THE MECHANISM OF NITRATION OF ANISOLE
IN THE
NITRIC ACID - ACETIC ANHYDRIDE
MIXTURES

A thesis presented for the
degree of Master of Science and Honours
in the University of Canterbury,
Christchurch, New Zealand.

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NOVEMBER, 1964

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ABSTRACT

A kinetic study of the nitration of anisole in acetic anhydride has been carried out. The concentrations of the reaction product were determined by ultraviolet spectroscopy. It was found that addition of acetic acid, sulphuric acid and lithium perchlorate accelerated the rate of reaction, but lithium nitrate retarded the reaction. The order dependence of the rate with respect to anisole is less than unity. The reaction is third order in nitric acid in the absence of added acetic acid, and second order in nitric acid in the presence of added acetic acid, and then first order in acetic acid. It is suggested that the non-integral order of anisole is the result of the simultaneous reactions, one of which is dependent on anisole concentration and the other independent of anisole. The reactive species in the two reactions are suggested to be two different protonated acetyl nitrates.

INTRODUCTION

Many preprarative nitrations involving nitric acid dissolved in acetic anhydride have been reported in literature. Kinetic studies showing the relative reactivity of a number of aromatic substrates and their halogen derivatives towards nitric acid in acetic anhydride have been made. Thus Tronov et.al.[1] found that aromatic substrates containing electron-donating groups nitrated faster than those aromatic substrates containing electron-withdrawing groups. Little,however, is known about the detailed mechanisms of nitration in nitric acid-acetic anhydride mixtures.

Such lack of knowledge of the details of the mechanism of nitration in nitric acid-acetic anhydride mixtures arises in part from uncertainty as to the nature and extent of the reaction between acetic anhydride and nitric acid. Attempts by Cohen and Wibaut[2] and by Paul[3] to elucidate the mechanism of nitration of benzene were unlikely to be successful when they assumed that nitric acid was present in acetic anhydride at stoichiometric concentration. A very large amount of evidence [4,5,6,7] now points to the fact that the reaction between nitric acid and excess acetic anhydride,leading to the formation of acetyl nitrate, is very rapid and goes virtually to completion :

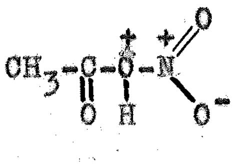
$$Ac_2O \quad + \quad HNO_3 \longrightarrow AcOH \quad + \quad AcONO_2 \qquad (1)$$

There is in fact some conflict between the experimental results of Cohen and Wibaut and of Paul. Cohen and Wibaut found a third order dependence on (stoichiometric) nitric acid of the rate of nitration of benzene in acetic anhydride solution. Paul claimed a second (2.2) order dependence. Both found a first order dependence on the benzene concentration. It appears then that little reliance can be placed on Paul's conclusion that the nitrating species is nitronium ion, NO_2^+ .

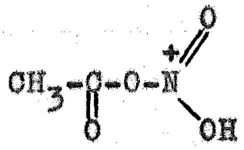
More recently it has been shown by Wright[8] that treatment of o-xylene and other methyl-substituted benzenes with nitric acid in acetic anhydride leads to the formation of acetoxy as well as nitro derivatives. Thus in the nitration of o-xylene with nitric acid in acetic anhydride it was found that in addition to 3-and 4-nitro-o-xylenes, 3,4-dimethylphenyl acetate was formed and it was a major product. Variation in the amount of nitric acid and addition of acetic acid did not affect the product composition. Addition of sulphuric acid which had a marked accelerating effect on the rate of nitration in acetic anhydride caused a very slight increase in the yield of acetoxy product. Sulphuric acid, therefore, catalysed the acetoxylation reaction. Furthermore, o-xylene was not acetoxylated when nitric acid was replaced by an equivalent amount of sulphuric acid. On the basis of these results, it was proposed that the acetoxylating species was the protonated acetyl nitrate.

The above suggestion is substantiated by Read's[9] work on the kinetics of nitration of o-xylene in nitric acid-acetic anhydride mixtures. He found that the acetoxylation: nitration rate ratio was constant throughout each run and from run to run under different conditions as when the concentrations of nitric acid and o-xylene were varied. This rate ratio was also unchanged in the presence of added acetic acid, sulphuric acid, and lithium nitrate even though the individual rates altered markedly. These results lead to the conclusion that either the same reactive species is responsible for both acetoxylation and nitration or, that separate acetoxylating and nitrating species must have a common precursor. This single species, or precursor to separate species, must contain both acetoxylating and nitrating groups and acetyl nitrate was suggested to be the most probable such entity. That acetyl nitrate is not the active reactive species was supported by the fact that the reaction was found to be zeroth-order in o-xylene concentration for both acetoxylation and nitration. Preformed acetyl nitrate (from nitric acid and acetic anhydride, cf. equation (1)) would react with o-xylene in a reaction whose rate must be dependent on the o-xylene concentration. Furthermore, the accelerating effect on the rates due to the presence of minute amount of added sulphuric acid indicated that the reactive species must be protonated, either formed from a protonated precursor, or formed in a protonation reaction. In each of these cases an essential step would seem to involve the reaction between acetyl nitrate and acid.

