

CHAPTER IV

DISCUSSION OF RESULTS AND CONCLUSIONS

Discussion of Results

1. Practical Aspects

Oxidation of phenols and their derivatives to 1,4-benzoquinones using thallium reagents has been known for a long time. Recently McKillop and Swann have studied the oxidation of phenols and hydroquinone with thallium (III) trifluoroacetate. They proposed the mechanism, calculated the chemical yield, and collected the products by crystallization technique. In the present study, spectroscopic technique has been developed in the quantitative determination of the oxidative product of hydroquinone and 4-aminophenol with thallium (III) salts. The amount of oxidised product was determined by extracting with chloroform. The absorbance of the solution was measured at 245 nm. and changed to corresponding concentration via calibration curve. For the purpose of comparison, the chemical yield of oxidised product can be used as measure of the oxidative power of various thallium (III) salts. It is worth mentioning that considerable time and effort were spent in developing the above technique which proved to be the reliable technique in producing quite a reproducible result in each set of measurements (see Table IV-XI).

Spectroscopic technique is better than crystallization technique in its convenience, accuracy and speed. However, there are many factors that have to be examined in designing the experiment described in the preceding chapter. In the purification process, 1,4-benzoquinone was purified not only by recrystallization, but also further purified by sublimation (see page 25). In order to get the best and consistent results, the optimum experimental conditions were investigated for hydroquinone-thallium (III) nitrate system and they were shown in Table I, II, III and Figures II, III and IV. The conditions that gave the maximum yield of product were 30 minutes at 20°C, mole ratio of hydroquinone: thallium (III) nitrate = 10:1 and these conditions were assumed to be the optimum conditions in other hydroquinone-thallium (III) salts system as well. For 4-aminophenol-thallium (III) nitrate system, the optimum experimental conditions were 6 hours at 40°C, mole ratio of 4-amino-phenol: thallium (III) nitrate = 10:1 and these conditions were assumed to be the optimum conditions in other 4-aminophenol-thallium (III) salts system as well. Oxidation of hydroquinone and 4-aminophenol yielded 1, 4-benzoquinone. Separation of the yellow product from the excess reagent was carried out by extracting with chloroform. In order to get rid of some impurities, the chloroform solution was washed with water and then dried with anhydrous sodium sulfate. In the presence of water, the chloroform solution was cloudy and shifted the maximum absorption of the solution. The absorbance of

the solution was measured at 245 nm. This method is better than other methods because the spectra of 1,4-benzoquinone in chloroform is highly reproducible.

