DISCUSSION OF RESULTS AND CONCLUSSIONS

4.1. Discussion of results

4.1.1. Practical aspects

Many factors require to be examined in designing experiments
described in the preceding chapter. It is the purpose of this
section to bring together some of these factors and problems for
consideration. In order to get the best and consistent results,
the optimum experimental conditions were first investigated for
thallium (III) sulphate-2, 3-butanediol system and they were shown
in Tables I and II and Figures II and III to be 20 hours at
$10 - 20^{\circ}C$ to give the maximum yield of product and these were
assumed to be the optimum conditions in other system as well.
When the experiment could not be completed in 20 hours, the reac-
tion was stopped by freezing the reaction mixture in the refrigerator
and it was continued on the next day. It was necessary to use the
cold trap (ether condenser) containing acetone-dry ice mixture of
$-70^{\circ}C$ to trap the susceptible volatile compounds such as formal-
dehyde (b.p. $-21^{\circ}C$), etc. and in the case of 2, 3-butanediol ice-
trap was sufficient. The solvent involved must be purified by
refluxing with 2, 4-dinitrophenylhydrazine in acid to remove any
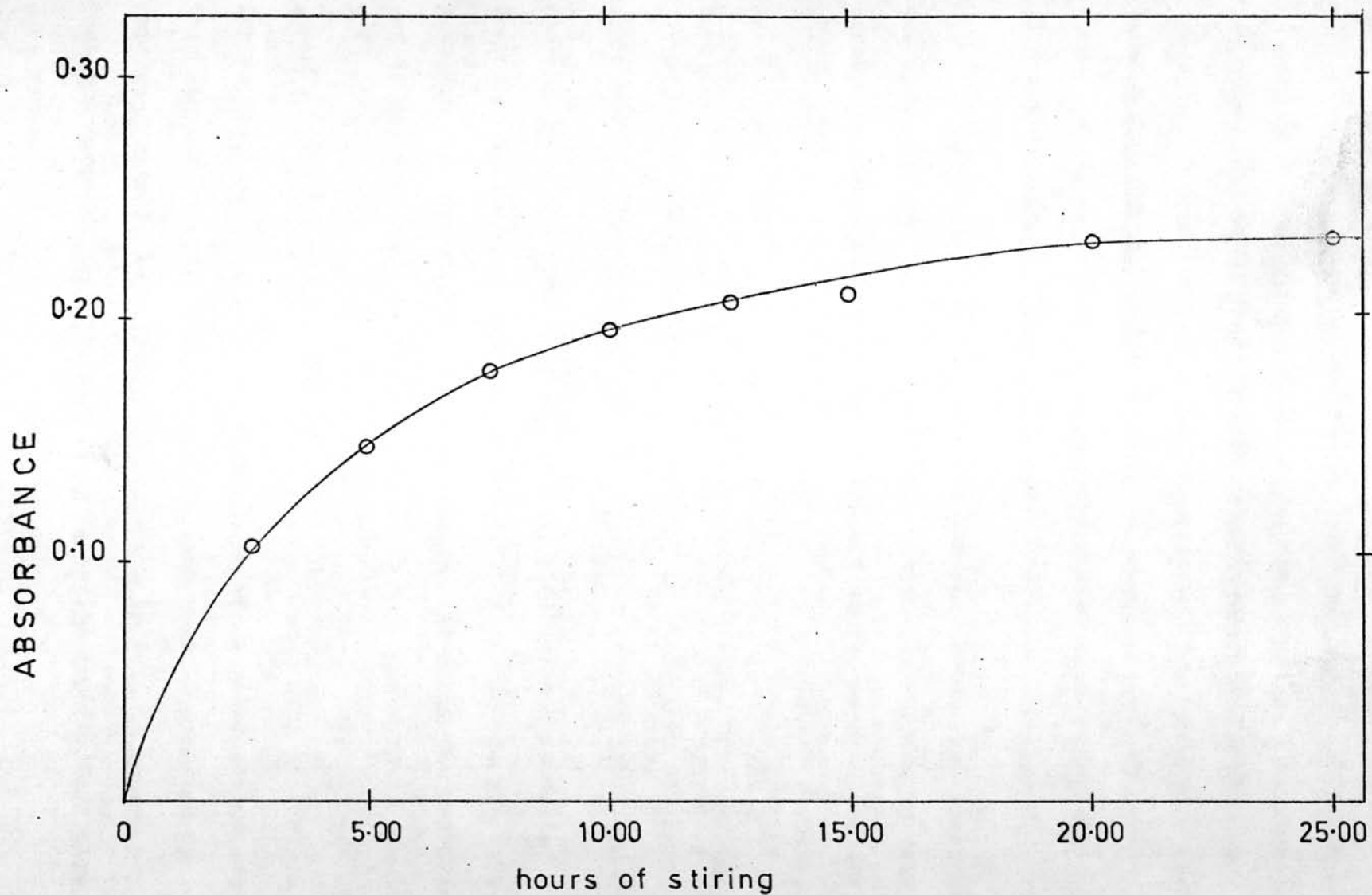carbonyl compound present, similarly 2, 4-dinitrophenylhydrazine

