

CHAPTER III

EXPERIMENTS

Chemicals

All chemicals used were of reagent grade, no further purification was attempted unless otherwise stated. Standard aqueous solutions were standardised by the conventional methods. Other major chemicals are tabulated below with manufacturers and important physical properties.⁽²³⁾

Chemical	Manufacturer	Mol.Wt.	B.P.(°C)	M.P.(°C)	Density (g/cm ³)
Hydroquinone	May & Baker	110.11	285 ⁷³⁰	173-4	1.328
1,4-Benzoquinone	BDH	108.10	Sub.	115.7	1.318
4-Aminophenol	BDH	109.13	Sub.par. d.110 ^{0.3}	186-7	-
Thallium(III) oxide	BDH	456.74	-20,875	717±5	-
Chloroform	Fisher	119.38	60.4-61°C	-63.5	1.4832

1. Preparation and Purification Methods.

The weighing of the materials mentioned below were carried out with a digital analytical balance Mettler H 43 with ± 0.1 mg. precision.

Thallium (III) oxide was the starting material for the preparation of thallium (III) salts. The concentrations of thallium (III) salts were determined by the conventional iodometric method using starch indicator and dead stop end point technique.⁽¹⁾

1.1 Thallium (III) Nitrate

5G.(0.011 mole) of thallium (III) oxide were dissolved in 15 cm³ of concentrated nitric acid at about 80°C, the reaction was complete in 30 minutes.⁽²⁾ Cooling of the pale yellow solution to 0°C yielded 7.1224 g. (0.016 mole, 70.50%) of colorless crystals of a trihydrate which was dried in vacuo over phosphorus pentoxide. Thallium (III) nitrate was very sensitive to moisture and must be stored in tightly sealed bottles.

A 4.2252×10^{-2} M. thallium (III) nitrate solution was prepared by dissolving 4.6945 g. of thallium (III) nitrate in 1 M. HNO₃ and the volume of this solution was made up to 250 cm³.

1.2 Thallium (III) Sulfate

5G.(0.011 mole) of thallium(III) oxide were dissolved in 20 cm³ of concentrated sulfuric acid at about 70°C, when the solution became cloudy the water was added slowly until the solution was clear. To complete the reaction, the solution was allowed to stir further for 30 minutes. Cooling the solution to 0°C yielded 8.3840 g. (0.010 mole, 93.06%) of colorless crystals of thallium (III) sulfate heptahydrate.

A 3.6665×10^{-2} M. thallium (III) sulfate solution was prepared by dissolving 7.5441 g. of thallium (III) sulfate in 1 M. H_2SO_4 and the volume of this solution was made up to 250 cm^3 .

1.3 Thallium (III) Chloride

5G.(0.011 mole) of thallium (III) oxide were dissolved in about 20 cm^3 of concentrated hydrochloric acid at about 60°C for 2-3 hours. Cooling of the pale yellowish-green solution to 0°C yielded 5.1912 g. (0.013 mole, 61.95%) of colorless crystals of thallium (III) chloride tetrahydrate.

A 4.2411×10^{-3} M. thallium (III) chloride solution was prepared by dissolving 0.4042 g. of thallium (III) chloride in 1 M. HCl. Since thallium (III) chloride was rather insoluble in its own acid, it was necessary to heat the solution gently and made the volume up to 250 cm^3 .

1.4 Thallium (III) Acetate

5G.(0.011 mole) of thallium (III) oxide were dissolved in about 30 cm^3 of glacial acetic acid at about 50°C for 4 hours. The residual solid was removed by suction filtration. Cooling of the pale yellow solution to 0°C yielded 6.1011 g. (0.016 mole, 72.50%) of colorless crystals of thallium (III) acetate.

A 2.0475×10^{-2} M. thallium (III) acetate solution was prepared by dissolving 1.9675 g. of thallium (III) acetate in glacial acetic acid and the volume of the solution was made up to 250 cm^3 .