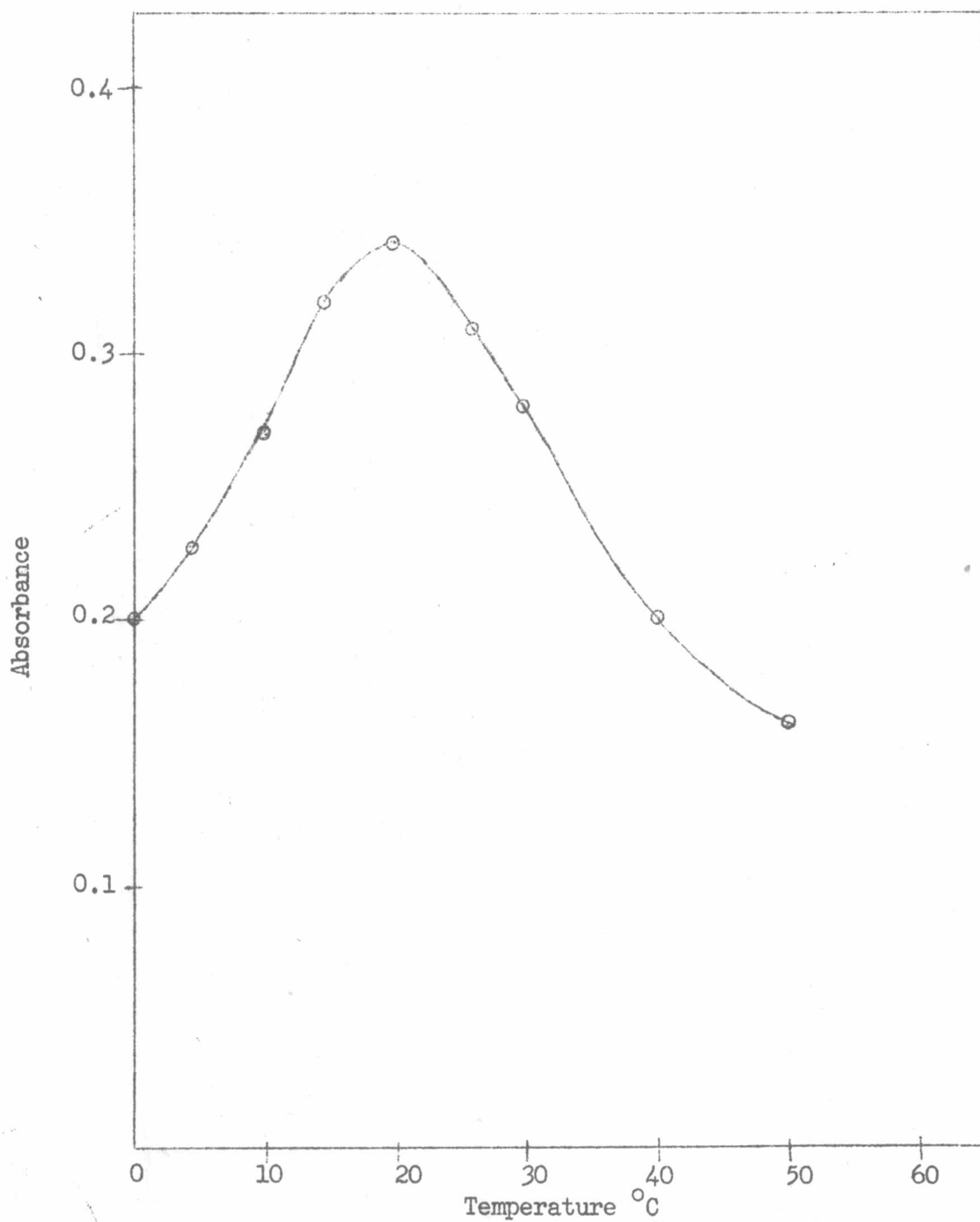


FIG II. VARIATION OF TEMPERATURE ON THE OXIDATION OF HYDROQUINONE WITH THALLIUM (III) NITRATE.