FIG. II   VARIATION OF TIME ON THE OXIDATION OF 2,3– BUTANEDIOL WITH THALLIUM (III) SULPHATE
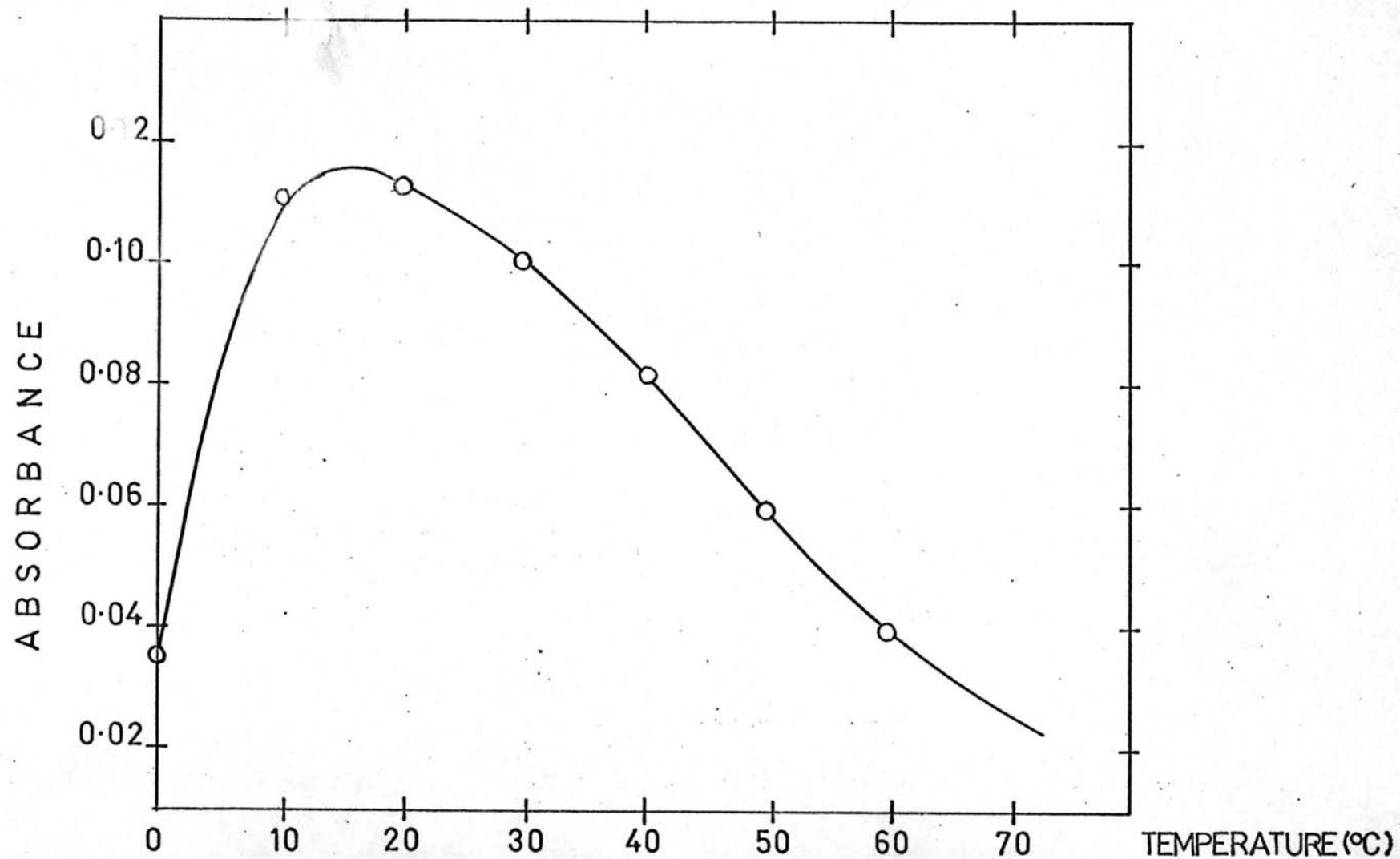
FIG. III VARIATION OF TEMPERATURE ON THE OXIDATION OF 2,3-BUTANEDIOL
WITH THALLIUM(III) SULPHATE

<u>TableI</u> <u>Variation of time on the oxidation of 2, 3-butonediol</u>

<u>with thallium (III) sulphate</u>

Mole ratio of thallium (III): 2, 3-butanediol = 1 : 21

Maximum wavelength: 335 nm.

