice-salt mixture.

The techniques described above were also applicable to other oxidants namely thallium (III) acetate, thallium (III) chloride, thallium (III) sulphate, and thallium (III) nitrate.

3.2. Chemicals

All chemicals otherwise mentioned were of Analar grade and used without further purification. Standard aqueous solutions were standardized by the conventional methods.

Other major chemicals are tabulated below with manufacturers and important physical properties:-

Chemicals	Manufacturers	Physical properties			References
		B.P(°C)	M.P(°C)	Sp.gr(gm/cc)	
ethylene glycol	BDH	197	-16	1.110	35
2,3-butanediol	Baker	183	34	1.048	
n-hexane	Baker	68.7	-	0.659	
Anhydrous sodium sulphate	BDH	-	500	-	
Thallium (III) oxide	BDH	-	875	759	

Some chemicals, however, could not be obtained with high purity commercially or they are not so stable. These had to be prepared in the laboratory. The methods of preparation are given in the following section.

3.2.1. Preparation methods

The weighings of the materials mentioned below were carried out with a digital analytical balance Satorius Model 2404 with ± 0.01 mg precision. When only a rough weight was needed, a Metler top pan balance type P 1000 was found to be sufficient.

The starting material for the preparation of thallium (III) salt is thallium (III) oxide. To prepare thallium (III) chloride, thallium (III) acetate, thallium (III) sulphate and thallium (III)

nitrate, just enough corresponding acids were added to dissolve about 5 gm. of thallium (III) oxide. The precipitate was obtained as a residue after the evaporation of the solution slowly and gently to avoid the thermal decomposition. The appropriate solutions of these salts were prepared as described below. Their concentrations were determined by the conventional iodometric method using a dead stop end point technique.

Thallium (III) acetate: It was prepared according to the method given in reference (7). The usual concentration used in this work was $6.260 \times 10^{-2} F$ in glacial acetic acid.

Thallium (III) sulphate: 5.0000 gm. of thallium (III) sulphate obtained from the above preparation were dissolved and made up to 250 ml solution with 1 F H_2SO_4 which yielded a solution of concentration of $4.742 \times 10^{-2} F$.

Thallium (III) nitrate: A solution of thallium (III) nitrate in 1 F HNO_3 with a concentration of $3.241 \times 10^{-2} F$ was prepared by dissolving 4.7022 gm. thallium (III) nitrate in 1 F HNO_3 and the solution was made to 250 ml with the same acid.

Thallium (III) chloride: Since dry thallium (III) chloride was rather insoluble in its own acid, according to reference (6) the moist thallium (III) chloride was suspended in water followed by the addition of just enough 1 F HCl to dissolve it, and to make 250 ml solution. The concentration of resulting solution was $7.805 \times 10^{-4} F$.

Lead (IV) acetate: A mixture of 550 gm. of glacial acetic acid and 185 gm. of acetic anhydride was placed in a 1-litre three-necked flask provided with a thermometer and a mercury sealed mechanical stirrer. The content was heated to 55 - 60°C, and 300 gm. of dry red lead powder were added in portions of 15 - 20 gm. at a time. A fresh addition was made only after the colour due to the preceding portion has almost disappeared. The temperature should not be allowed to rise above 65°C. Towards the end of the reaction it was necessary to warm the flask cautiously to about 80°C in order to complete the reaction. At the end of the reaction, the thick and dark solution was cooled and the precipitate was filtered off and washed with glacial acetic acid containing a little acetic anhydride. The solution was then treated with a little decolourising carbon, filtered through a hot funnel and cooled. The colourless crystalline solid was filtered off and dried in a vacuum desiccator over potassium hydroxide pellets. The usual yield obtained by this method was about 90%.

Lead (IV) acetate (7.66179 gm) was weighed and dissolved in glacial acetic acid in a 250-ml volumetric flask. This gave a solution of concentration of $4.1020 \times 10^{-2} F$.

Carbonyl free alcohol: The laboratory grade alcohols were refluxed for one hour with excess 2, 4-dinitrophenylhydrazine mixed with few drops of concentrated hydrochloric acid. The alcohol was then distilled from an all glass distillation apparatus at 78°C.

2, 4-dinitrophenylhydrazine: The laboratory grade 2, 4-dinitrophenylhydrazine was recrystallized in a carbonyl free-alcohol to remove some impurities and certain phenylhydrazone contaminant.

Standard formaldehyde-2, 4-dinitrophenylhydrazone: 3.0 g. of pure 2, 4-dinitrophenylhydrazine were dissolved in solution containing 15 ml of concentrated sulphuric acid and 20 ml of water, 70 ml of 95% carbonyl free ethyl alcohol were added, the solution was mixed thoroughly and filtered off the undissolved part.

A solution of 100 ml of the above 2, 4-dinitrophenylhydrazine reagent was placed in a 250-ml round bottom flask, and into it was added 5 ml of formalin solution. The mixture was refluxed for one hour at 50°C, after which the content was cooled and the yellow precipitate was filtered off. The precipitate was recrystallized in 95% carbonyl free ethyl alcohol until its melting point range was 166 - 167°C. The prepared formaldehyde-2, 4-dinitrophenylhydrazone was identified and checked for its purity using a Pye-unicam double beam recording infrared spectrometer model SP 200 G.

Acetaldehyde-2, 4-dinitrophenylhydrazone: The procedure was the same as above, with the difference only in that acetaldehyde solution was used instead. The recrystallization process was carried out until the product melted at 164 - 165°C.