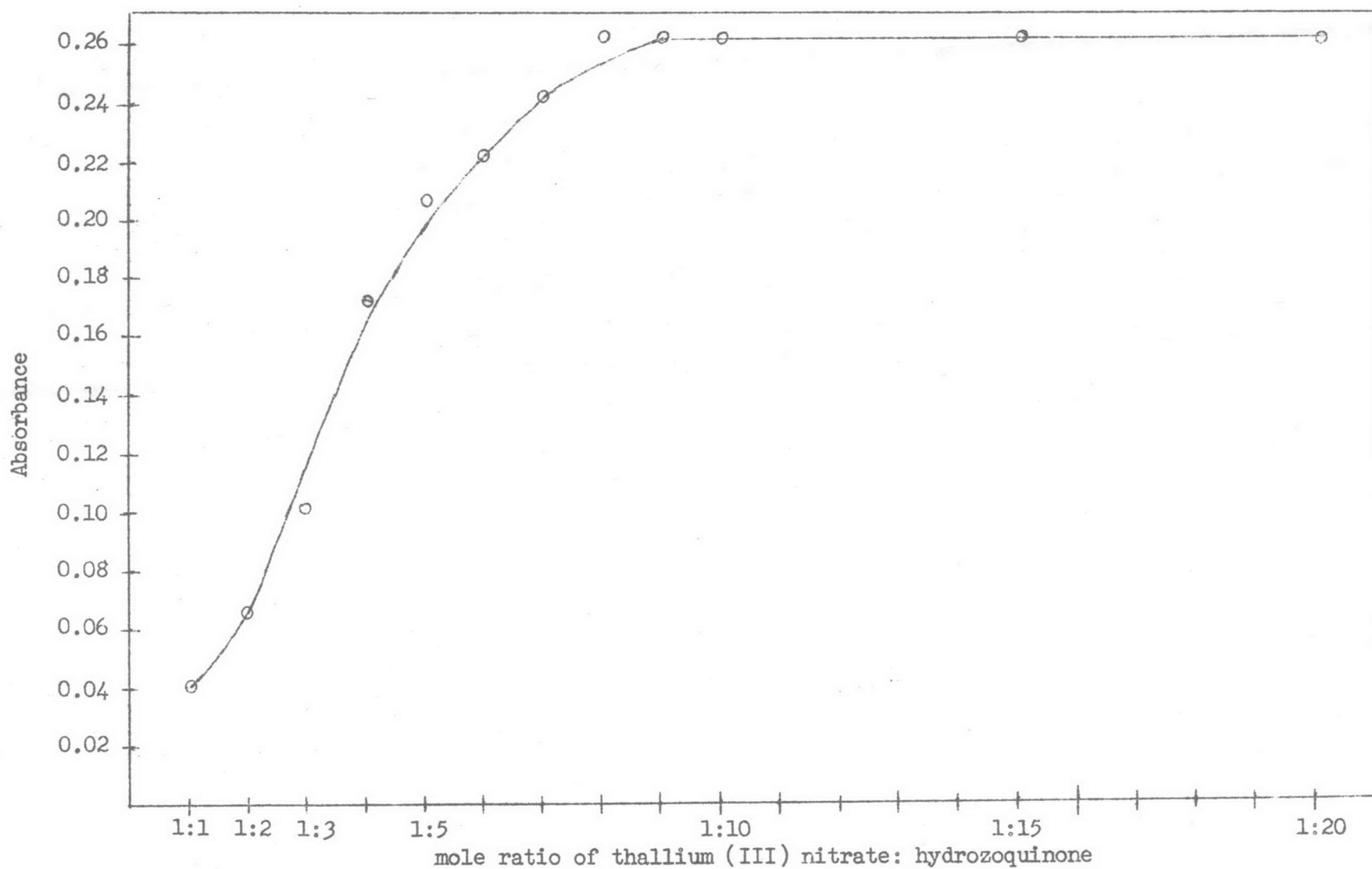


FIG III. VARIATION OF MOLE RATIO OF THALLIUM (III) NITRATE: HYDROQUINONE ON THE OXIDATION OF HYDROQUINONE WITH THALLIUM (III) NITRATE.