Experiment	Time (hour)	Refluxing temperature ($^\circ$C)	Absorbance
1	2.50	15 - 20	0.110
2	5.00	15 - 20	0.150
3	7.50	15 - 20	0.180
4	10.00	15 - 20	0.190
5	12.50	15 - 20	0.210
6	15.00	15 - 20	0.215
7	20.00	15 - 20	0.236
8	25.00	15 - 20	0.236

Table II   Variation of temperature on the oxidation of

2, 3-butanediol with thallium (III) sulphate

Mole ratio of thallium (III):   2, 3-butanediol = 1 : 21

Maximum wavelength: 335 nm.

Refluxing time: 5 hours

Experiment	Refluxing temperature ($^\circ$C)	Absorbance
1	0 - 2	0.035
2	10 - 12	0.110
3	18 - 20	0.111
4	29 - 30	0.100
5	39 - 40	0.081
6	49 - 50	0.060
7	59 - 60	0.040

was also recrystallized to remove the possible contaminant phenyl-
hydrazone.   It is worth mentioning that considerable time and
effort were spent in the developing the above technique which
proved to be the reliable technique in producing quite a reproducible
result in each set of measurements (see Table III - Table XII)

Table III   Oxidation of 2, 3-butanediol with lead (IV) acetate

Mole ratio of lead (IV): 2, 3-butanediol = 1 : 10

Refluxing temperature: 15 - 20°C

Reacting time: 20 hours

Maximum wavelength: 335 nm.

Experiment	Absorbance	Amount (mole)	Percentage yield
1	0.130	7.74 X 10^{-4}	65.96
2	0.128	7.47. X 10^{-4}	63.63
3	0.125	7.19 X 10^{-4}	61.25
			Mean 63.60

Table IV Oxidation of 2,3-butanediol with thallium (III) chloride

Mole ratio of thallium (III): 2,3-butanediol = 1 : 34

Refluxing temperature: 15 - 20°C

reacting time: 20 hours

Maximum wavelength: 335 nm.

Experiment	Absorbance	Amount (mole)	Percentage yield
1	0.040	2.49 X 10^{-4}	71.00
2	0.041	2.49 X 10^{-4}	71.00
3	0.043	2.49 X 10^{-4}	71.00
			Mean 71.00

Table V   Oxidation of 2,3-butanediol with thallium (III) acetate

Mole ratio of thallium (III): 2,3-butanediol = 1 : 31

Refluxing temperature: 15 - 20°C

Reacting time: 20 hours

Maximum wavelength: 335 nm.

Experiment	Absorbance	Amount (mole)	Percentage yield
1	0.090	2.76×10^{-4}	73.69
2	0.084	2.62×10^{-4}	70.00
3	0.089	2.76×10^{-4}	73.69
			Mean 72.46

Table VI   Oxidation of 2,3-butanediol with thallium (III) sulphate

Mole ratio of thallium (III): 2,3-butanediol = 1 : 34

Refluxing temperature: 15 - 20°C

Reacting time: 20 hours

Maximum wavelength: 335 nm.

Experiment	Absorbance	Amount (mole)	Percentage yield
1	0.065	7.19×10^{-4}	75.87
2	0.060	6.86×10^{-4}	72.37
3	0.065	7.19×10^{-4}	75.87
			Mean 74.70

Table VII   Oxidation of 2,3-butanediol with thallium (III) nitrate

Mole ratio of thallium (III): 2,3-butanediol = 1 : 31

Refluxing temperature: 15 - 20°C

Reacting time: 20 hours

Maximum wavelength: 335 nm

Experiment	Absorbance	Amount (mole)	Percentage yield
1	0.021	2.54×10^{-4}	78.55
2	0.022	2.54×10^{-4}	78.55
3	0.023	2.54×10^{-4}	78.55
			Mean 78.55

Table VIII   Oxidation of ethylene glycol with lead (IV) acetate

Mole ratio of thallium: ethylene glycol = 1 : 16

Refluxing temperature: 15 - 20°C

Reacting time: 20 hours

Maximum wavelength: 330 nm.

Experiment	Absorbance	Amount (mole)	Percentage yield
1	0.526	8.70×10^{-4}	70.16
2	0.530	8.82×10^{-4}	71.17
3	0.529	8.80×10^{-4}	70.96
			Mean 70.76

Table IX Oxidation of ethylene glycol with thallium (III) chloride

Mole ratio of thallium (III): ethylene glycol = 1 : 57

Refluxing temperature: 15 - 20°C

Reacting time: 20 hours

Maximum wavelength: 330 nm.