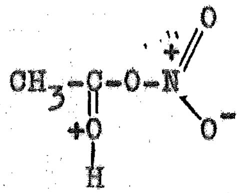
When m-xylene was used as the substrate the sum of rates of acetoxylation plus nitration was the same as that for o-xylene, but the individual rates differed markedly. Read therefore concluded that the acetoxylating and nitrating species were identical, for only then could he explain the observations that the ratio of the rate of acetoxylation to nitration is dependent on the nature of the substrate but is independent of the concentration of a particular substrate. Of possible acetoxylating and nitrating species, formed from acetyl nitrate and acid, only protonated acetyl nitrate could be both. It was therefore concluded that the acetoxylating species was the nitrating species and that this was one of the following protonated acetyl nitrates :



(I)



(II)



(III)

The reactive species in nitration and acetoxylation of o-xylene in nitric acid-acetic anhydride mixture is then protonated acetyl nitrate which is formed in a slow step. On this assumption the overall mechanism is written as follows:

$$HNO_3 + Ac_2O \rightleftharpoons AcONO_2 + AcOH$$

$$AcONO_2 + HA \xrightarrow{slow} AcONO_2H^+A^-$$

$$AcONO_2H^+A^- + ArH \xrightarrow{fast} ArOAc + HNO_2 + HA$$

$$AcONO_2H^+A^- + ArH \xrightarrow{fast} ArNO_2 + AcOH + HA$$

In confirmation of this mechanism Read showed that the reaction was zeroth-order in o-xylene and third order in nitric acid, in the absence of added acetic acid, and second order in nitric acid and first order in acetic acid when acetic acid was added. In addition he demonstrated that, as would be predicted from the mechanism, sulphuric acid exerted a marked catalytical effect and lithium nitrate was an anticatalyst. It was not possible to discriminate between the three protonated acetyl nitrates on the basis of the kinetic results. Read suggested that the least reactive species(present in highest concentration),that protonated on the carbonyl group,was the least likely active entity since it seemed unlikely that protonation on the carbonyl group would be slow enough to be rate-determining.

The question arises as to what happens when a more active substrate than o-xylene is used. From Wright's findings[8] as the substrate is made more activated, i.e. more methyl groups are added, the yield of acetoxy compounds increases, at least in the unhindered positions. Now anisole is rather more reactive towards electrophiles than is o-xylene. σ^+_{4-OMe} is -0.764[10] whereas $\sigma^+_{4-Me} + \sigma^+_{3-Me} = -0.375$[10]. Since ρ for nitration is -6.5[10] anisole should be substituted in the 4-position $10^{-6.5(-0.764 + 0.375)} = 340$ times as fast as o-xylene. It seems unlikely that acetoxylation of anisole does occur since no acetoxy compound, formed from the reaction of anisole with nitric acid, has been reported in the literature. An explanation of the absence of acetoxylation of anisole must be sought in terms of a different mechanism of nitration to that which occurs in the case of o-xylene, where reaction with a particular protonated acetyl nitrate leads to both acetoxylation and nitration. In the work described in this thesis the kinetics of nitration of anisole in acetic anhydride have been investigated in an attempt to elucidate the mechanism of the reaction.

EXPERIMENTAL

Melting points and boiling points are uncorrected. Unless otherwise stated, reference values are given in Beilstein " Handbuch der Organischer Chemie ".