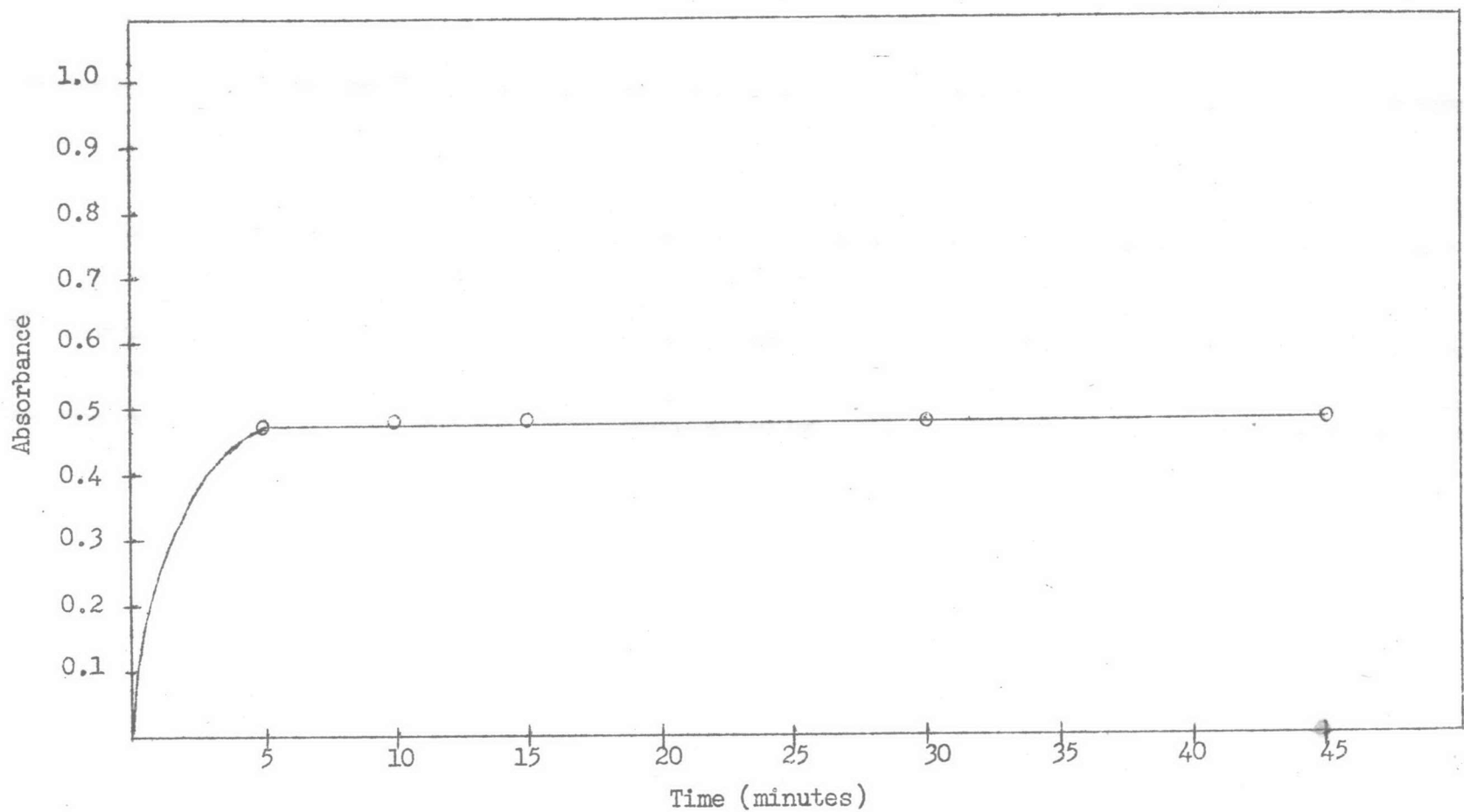


FIG IV. VARIATION OF TIME ON THE OXIDATION OF HYDROQUINONE WITH THALLIUM (III) NITRATE.

Table I

Variation of temperature on the oxidation of hydroquinone
with thallium (III) nitrate.

Mole ratio: thallium (III) nitrate: hydroquinone = 1 : 10

Reaction time: 15 minutes

Maximum wavelength: 245 nm.

| Experiment | Reaction temperature ($^{\circ}\text{C}$) | Absorbance |
|------------|---|------------|
| 1 | 0 ± 1 | 0.200 |
| 2 | 5 ± 1 | 0.230 |
| 3 | 10 ± 1 | 0.270 |
| 4 | 15 ± 1 | 0.320 |
| 5 | 20 ± 1 | 0.340 |
| 6 | 25 ± 1 | 0.315 |
| 7 | 30 ± 1 | 0.280 |
| 8 | 40 ± 1 | 0.200 |
| 9 | 50 ± 1 | 0.160 |

Table II

Variation of mole ratio of thallium (III) nitrate:
hydroquinone on the oxidation of hydroquinone with
thallium (III) nitrate

Reaction temperature : 20°C
Reaction time : 15 minutes
Maximum wavelength : 245 nm.

| Experiment | Mole ratio of thallium (III) nitrate: hydroquinone | Absorbance |
|------------|---|------------|
| 1 | 1:1 | 0.040 |
| 2 | 1:2 | 0.065 |
| 3 | 1:3 | 0.100 |
| 4 | 1:4 | 0.170 |
| 5 | 1:5 | 0.205 |
| 6 | 1:6 | 0.220 |
| 7 | 1:7 | 0.240 |
| 8 | 1:8 | 0.260 |
| 9 | 1:9 | 0.260 |
| 10 | 1:10 | 0.260 |
| 11 | 1:15 | 0.260 |
| 12 | 1:20 | 0.260 |

Table III

Variation of time on the oxidation of hydroquinone
with thallium (III) nitrate.

Mole ratio : thallium (III) nitrate : hydroquinone = 1:10

Reaction temperature : 20°C

Maximum wavelength : 245 nm.

| Experiment | Reaction time (minutes) | Absorbance |
|------------|-------------------------|------------|
| 1 | 5 | 0.480 |
| 2 | 10 | 0.485 |
| 3 | 15 | 0.485 |
| 4 | 30 | 0.480 |
| 5 | 45 | 0.480 |
| 6 | 60 | 0.480 |
| 7 | 90 | 0.480 |

Table IVOxidation of hydroquinone with thallium (III) nitrate.