Experiment	Absorbance	Amount (mole)	Percentage yield
1	0.050	3.14 X 10^{-4}	89.75
2	0.052	3.14 X 10^{-4}	89.75
3	0.049	3.14 X 10^{-4}	89.75
			Mean 89.75

Table X Oxidation of ethylene glycol with thallium (III) acetate

Mole ratio of thallium (III): ethylene glycol = 1 : 53

Refluxing temperature: 15 - 20°C

Reacting time: 20 hours

Maximum wavelength: 330 nm.

Experiment	Absorbance	Amount (mole)	Percentage yield
1	0.210	3.51 X 10^{-4}	93.75
2	0.212	3.52 X 10^{-4}	93.75
3	0.220	3.56 X 10^{-4}	94.86
			Mean 94.16

Table XI Oxidation of ethylene glycol with thallium (III) sulphate

Mole ratio of thallium (III):   ethylene glycol = 1 : 21

Refluxing time: 20 hours

Maximum wavelength: 330 nm.

Experiment	Absorbance	Amount (mole)	Percentage yield
1	0.420	9.12×10^{-4}	96.17
2	0.420	9.12×10^{-4}	96.17
3	0.420	9.12×10^{-4}	96.17
			Mean 96.17

Table XII Oxidation of ethylene glycol with thallium (III) nitrate

Mole ratio of thallium (III):   ethylene glycol =1 : 21

Refluxing temperature: 15 - 20 $^{\circ}$C
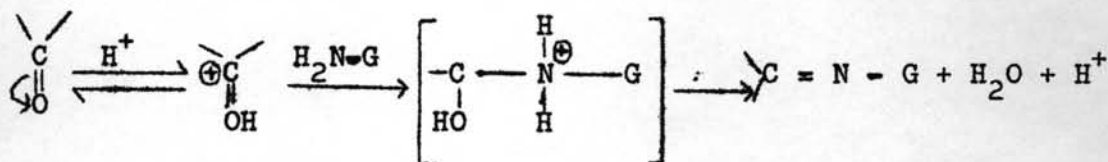
Reacting time: 20 hours

Maximum wavelength: 330 nm.

Experiment	Absorbance	Amount (mole)	Percentage yield
1	0.070	9.27×10^{-4}	98.71
2	0.070	9.27×10^{-4}	98.71
3	0.070	9.27×10^{-4}	98.71
			Mean 98.71

The analytical method was based on the condensation of the carbonyl compound with 2, 4-dinitrophenylhydrazine. Separation of the yellow product from the excess reagent was carried out by extracting with n-hexane which was a very effective solvent for the system. The absorbance of the solution was measured at 330 nm. for formaldehyde-2, 4-dinitrophenylhydrazone and 335 nm. for acetaldehyde-2, 4-dinitrophenylhydrazone. This procedure represents an improvement over existing methods because any reagent interference is eliminated. Besides, the spectra of the pure, neutral 2, 4-dinitrophenylhydrazone was highly reproducible. In addition, this method was very specific for carbonyl compound. The extraction of the hydrazone derivative with n-hexane has increased the specificity especially for the lower molecular weight carbonyl 2, 4-dinitrophenylhydrazone. The absorbances for a set of solutions and solvent determined according to the above procedure, were constant with $\pm$ 0.02 absorbance unit when the prepared solution was used within 4 - 5 days. Methanol was added in the separatory funnel before adding n-hexane in order to decrease the solubility of the formaldehyde or acetaldehyde-2, 4-dinitrophenylhydrazones in the aqueous-alcohol phase (see page 19). The addition of more water might be more effective, but rather serious emulsion difficulties resulted. The system was found to obey Beer's Law from 3 to 300 ppm. of the hydrazone derivative.

It is generally known that the condensation between carbonyl compound and ammonium derivative involves nucleophilic attack by the

basic nitrogen compound on carbonyl carbon. Protonation of carbonyl oxygen makes carbonyl carbon more susceptible to nucleophilic attack, in so far as the carbonyl compound is concerned, then addition will be favoured by high acidity as indicated in the following equation:-

$$\begin{array}{c} \diagdown \diagup \\ C \\ \parallel \\ O \end{array} \xrightarrow{\text{H}^+} \overset{\oplus}{C} \begin{array}{c} \diagdown \diagup \\ \parallel \\ OH \end{array} \xrightarrow{\text{H}_2\text{N-G}} \left[\begin{array}{ccc} & & \overset{H}{\underset{|}{\overset{|}{\overset{\oplus}{N}}}} \\ -C & \longleftarrow & \overset{|}{N} \\ \underset{HO}{|} & & \underset{H}{|} \end{array} G \right] \therefore \begin{array}{c} \diagdown \diagup \\ C \end{array} = N - G + H_2O + H^+$$

Thus the solution was made acid to ensure the right condition for the formation of the hydrazone derivative.