1.5 Purification of 1,4-Benzoquinone

Technical grade 1,4-benzoquinone was purified by recrystallization from petroleum-ether 3 times and then further purified by sublimation twice. The purified 1,4-benzoquinone was checked for its purity by using a Pye unicam double beam recording infrared spectrophotometer model 200 G, and thin-layer chromatography, using E. Merck silica gel-G (Darmstadt) as absorbance and methanol:chloroform (= 1:19) mixture as eluent, the Rf value of 1,4-benzoquinone is 0.64.

1.6 Standard 1×10^{-4} M. 1,4-Benzoquinone Solution

1,4-Benzoquinone 0.1081 g. (0.001 mole) was dissolved in chloroform in 10 cm³ volumetric flask. A 1 cm³ aliquot was pipetted and diluted to 10 cm³. A 1 cm³ of the latter solution was pipetted and made up to 100 cm³ with chloroform in a volumetric flask. The solution obtained, was 1×10^{-4} M. 1,4-benzoquinone solution.

The Oxidation Process

Throughout this work the Perkin-Elmer double beam grating spectrophotometer model 124 was used for the determination of the concentration of 1,4-benzoquinone. The calibration curve was first constructed for standard solution of 1,4-benzoquinone as shown in Appendix. The techniques described below was also applicable to other oxidants namely thallium (III) sulfate, thallium (III) chloride, and thallium (III) acetate. All the experiments reported in this thesis were performed in triplicates.



1. Oxidation of Hydroquinone

A 15 cm³ solution of 4.2252 x 10⁻² M. thallium (III) nitrate was pipetted into a 25 cm³ beaker, cooled to 20°C, and then poured into a 100 cm³ round-bottomed flask which contained 6.3378 x 10⁻³ moles of hydroquinone. The content was stirred by means of magnetic stirrer and the temperature was controlled at 20 ± 1°C for 30 minutes. After the reaction was completed, the bulk of the acid was then removed by evaporation under reduced pressure in the rotary evaporator and the residue was poured into 50 cm³ ice-water. The 1,4-benzoquinone which separated at this stage was extracted with 30 cm³ of chloroform, then reextracted with 20 cm³ of chloroform 3 times, until the chloroform and the aqueous layers became colorless. The combined chloroform extracts were washed with water and dried over anhydrous sodium sulfate, then transferred into a 100 cm³ volumetric flask and made up to its volume with chloroform. A 0.1 cm³ aliquot was pipetted into a 25 cm³ volumetric flask and diluted to the mark with chloroform. The maximum absorbance of this solution occurred at 245 nm. (Fig I) using a 1 cm. quartz cell with chloroform as reference.

2. Oxidation of 4-Aminophenol

A 15 cm³ solution of 4.2252 x 10⁻² M. thallium (III) nitrate was pipetted into a 100 cm³ round-bottomed flask which contained a 6.3378 x 10⁻³ moles of 4-aminophenol. The reaction mixture was refluxed under controlled temperature at 40 ± 3°C and