Mole ratio : thallium (III) nitrate : hydroquinone = 1:10

Reaction temperature : $20 \pm 1^{\circ}\text{C}$

Reaction time : 30 minutes

Maximum wavelength : 245 nm.

| Experiment | Absorbance | Amount (mole) | Percentage yield |
|------------|------------|-------------------------|------------------|
| 1 | 0.480 | 58.125×10^{-5} | 91.61 |
| 2 | 0.480 | 58.125×10^{-5} | 91.61 |
| 3 | 0.480 | 58.125×10^{-5} | 91.61 |
| | | | Mean 91.61 |

Table VOxidation of hydroquinone with thallium (III) sulfate.

Mole ratio : thallium (III) sulfate : hydroquinone = 1:10

Reaction temperature : $20 \pm 1^{\circ}\text{C}$

Reaction time : 30 minutes

Maximum wavelength : 245 nm.

| Experiment | Absorbance | Amount (mole) | Percentage yield |
|------------|------------|--------------------------|------------------|
| 1 | 0.400 | 48.4375×10^{-5} | 88.07 |
| 2 | 0.405 | 48.9050×10^{-5} | 88.92 |
| 3 | 0.410 | 49.3750×10^{-5} | 89.78 |
| | | | Mean 88.92 |

Table VIOxidation of hydroquinone with thallium (III) chloride.

Mole ratio : thallium (III) chloride : hydroquinone = 1:10

Reaction temperature : $20 \pm 1^{\circ}\text{C}$

Reaction time : 30 minutes

Maximum wavelength : 245 nm.

| Experiment | Absorbance | Amount (mole) | Percentage yield |
|------------|------------|-------------------------|------------------|
| 1 | 0.270 | 33.500×10^{-5} | 76.63 |
| 2 | 0.270 | 33.500×10^{-5} | 76.63 |
| 3 | 0.275 | 33.125×10^{-5} | 78.10 |
| | | | Mean 77.12 |

Table VIIOxidation of hydroquinone with thallium (III) acetate.

Mole ratio : thallium (III) acetate : hydroquinone = 1:10

Reaction temperature : $20 \pm 1^{\circ}\text{C}$

Reaction time : 30 minutes

Maximum wavelength : 245 nm.

| Experiment | Absorbance | Amount (mole) | Percentage yield |
|------------|------------|--------------------------|------------------|
| 1 | 0.210 | 25.0000×10^{-5} | 81.40 |
| 2 | 0.220 | 26.5625×10^{-5} | 86.49 |
| 3 | 0.210 | 25.0000×10^{-5} | 81.40 |
| | | | Mean 83.10 |

Table VIIIOxidation of 4-aminophenol with thallium (III) nitrate.

Mole ratio : thallium (III) nitrate : 4-aminophenol = 1:10

Reaction temperature : $40 \pm 3^{\circ}\text{C}$

Reaction time : 6 hours.

Maximum wavelength : 245 nm.

| Experiment | Absorbance | Amount (mole) | Percentage yield |
|------------|------------|--------------------------|------------------|
| 1 | 0.375 | 45.3125×10^{-5} | 71.49 |
| 2 | 0.375 | 45.3125×10^{-5} | 71.49 |
| 3 | 0.370 | 44.6875×10^{-5} | 70.51 |
| | | | Mean 71.16 |

Table IXOxidation of 4-aminophenol with thallium (III) sulfate.

Mole ratio : thallium (III) sulfate: 4-aminophenol = 1:10

Reaction temperature : $40 \pm 3^{\circ}\text{C}$

Reaction time : 6 hours

Maximum wavelength : 245 nm.

| Experiment | Absorbance | Amount (mole) | Percentage yield |
|------------|------------|-------------------------|------------------|
| 1 | 0.300 | 36.250×10^{-5} | 65.91 |
| 2 | 0.300 | 36.250×10^{-5} | 65.91 |
| 3 | 0.305 | 36.875×10^{-5} | 67.05 |
| | | | Mean 66.29 |

Table XOxidation of 4-aminophenol with thallium (III) chloride.