Before extracting, the solution must be neutralized (see page 19), since the presence of either proton or hydroxyl ion can shift the position of the maximum wavelength markedly. For the presence of the available proton, the explanation for wavelength shift is that proton can undergo protonation to the unshared pair electron of nitrogen resulting in pronounced effect on the position of the maximum wavelength.

On the other hand, in the presence of alkaline solution, an effect of bathochromic shift to visible region is observed. The disadvantage is on the decrease of the molar absorptivity rather rapidly with time evidently the coloured species formed is unstable and is as half as sensitive (36).

The analysis of the residue was carried out to ensure that the oxidation by the added oxidant took place as expected. Thallium (I) salts were detected after the reaction had been completed.

They were identified by means of characteristic microcrystalline white precipitate as benzoate or tartarate (37). When lead (IV) acetate was used as an oxidant the presence of lead (II) acetate was evident by the yellow precipitate upon the addition of potassium dichromate. Test with α-napthylamine showed the absence of thallium (III) salts, which indicated that they were entirely used up in the oxidation process.

4.1.2. Theoretical aspect

Oxidative yields and their formal potential

As mentioned in chapter I, the ease of the reduction of thallium (III) to thallium (I) salts vary greatly with the nature of anions present, Thus as shown in Table XIII , the presence of chloride ion stabilizes thallium (III) more than thallium(I) by the formation of complexes and therefore the potential is lowered. The published values of the reduction potentials of the oxidants employed in this work are given in the table XIII.

Table XIII The reduction potentials of various salts and
percentage yields of the hydrazone derivatives

Oxidant used	E_f^o in volt	Percentage yield of F-2,4-DNPH[*]	Percentage yield of A-2,4-DNPH[**]
lead (IV) acetate	-	70.76	63.60
thallium(III) chloride	0.789 (6)	89.75	71.00
thallium(III) acetate	0.9518 to 1.048(7)	94.16	72.46
thallium(III) sulphate	1.2207(8)	96.17	74.70
thallium(III) nitrate	1.2303(9)	98.71	78.55

[*] F-2, 4-DNPH stands for formaldehyde-2, 4-dinitrophenylhydrazone

[**] A-2, 4-DNPH stands for acetaldehyde-2, 4-dinitrophenylhydrazone

The study of these figures reveals that thallium (III) nitrate
should be the strongest oxidant whereas thallium (III) chloride is
the weakest while thallium (III) sulphate and thallium (III) acetate
are the second and the third with respect to the oxidizing power
respectively. The percentage yield of the products correlates very
well with the formal potentials that is the more the potentials are,
the more the products form. Since standard potential of lead (IV)
acetate in glacial acetic acid was not given in the Table of Latimer
(38), the tentative prediction of the oxidizing power can be made
based on the percentage yield of the product. The potential of
lead (IV) acetate should be lower than that of thallium (III) chloride.

Under the IUPAC convention, strong oxidizing agents such as thallium (III) nitrate have large positive electrode potentials with respect to hydrogen half-cell, it indicates that the oxidation reaction tends to occur spontaneously. The reverse is also true for the reduction process whereby thallium (III) nitrate is itself reduced more easily than thallium (III) acetate whose electrode potential is less positive.

Oxidative yields and the structures of two glycols

Following the mechanism of glycol oxidation with lead (IV) acetate proposing by Criegee (13), it is possible to propose the mechanism of glycol oxidation with thallium (III) salts by the similar pathway through cyclic ester intermediate as:-
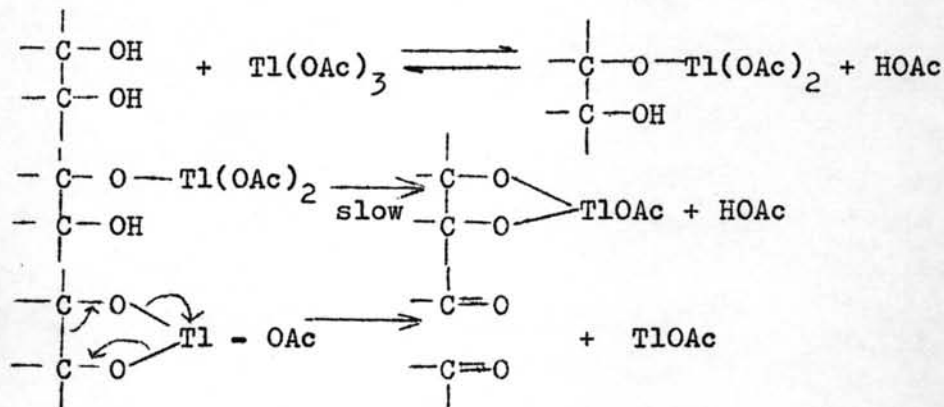
Considering the structure of ethylene glycol and 2,3-butanediol, the later has the additional two methyl groups. There is evidence that the methyl group is not an electron-releasing group when connected to saturated carbon, it either has no effect, or is slightly electron-withdrawing (39). The oxidative yields