Preparation and Purification of Compounds

Anisole

Anisole(Hopkin and Williams Ltd.)(200 ml.) was washed several times with 1N sodium hydroxide and then with distilled water until the washings were neutral to litmus. After drying over anhydrous magnesium sulphate, the anisole was distilled and a middle fraction was collected,b.p. 152°(155°).

p-Nitroanisole

The method used was similar to that of Vogel[11]. Sodium hydroxide pellets(11 g.) were dissolved in water(100 ml.) and p-nitrophenol (35.5 g.) was added. Dimethyl sulphate (24 ml.) was then added dropwise, with shaking. The mixture was refluxed for an hour. It was then allowed to cool and water (100 ml.) was added. The precipitate formed was washed with 4N sodium hydroxide and then with distilled water. It was recrystallised twice from absolute alcohol, m.p. 53.5°-54.5° (54°).

o-Nitroanisole

The method used was similar to that described above except that o-nitrophenol was used. After refluxing, the mixture of o-nitrophenol, sodium hydroxide, and dimethyl sulphate was cooled and water(100 ml.) was added. Two layers were formed. The lower layer was washed with water. Carbon tetrachloride was added and the solution was washed with dilute sulphuric acid and then with water until the washings were neutral. After drying over silica gel and removal of carbon tetrachloride the mixture was distilled under reduced pressure. The distillate, collected at 92°-96°/18 mm. was washed with 0.1N sodium hydroxide until a red colour no longer formed in the aqueous layer. The organic layer was then washed with water, dried and distilled under reduced pressure. The yellow distillate was collected at 106°-108°/20 mm.(277°/760 mm.).

Acetic anhydride

Acetic anhydride(Riedel de Haen,R.G.) was fractionated under reduced pressure through a six foot column packed with helices. The first 10% of the distillate which contained most of the acetic acid impurity was discarded and the pure acetic anhydride was collected at 60°/55 mm.[8].

Acetic acid

Acetic acid(B.D.H.,AnalaR) of a purity not less than 99.6% was used without purification.

o-Xylene

o-Xylene(b.D.H.) was used without further purification.

2-Propanol

2-Propanol(Shell Co.) was used without further purification.

Carbon tetrachloride

Carbon tetrachloride(B.D.H.,AnalaR and Riedel de Haen, R.G.) was used without further purification.

Lithium carbonate

Lithium carbonate(B.D.H.) was dried in oven at 140° for several days and was used without further purification.

Sodium hydroxide

Sodium hydroxide pellets(B.D.H.,AnalaR) were used without further purification.

Sulphuric acid

Sulphuric acid(Riedel de Haen,R.G.), 95-97%, $d_{20}1.83$, was used without further purification.

Crystal violet

Crystal violet(B.D.H.,AnalaR) was used without further purification.

Nitric acid

Nitric acid was purified by distilling a mixture of one volume of fuming nitric acid(B.D.H.,AnalaR, s.g. =1.5) and two volumes of 98% sulphuric acid(B.D.H.,AnalaR) under reduced pressure. The colourless distillate was collected in a trap cooled in a mixture of dry ice and acetone. The first 10% of the distillate was discarded. It has previously been shown[8] that the acid prepared in this way analysed as 99.8 ± 0.3%.

Preparation of Reagents

Sodium hydroxide

Sodium hydroxide(B.D.H.,AnalaR) pellets were dissolved in distilled water to give a 4N solution.

Acetic acid

Acetic acid(B.D.H.,AnalaR) was dissolved in purified acetic anhydride to give a 1M solution.

Sulphuric acid

The required concentration of sulphuric acid solution was prepared by dissolving an appropriate amount of sulphuric acid(Riedel de Haen,R.G.) in purified acetic anhydride.

Lithium nitrate

Lithium carbonate(B.D.H.)(0.0190g.) was dissolved in AnalaR glacial acetic acid(15g.) and the resulting solution was diluted with acetic anhydride(Riedel de Haen,R.G.) to 25 ml.. After diluting the solution with 1M acetic acid solution, distilled nitric acid was added to produce the required lithium nitrate solution.

Lithium perchlorate

Lithium carbonate(B.D.H.)(0.0753g.) and perchloric acid (B.D.H.,AnalaR)(0.3546g.) were separately dissolved in glacial acetic acid(B.D.H.,AnalaR) and were made up to 50 ml.. 3 ml. of the lithium acetate solution were then titrated with perchloric acid solution to the basic side of the end-point using crystal violet as the indicator. The lithium acetate and perchloric acid solutions were then mixed in the appropriate proportions by volume and the mixture was diluted with acetic anhydride(Riedel de Haen,R.G.) to produce a solution containing 1M acetic acid and the required concentration of lithium perchlorate.

Crystal violet

Crystal violet(1g.) was dissolved in glacial acetic acid(100 ml.).

Determination of the Extinction Coefficient

Kinetics of nitration of anisole were followed by UV specrophotometric analysis of the reaction products. 2-Propanol was used as the solvent. It was verified that the solvent did not absorb above 270 mμ.