Mole ratio : thallium (III) chloride : 4-aminophenol = 1:10

Reaction temperature : $40 \pm 3^{\circ}\text{C}$

Reaction time : 6 hours

Maximum wavelength : 245 nm.

| Experiment | Absorbance | Amount (mole) | Percentage yield |
|------------|------------|--------------------------|------------------|
| 1 | 0.200 | 24.2187×10^{-5} | 56.18 |
| 2 | 0.200 | 24.2187×10^{-5} | 56.18 |
| 3 | 0.195 | 23.7500×10^{-5} | 55.09 |
| | | | Mean 55.82 |

Table XIOxidation of 4-aminophenol with thallium (III) acetate.

Mole ratio : thallium (III) acetate : 4-aminophenol = 1:10

Reaction temperature : $40 \pm 3^{\circ}\text{C}$

Reaction time : 6 hours

Maximum wavelength : 245 nm.

| Experiment | Absorbance | Amount (mole) | Percentage yield |
|------------|------------|------------------------|------------------|
| 1 | 0.155 | 18.75×10^{-5} | 61.05 |
| 2 | 0.155 | 18.75×10^{-5} | 61.05 |
| 3 | 0.155 | 18.75×10^{-5} | 61.05 |
| | | | Mean 61.05 |

2. Theoretical Aspects

2.1 Oxidative Yield and Their Formal Reduction Potential

Table XII

The formal reduction potentials and percentage yield of 1,4-benzoquinone

| Thallium (III) salt | E_f^0 (v) | Percentage yield of 1,4-benzoquinone(%) | |
|-------------------------|-----------------------|---|-------------------------|
| | | Hydroquinone substrate | 4-Aminophenol substrate |
| Thallium (III) nitrate | +1.2303 | 91.61 | 71.16 |
| Thallium (III) sulfate | +1.2207 | 88.92 | 66.29 |
| Thallium (III) acetate | +0.9518 to +1.0488 | 83.10 | 61.05 |
| Thallium (III) chloride | +0.784 | 77.12 | 55.82 |

Any oxidation-reduction reaction may be broken up into two "half-reactions" that indicate the mechanism by which electrons are transferred from the reducing agent to the oxidising agent. The experimental determination of the absolute potential of any half-reaction is a difficult problem, but since any chemical reaction involves only the difference in potential between two half-reactions, the determination of absolute value is unnecessary. For this reason the procedure has come into general use of choosing the potential of some one half-reaction as an arbitrary zero and using this as a reference half-reaction for potential of all other

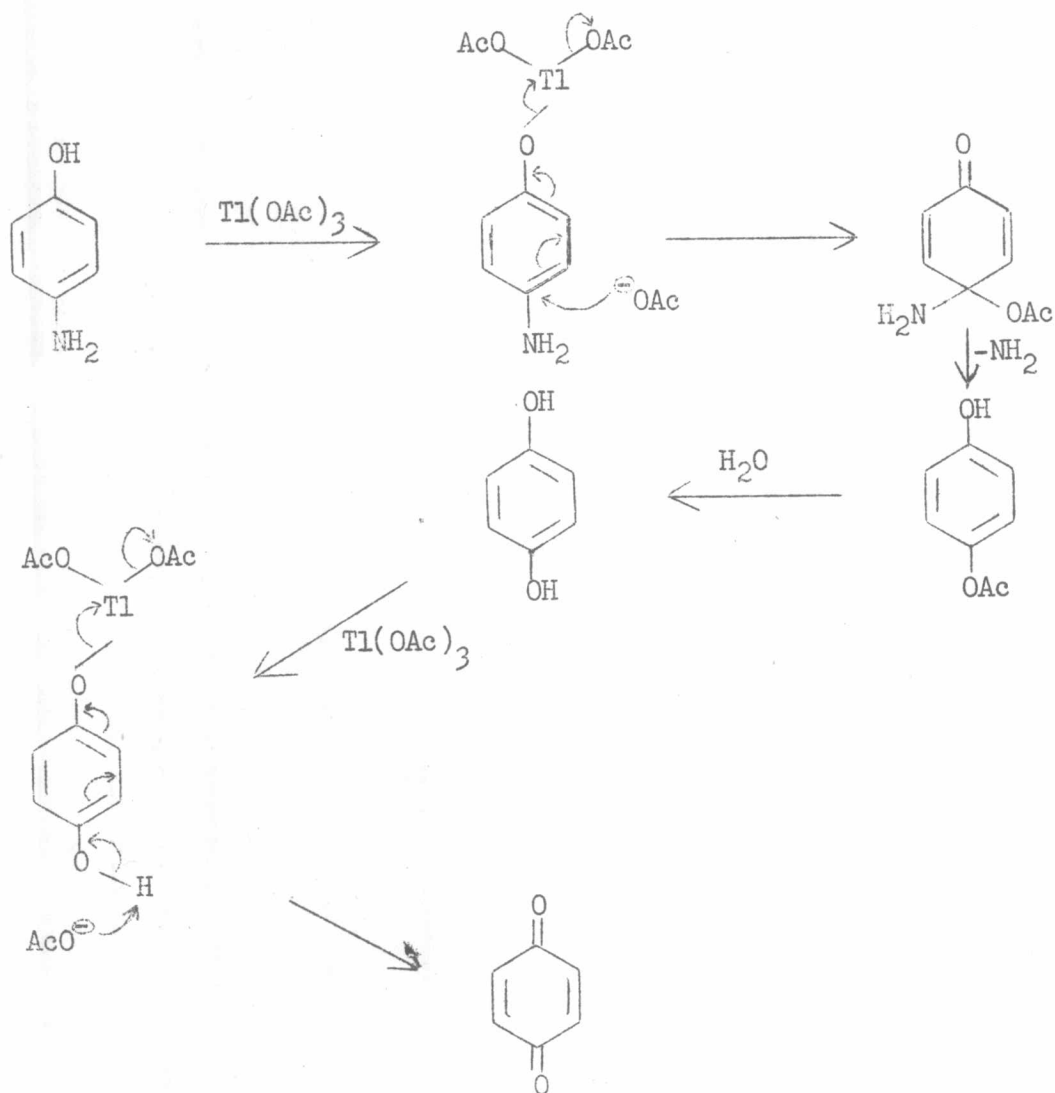
half-reactions. The reference half-reaction so chosen is the hydrogen gas-hydrogen ion couple.⁽⁷⁾