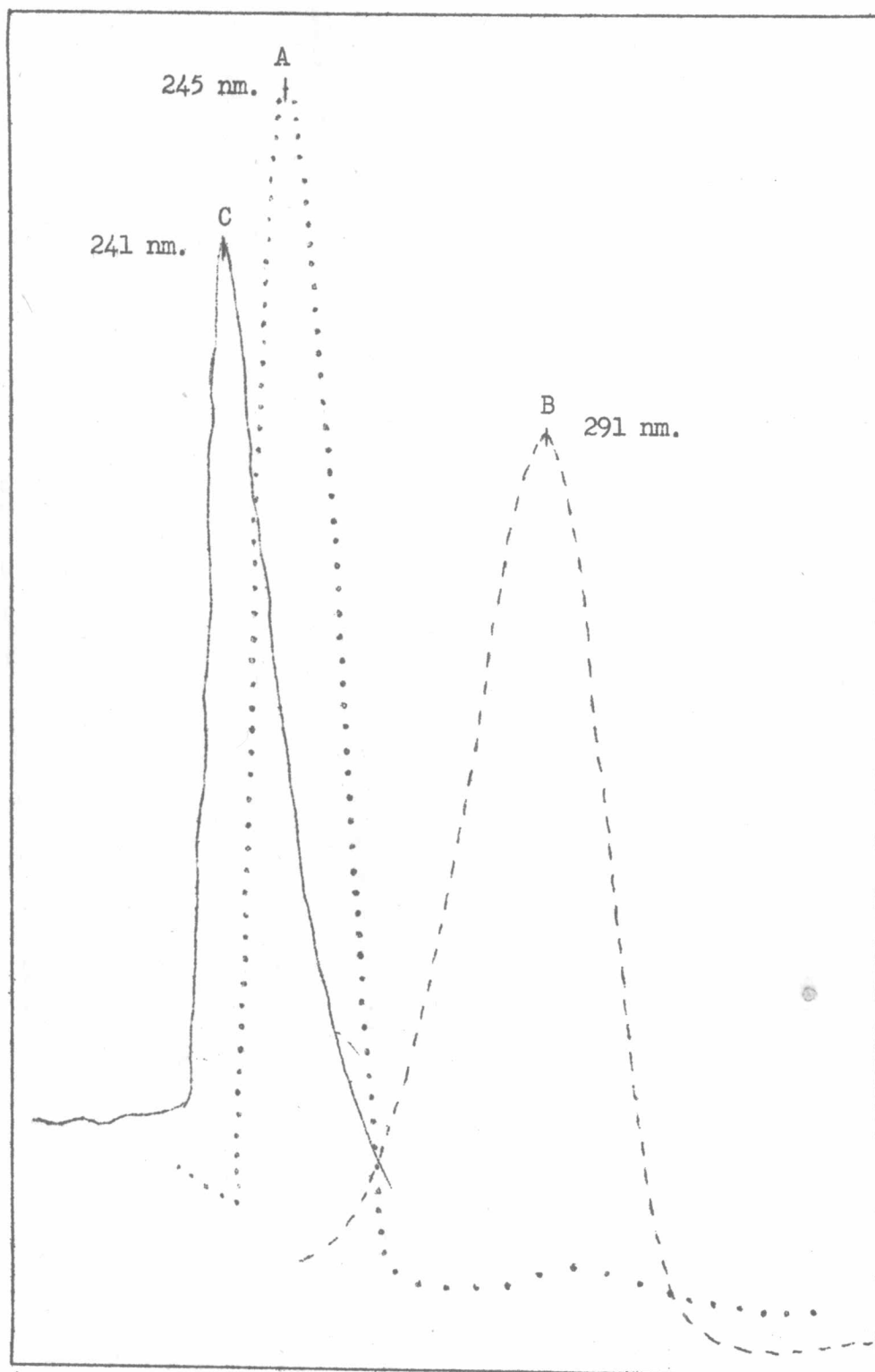


FIG I. ABSORPTION SPECTRA OF 1,4-BENZOQUINONE IN CHLOROFORM (CURVE A), HYDROQUINONE IN CHLOROFORM (CURVE B), AND 4-AMINOPHENOL IN CHLOROFORM (CURVE C)

stirred by magnetic stirrer for 6 hours. After the reaction was completed, the bulk of the acid was then removed by evaporation under reduced pressure in the rotary evaporator. The residue was poured into 50 cm³ ice-water, 30 cm³ of chloroform added, contents well mixed, filtered by suction pump and the precipitate washed with a little chloroform. After the chloroform layer was removed, the aqueous layer was reextracted with 20 cm³ of chloroform 3 times, until the chloroform layer became colorless. The combined chloroform extracts were washed with water and dried over anhydrous sodium sulfate, then transferred into a 100 cm³ volumetric flask and made up to its volume with chloroform. A 0.1 cm³ aliquot was pipetted into a 25 cm³ volumetric flask and diluted to the mark with chloroform. The maximum absorbance of this solution occurred at 245 nm. (Fig I) using a 1 cm. quartz cell with chloroform as reference.