Gas chromatographic analysis(Pye Argon Chromatograph) of product mixtures indicated that o- and p-nitroanisoles were the only two products formed under our conditions (anisole was in excess of the nitric acid). Griffiths et.al.[12] have measured the isomer distribution obtained on the nitration of anisole with nitric acid in acetic anhydride as being 73% o- and 27% p-nitroanisoles. The spectra of pure o- and p-nitroanisoles in 2-propanol were determined and the extinction coefficients at the wavelength of maximum absorption(307 mμ)of the nitration product mixture were 2,100 and 10,380 l.mole^{-1}cm.$^{-1}$ respectively. From these values and the isomer distribution determined by Griffiths et.al. the extinction coefficient of the product mixture at 307 mμ was calculated to be 4337 l.mole^{-1}cm.$^{-1}$.

Kinetic method

A 25 ml. volumetric flask containing 10 ml. of acetic anhydride was weighed and an appropriate amount of distilled nitric acid was added. The flasked was weighed again and the volume was made up to 25 ml. with acetic anhydride. Volumetric dilution of this standard solution would give a nitric acid solution of the required concentration for a kinetic run. Only freshly prepared nitric acid solutions were used for kinetic runs. A soultion of anisole in acetic anhydride was prepared similarly. The solutions of nitric acid and anisole were placed in a thermostated water bath which was maintained at 25.00 ± 0.03° by means of a mercury-toluene regulator and an electric heater. After 30 minutes equal volumes (20 ml.) of the solutions were mixed and were shaken to ensure homogeneity. Eight samples (4 ml. each) of the reaction mixture were withdrawn at suitable time intervals and were diluted to 100 ml. with 2-propanol. The spectrum of each solution was scanned from 295 mμ to 315 mμ using the Beckman DK-2A spectrophotometer. 2-Prppanol was used in the reference cell. Cells of 1 cm. path length were used. From the optical densities of the solutions at 307 mμ ($\lambda_{max.}$) the concentration of the product mixture was calculated. It was verified that the separate solutions of nitric acid and anisole in acetic anhydride, when diluted as above with 2-propanol, showed no absorption at 307 mμ.

In the kinetic runs with o-xylene the aliquots of the reaction mixture were quenched in 50 ml. of 4N sodium hydroxide and were extracted (5x4 ml.) with AnalaR carbon tetrachloride[8]. The combined carbon tetrachloride layers were diluted with 2-propanol and the spectrum was run(2-propanol in the reference cell) on the Beckman DK-2A spectrophotometer. The alkaline layer was centrifuged and diluted to 100 ml. with distilled water. The spectrum of the solution was also determined (distilled water reference). From the optical densities of the carbon tetrachloride extracts at 300 mμ and of the alkaline extracts at 295 mμ the concentrations of the products, nitroxylenes and phenyl acetate, could be evaluated. The extinction coefficients used for these calculations were those measured by Read[8]:

$$\varepsilon_{\text{nitroxylenes}} = 3673 \text{m}\mu \text{ , } \quad \varepsilon_{\text{phenoxide}} = 4912 \text{ m}\mu .$$

RESULTS

Tables and Graphs

The following Tables and Graphs represent the typical runs carried out under different conditions.

From the proposed mechanism of the reaction (p. 44) an integrated rate equation $F(m) = 1 + \alpha t$ is derived. α is a constant and $F(m)$ has the form

$$F(m) = \frac{1}{1-m} + \frac{1-a}{2(1+a)} \ln(1+m) - \frac{1-3a}{2(1-a)} \ln(1-m) - \frac{2a^2}{1-a^2} \ln(1-am)$$

where m is the fraction of nitric acid consumed and a is the ratio of the initial concentrations of nitric acid : anisole. Table I represents the data of a typical run and the function $F(m)$ is plotted against time(t) in Graph I.

However, for most runs only initial rates (up to 20% reaction) were measured and in such cases an approximate form of the function $F(m)$ was used : $F(m) = \frac{1}{1-m}$. In a few cases, in particular for runs No. 3 to 9 used to derive the order with respect to anisole (Graph III) the function $F(m) = \frac{1}{1-m} + m$ was employed. A typical example of these runs is shown in Table II and Graph III. Within experimental error the two approximate expressions for $F(m)$ lead to identical rate constants where allowance is made for the factor of 2 difference in the slopes of the F(m) vs t plots. Order plots showing the dependence of the rate on the concentrations of nitric acid and acetic acid are shown in Graphs IV and V.

The effects of added acetic acid, sulphuric acid, lithium nitrate and lithium perchlorate can be observed from the data recorded in Tables III, IV, V and VI respectively and their respective F(m) vs t plots are shown in Graphs VI, VII, VIII and IX.

Results of o-xylene runs in purified and unpurified acetic anhydride are collected in Tables VII and VIII respectively and are plotted in Graph X.