A positive value for E_f° will mean that the oxidised form of the half-reaction is a better oxidising agent than H^+ and, similarly, a negative E_f° will mean that the reduced form of the half-reaction is a better reducing agent than H_2 . Thus as shown in Table XII, the more positive the E_f° value should be the more stronger oxidant. So thallium (III) nitrate should be the strongest oxidant whereas thallium (III) chloride is the weakest while thallium (III) sulfate and thallium (III) acetate are the second and the third respectively. The percentage yield of the products correlate very well with the E_f° value that is the more the E_f° value are, the more the product form.

2.2 Mechanism of the Reaction

McKillop and Swann have proposed the mechanism of the oxidation of phenols and hydroquinones with thallium (III) trifluoroacetate. In the same way, the mechanism of hydroquinone and 4-aminophenol oxidation with other thallium (III) salts are proposed by the similar pathway as follows:



From the proposed mechanism, the hydroquinone was oxidised in only one step. In contrast, the 4-aminophenol was oxidised with thallium (III) acetate, followed by loss of the amino group and then the hydroquinone intermediate was further oxidised with the other molecule of thallium (III) acetate. Thus the oxidative product using 4-aminophenol as substrate gave lower yield than that using hydroquinone.

Conclusions

There are many oxidants used in organic synthesis, but each oxidant could only have an efficiency for the suitable corresponding system: such as Tollen's reagent can oxidise the corresponding aldehydic compound, it can not oxidise the ketonic or alcoholic compound. Thus the best oxidant not only has the ability to oxidise organic compounds, but also has the specificity and gives high quantitative yield. In case of the oxidation of hydroquinone with thallium (III) salts it is one of the best for preparation and quantitative determination of 1,4-benzoquinone.

The study of the oxidative properties of thallium (III) salts on ethylene glycol and 2, 3-butanediol⁽⁶⁾ supported and agreed well with the oxidising power of thallium (III) salts in this thesis.

Suggestion for Future Works.

The work can be continued in various aspects, all of which are worth investigating. The oxidising power of thallium (III) salts may be studied with other substrates, for example, substituted phenol, aldehyde etc. Other techniques can also be used in the determination of the oxidative products such as crystallization and the reaction may be run in organic solvent instead of aqueous solution. On the other hand, other thallium reagents (eg Tl_2O_3 in EtOH) may be used as the oxidising agent for these substrates.