from ethylene glycol are larger than that of 2,3-butanediol because the cyclic ester intermediate of ethylene glycol is more reactive than that of 2,3-butanediol. The difference in reactivity is due to steric effect. 2,3-butanediol is the larger molecule and the diol group is more hindered to the attack by thallium (III) salts, therefore its cyclic ester intermediate is not so stable resulting in the lower yield.

4.2. Conclusions

Although there are indications that the number of new oxidants suitable for the organic system is increasing, the new and more powerful ones are still sought for. From the results given in Table XIII, conclusion can be drawn that thallium (III) salts under investigation, namely thallium (III) chloride, thallium (III) acetate, thallium (III) sulphate and thallium (III) nitrate are the promising ones. They are stronger oxidants than lead (IV) acetate but mild enough to be used with 1,2-glycol which are know to be cleaved under a mild condition.

As far as the oxidation product yields are concerned the oxidizing power of the product are so good that olefins are often converted to glycol and then cleaved with lead (IV) acetate rather than being cleaved directly with ozone or dichromate or permanganate. This should be true also for thallium (III) salts which have been found in this work to be stronger oxidants than lead (IV) acetate. Lead (IV) acetate and thallium (III) salts are complementary since lead (IV) acetate

is best used in organic solvents while thallium (III) salts are used in aqueous solvents. Their major use may be employed a great deal in structural determination of the carbohydrates.(40).

The additional information resulting from this work is the approximate order of the reduction potential of lead (IV) acetate in glacial acetic acid which is unavailable in the literature The emf measurement will, however, give a strong proof whether the estimation is valid.

4.3. Suggestion for the further works

The work can be continued in various aspects, all of which are worth investigating. For example, it is interesting to measure the redox potential of lead (IV)/lead (II) electrode in glacial acetic acid in order to test the validity of the prediction made tentatively in this work. Aldehyde was the only product concerned here; therefore further investigation of other oxidative products may be carried out to see whether the glycol has been over oxidized in which case the investigation can be extended further to see the effect of temperature on the product distribution. Other instrumental techniques can also be introduced in the determination of the oxidative products such as gas chromatographic method.

APPENDIX I

Calibration curve of standard acetaldehyde-2, 4-dinitrophenyl-hydrazone (A-2, 4-DNPH)

Stock solution of 1.107×10^{-4} F of A-2, 4-DNPH was prepared in n-hexane and the following dilutions were made. The absorbance of the resulting solutions were measured at 335 nm.

ml of stock solution of A-2, 4-DNPH	Final volume (ml)	Absorbance
1	25	0.095
2	25	0.190
3	25	0.290
4	25	0.380
5	25	0.480
6	25	0.570
7	25	0.665
8	25	0.760
9	25	0.860
10	25	0.940