Table IX shows the slopes of the order plots of anisole, nitric acid and acetic acid in acetic anhydride and in purified acetic anhydride containing added acetic acid.

The rates of all the reactions are summarised in Table X.

TABLE I

Nitration of Anisole in pure Acetic Anhydride

$[HNO_3] = 0.0511$ M $\qquad f = 150$

$[\text{Anisole}] = 0.201$ M $\qquad \mathcal{E}_m = 4337$ at 307 mμ

$$F(m) = \frac{1}{1-m} + \frac{1-a}{2(1+a)}\ln(1+m) - \frac{1-3a}{2(1-a)}\ln(1-m) - \frac{2a^2}{1-a^2}\ln(1-am)$$

t/min.	D.	$C_m \times 10^2$	m	F(m)
3	0.040	0.1383	0.0271	1.041
6	0.065	0.2250	0.0441	1.068
9	0.097	0.3355	0.0657	1.103
12	0.124	0.4288	0.0840	1.133
15	0.150	0.5188	0.1016	1.163
20	0.190	0.6571	0.1287	1.210
25	0.223	0.7712	0.1511	1.251
30	0.252	0.8715	0.1707	1.289
35	0.283	0.9787	0.1917	1.330
40	0.310	1.0721	0.2100	1.368
70	0.442	1.5280	0.2993	1.573
100	0.545	1.8831	0.3689	1.765
130	0.636	2.2000	0.4310	1.970
160	0.715	2.4730	0.4845	2.181
190	0.776	2.6820	0.5254	2.371

Initial slope of F(m) vs t plot is 1.7×10^{-4} sec.$^{-1}$.

$$a = \frac{[HNO_3]}{[\text{Anisole}]}$$

f = dilution factor

C_m = concentration of reaction products

D. = optical density at 307 mμ

$$m = \frac{[\text{reaction products}]}{\text{initial } [HNO_3]}$$

= fraction of reaction

$\mathcal{E}_m$ = extinction coefficient of reaction products

TABLE II

Nitration of Anisole in Acetic Anhydride

$[HNO_3] = 0.0518$ M $\qquad f = 150$

$[\text{Anisole}] = 0.101$ M $\qquad \varepsilon_m = 4337$ at 307 $m\mu$

$F(m) = \frac{1}{1-m} + m$

t/min.	D.	$C_m \times 10^2$	m	$\frac{1}{1-m} + m$
5	0.115	0.3966	0.0766	1.160
10	0.199	0.6871	0.1328	1.286
15	0.273	0.9447	0.2825	1.406
20	0.329	1.1380	0.2199	1.502
25	0.391	1.3530	0.2614	1.615
30	0.443	1.5330	0.2962	1.717
35	0.483	1.6690	0.3225	1.799
40	0.524	1.8110	0.3500	1.889

Slope of F(m) vs t plot is 4.6×10^{-4} sec.$^{-1}$

TABLE III

Nitration of Anisole in pure Acetic Anhydride with added Acetic acid

$[HNO_3] = 0.0517$ M $\qquad f = 150$

$[\text{Anisole}] = 0.320$ M $\qquad \varepsilon_m = 4337$ at 307 $m\mu$

$[AcOH] = 1.00$ M $\qquad F(m) = \frac{1}{1-m}$

t/min.	D.	$C_m \times 10^2$	m	$\frac{1}{1-m}$
2	0.131	0.4554	0.0882	1.097
4	0.253	0.8733	0.1691	1.204
6	0.358	1.2390	0.2399	1.316
8	0.438	1.5130	0.2929	1.414
10	0.517	1.7870	0.3460	1.529
12	0.575	1.9890	0.3851	1.626
14	0.633	2.1900	0.4240	1.736
16	0.692	2.3920	0.4631	1.863

Slope of F(m) vs t plot is 8.68×10^{-4} sec.$^{-1}$

TABLE IV

Nitration of Anisole in pure Acetic Anhydride with added sulphuric acid

$[HNO_3]$ = 0.0506 M f = 150

[Anisole] = 0.402 M ε_m = 4337 at 307 mμ

$[H_2SO_4]$ = 0.00 M $F(m) = \frac{1}{1-m}$

t/min.	D.	C_m x10^2	m	$\frac{1}{1-m}$
5	0.083	0.2882	0.0569	1.060
10	0.150	0.5188	0.1025	1.114
15	0.217	0.7493	0.1480	1.174
20	0.267	0.9222	0.1822	1.223
25	0.313	1.0840	0.2141	1.272
30	0.361	1.2480	0.2465	1.327
35	0.405	1.4010	0.2767	1.383
40	0.448	1.5480	0.3058	1.441

Slope of F(m) vs t plot is 1.81 x 10^{-4}sec.$^{-1}$

$[HNO_3]$=0.0504 M f= 150

[Anisole] = 0.402 M ε_m = 4337 at 307 mμ

$[H_2SO_4]$ = 4.04 x10^{-5} M $F(m) = \frac{1}{1-m}$

t/min.	D.	C_mx10^2	m	$\frac{1}{1-m}$
2	0.127	0.4381	0.0869	1.095
4	0.267	0.9222	0.1829	1.224
6	0.393	1.3600	0.2697	1.369
8	0.478	1.6540	0.3280	1.488
10	0.582	2.0120	0.3990	1.664
12	0.662	2.2880	0.4538	1.831
14	0.725	2.5070	0.4972	1.989
16	0.815	2.8190	0.5591	2.268

Slope of F(m) vs t plot is 13.21 x 10^{-4}sec.$^{-1}$

TABLE V

Nitration of Anisole in Acetic Anhydride with added Lithium Nitrate and Acetic Acid

$[HNO_3]$ = 0.0545 M   f= 150

[Anisole] = 0.4013 M ε_m = 4337 at 307 mμ

$[LiNO_3]$ = 1.03×10^{-3} M $F(m) = \frac{1}{1-m}$

[AcOH] = 1.001 M

t/min.	D.	$C_m \times 10^2$	m	$\frac{1}{1-m}$
3	0.055	0.1902	0.0349	1.036
6	0.108	0.3747	0.0688	1.074
9	0.162	0.5608	0.1029	1.115
12	0.205	0.7090	0.1301	1.150
15	0.249	0.8611	0.1580	1.188
18	0.292	1.0090	0.1852	1.227
21	0.329	1.1400	0.2092	1.265
24	0.368	1.2720	0.2334	1.305

Slope of F(m) vs t plot is 2.10×10^{-4} sec.$^{-1}$

TABLE VI

Nitration of Anisole in Acetic Anhydride with added Lithium Perchlorate and Acetic Acid

$[HNO_3]$= 0.0521 M   f = 150

[Anisole] =0.4014 M ε_m = 4337 at 307 mμ

$[LiClO_4]$ = 1.20×10^{-3}M $F(m) = \frac{1}{1-m}$

[AcOH] = 1.001 M

t/min.	D.	$C_m \times 10^2$	m	$\frac{1}{1-m}$
3	0.434	1.5020	0.2886	1.406
6	0.746	1.5790	0.4955	1.982
9	0.859	2.9710	0.5708	2.330
12	0.959	3.3170	0.6373	2.757
15	1.048	3.6260	0.6966	3.296
18	1.097	3.7960	0.7293	3.694
21	1.131	3.9110	0.7514	4.023
24	1.193	4.1270	0.7929	4.829

Slope of F(m) vs t plot is 25.40×10^{-4}sec.$^{-1}$

TABLE VII

Concurrent Acetoxylation and Nitration of o-Xylene in Acetic Anhydride. Zero Order Dependence of the Rates of Acetoxylation and Nitration on the o-Xylene Concentration

$[\text{o-Xylene}] = 0.414$ M

$[HNO_3] = 0.0537$ M

$F(m) = \frac{1}{1-m}$

$f = 50$

$\varepsilon_N = 3673$ at 300 mμ

$D(\text{blank}) = 0.065$

$D_N = D - D(\text{blank})$

t/min.	D_N	m	$\frac{1}{1-m}$
5	0.094	0.0416	1.043
10	0.204	0.0907	1.100
15	0.256	0.1138	1.128
20	0.320	0.1423	1.166
25	0.381	0.1694	1.204
30	0.437	0.1944	1.241
35	0.570	0.2534	1.339
40	0.533	0.2370	1.311

Slope of F(m) vs t plot is 1.28×10^{-4} sec.$^{-1}$

D = measured optical density of carbon tetrachloride extract

D_N = optical density of the nitroxylene mixture in alcohol

f = dilution factor

ε_N = extinction coefficient of nitroxylene mixture

TABLE VIII

Concurrent Acetoxylation and Nitration of o-Xylene in purified Acetic Anhydride. Zero Order Dependence of the Rates of Acetoxylation and Nitration on the o-Xylene Concentration