Molar absorptivity of A-2, 4-DNPH is 21,954 cm^2-mole^{-1}

Plot of absorbance versus concentration of A-2, 4- DNPH is shown in Figure IV.
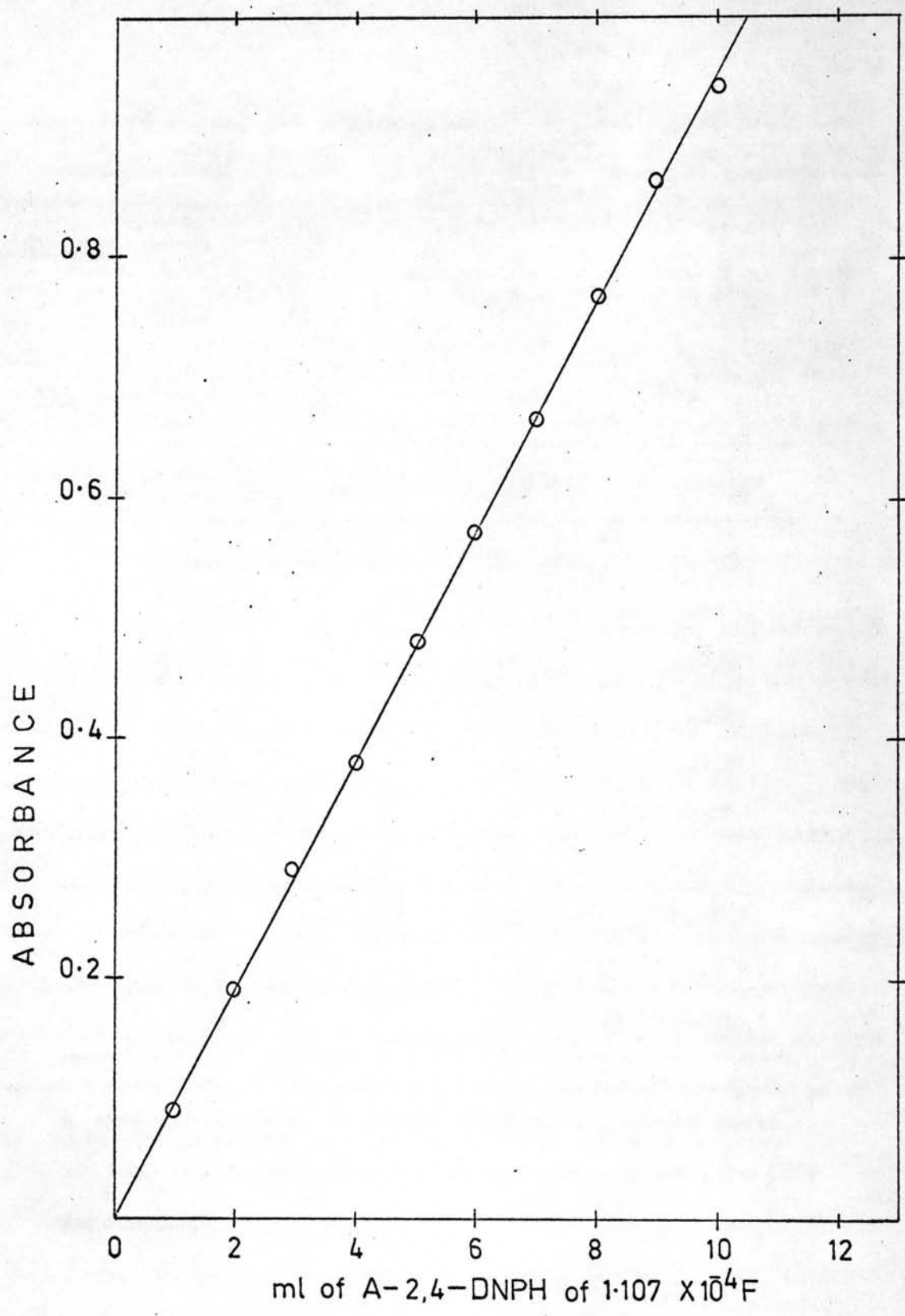
FIG. IV   CALIBRATION CURVE OF STANDARD
A-2,4-DNPH

APPENDIX II

Calibration curve of standard formaldehyde-2, 4-dinitrophenyl-hydrazone (F-2, 4-DNPH)

Stock solution of 3.314×10^{-5}F of F-2, 4-DNPH was prepared in n-hexane and the following dilutions were made. The absorbance of the solution were measured at 330 nm.

ml of stock solution of F-2, 4-DNPH	Final volume (ml)	Absorbance
2	25	0.051
4	25	0.110
6	25	0.154
8	25	0.201
10	25	0.249
12	25	0.309
14	25	0.347
16	25	0.383
18	25	0.446
20	25	0.505