[o-Xylene] = 0.414 M

$[HNO_3]$ = 0.0506 M

$F(m) = \frac{1}{1-m}$

f = 10

ε_N = 3673 at 300 mμ

D(blank) = 0.012

D_N = D-D(blank)

t/min.	D_N	m	$\frac{1}{1-m}$
5	0.123	0.0116	1.012
10	0.258	0.0244	1.025
15	0.378	0.0357	1.037
20	0.514	0.0486	1.051
26	0.640	0.0605	1.064
30	0.740	0.0699	1.075
35	0.770	0.0728	1.079
40	0.865	0.0818	1.089

Slope of F(m) vs t plot is 0.41 x 10^{-4}sec.$^{-1}$

TABLE IX

Summary of Slopes of Order Plot

Acetic Anhydride	[AcOH]	[Anisole]	$[HNO_3]$	Slopes of Order Plot
Purified	1M	0.05-0.40 M	0.05 M	0.75 ± 0.13
Purified	1M	0.4M	0.022-0.101M	2.49 ± 0.09
Purified	0.35-2.22M	0.4M	0.05M	1.03 ± 0.12
Purified	—	0.4M	0.011-0.098M	2.94 ± 0.13
Unpurified	—	0.025-0.203M	0.05M	0.76 ± 0.13

Summary of Rates

TABLE X

Run No.	[HNO_3](M)	[Anisole](M)	[AcOH](M)	Ratex10^6 mole l^{-1} sec.$^{-1}$	kx10^2 l^3 mole^{-3} sec.$^{-1}$
1	0.0511	0.2010	—	5.97	22.2
2	0.0510	0.4017	—	4.90	9.2
3	0.0562	0.0251	—	5.56	124.92
4	0.0585	0.0517	—	9.48	91.58
5	0.0525	0.1006	—	12.6	86.56
6	0.0526	0.1488	—	14.67	67.74
7	0.0515	0.2028	—	19.73	71.21
8	0.0518	0.1014	—	10.72	76.05
9	0.0516	0.2009	—	23.22	84.12
10	0.0334	0.3940	—	3.88	26.4
11	0.0212	0.0500	—	0.95	200.27
12	0.0208	0.0500	—	0.92	203.40
13	0.1027	0.3940	—	47.24	10.65
14	0.0735	0.3940	—	14.77	9.44
15	0.0111	0.3991	—	0.16	29.30
16	0.0330	0.3991	—	2.05	14.27
17	0.0536	0.3991	—	6.86	11.15
18	0.0665	0.3991	—	9.98	8.50
19	0.0977	0.3991	—	42.99	11.53
20	0.0804	0.4109	—	32.16	15.06
21	0.0518	0.2000	—	26.94	96.90
22	0.0163	0.4109	—	0.23	12.82
23	0.0244	0.4109	—	0.81	13.49
24	0.0481	0.4002	0.3489	16.45	4.48
25	0.0529	0.4371	2.2218	117.54	4.23
26	0.0549	0.4215	0.8888	43.98	3.67
27	0.0574	0.3802	1.3856	81.51	4.07
28	0.0548	0.4027	1.7147	71.24	3.33
29	0.0534	0.3905	1.8498	101.46	4.79
30	0.0529	0.4026	1.4058	55.12	3.35
31	0.0512	0.3998	1.0005	47.41	4.30
32	0.0517	0.3998	1.0005	48.08	4.28
33	0.0516	0.3198	1.0005	44.79	5.00
34	0.0514	0.1999	1.0005	22.82	4.11
35	0.0514	0.1999	1.0005	25.60	4.61
36	0.0513	0.1004	1.0005	19.49	7.01
37	0.0514	0.0502	1.0005	9.36	6.71
38	0.0767	0.4040	1.0133	122.72	4.74
39	0.1012	0.4040	1.0133	281.13	6.10
40	0.0550	0.4040	1.0133	45.32	3.47
41	0.0313	0.4040	1.0133	12.36	2.99
42	0.0116	0.4040	1.0133	1.52	2.73

Run No.	$[HNO_3]$(M)	[Anisole](M)	[AcOH] (M)	Rate x10^6 mole 1^{-1} sec.$^{-1}$	k x10^2 1^3 mole^3 sec.$^{-1}$
43	0.0797	0.4041	1.0100	165.22	5.91
44	0.0532	0.4041	1.0100	44.32	3.65
45	0.0611	0.4040	1.0100	95.32	5.90
46	0.0215	0.4040	1.0100	6.58	3.41
47	0.0527	0.4040	1.0100	41.05	3.44
48	0.0118	0.4004	1.0095	1.77	3.11
49	0.0309	0.4004	1.0024	12.95	3.28
50	0.0504	0.4004	1.0024	42.49	3.97
51	0.0721	0.4004	1.0024	89.26	3.99
52	0.1006	0.4004	1.0024	214.78	4.80