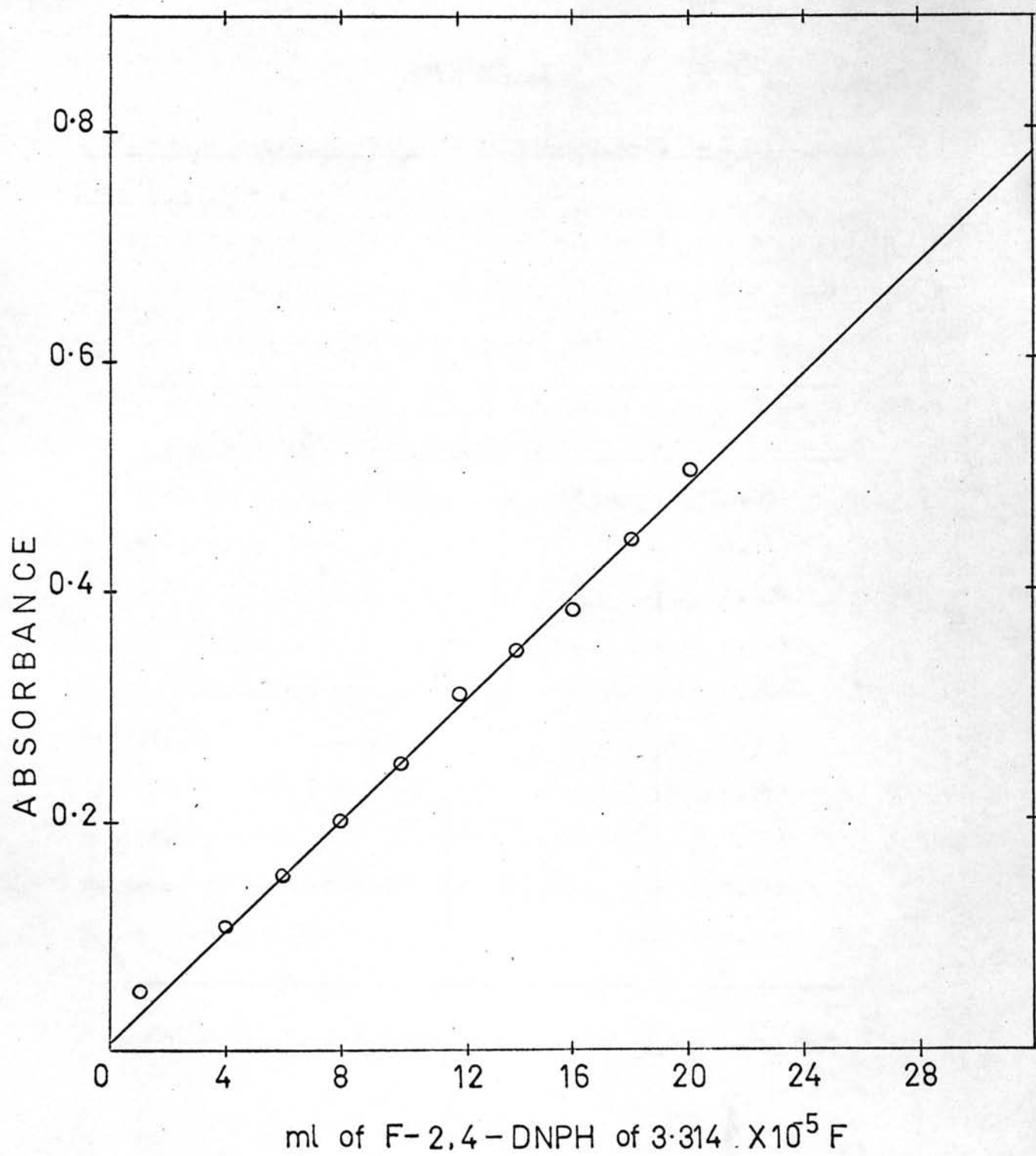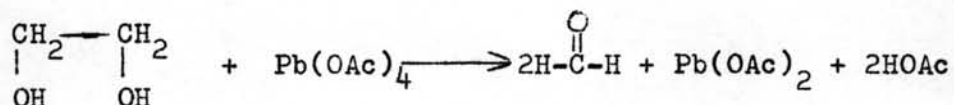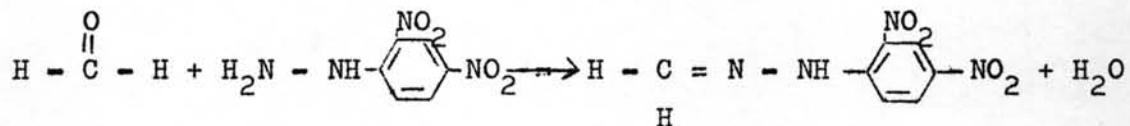Molar absorptivity of F-2, 4-DNPH is 18,894 cm^2-mole^{-1}

FIG V   CALIBRATION CURVE OF STANDARD-F-2,4-DNPH

APPENDIX III

Calculation of the oxidative yield

Ethylene glycol was oxidized by lead (IV) acetate yielding the following product.

$$CH_2\!-\!CH_2 \quad + \quad Pb(OAc)_4 \longrightarrow 2H\!-\!\overset{O}{\overset{\|}{C}}\!-\!H \; + \; Pb(OAc)_2 \; + \; 2HOAc$$
$$\underset{OH}{|} \quad \underset{OH}{|}$$

Formaldehyde reacted with 2,4-dinitrophenylhydrazine yielding the formaldehyde-2, 4-dinitrophenylhydrazone.

$$H - \overset{O}{\overset{\|}{C}} - H + H_2N - NH-\!\!\left\langle\!\!\!\begin{array}{c}NO_2\\ \\ \end{array}\!\!\!\right\rangle\!\!-NO_2 \longrightarrow H - \underset{H}{\overset{}{C}} = N - NH -\!\!\left\langle\!\!\!\begin{array}{c}NO_2\\ \\ \end{array}\!\!\!\right\rangle\!\!- NO_2 + H_2O$$

Theoretical yield was calculated from the amount of moles of lead (IV) acetate used.

Practical yield was calculated from the calibration curve of formaldehyde-2, 4-dinitrophenylhydrazone and converted to the original concentration by dilution factor.