Run No.	$[HNO_3]$(M)	[Anisole](M)	$[H_2SO_4]$(M) x 10^5	Rate x10^6 mole 1^{-1} sec.$^{-1}$
53	0.0506	0.4017	—	9.16
54	0.0503	0.4017	—	8.45
55	0.0506	0.4017	4.0	51.97
56	0.0504	0.4017	4.0	51.76
57	0.0507	0.4008	1.0	15.36
58	0.0509	0.4008	1.0	14.91

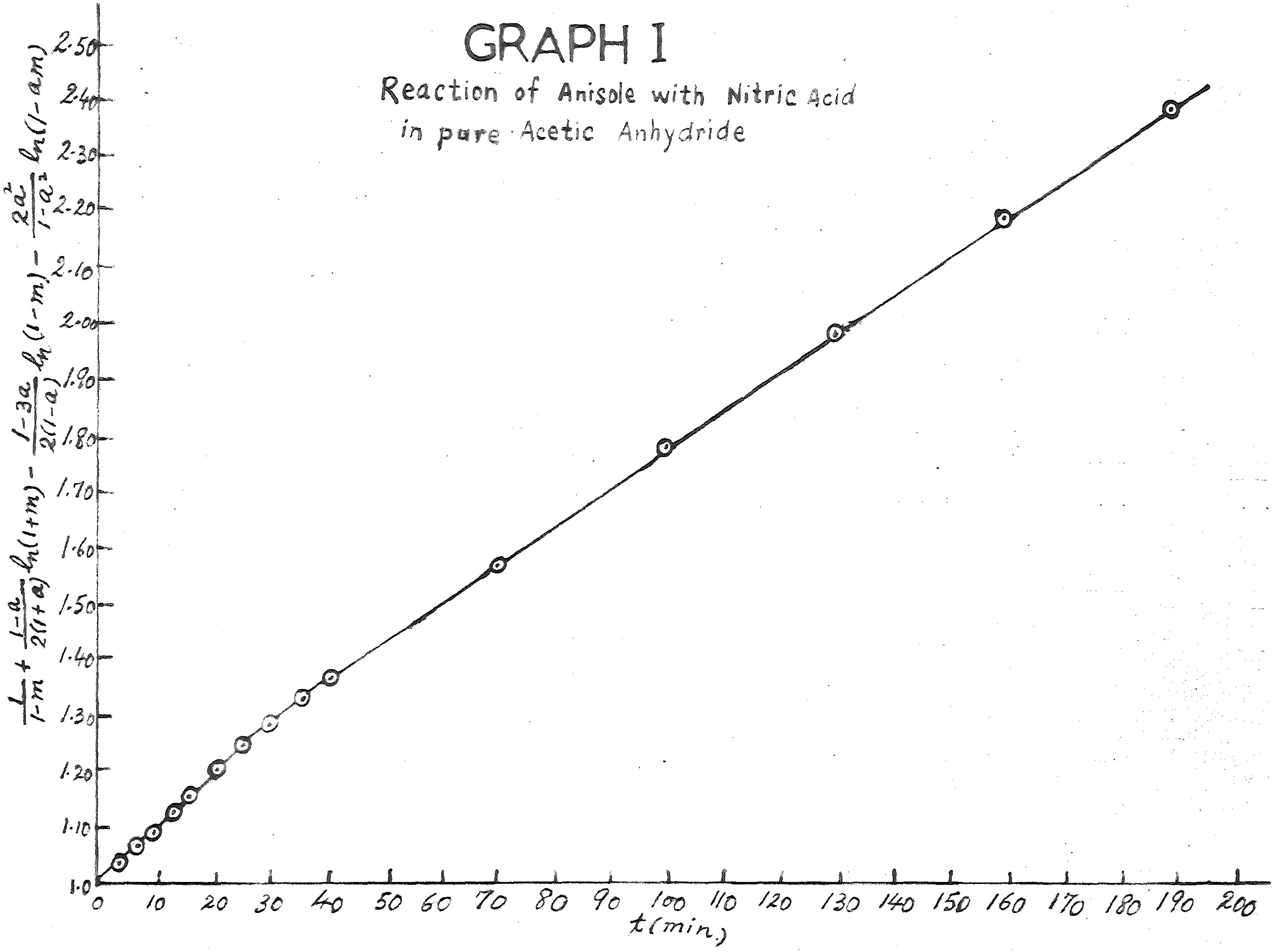
Run No.	$[HNO_3]$(M)	[Anisole](M)	[AcOH](M)	$[LiNO_3]$(M) x10^3	Rate x10^6 mole 1^{-1} sec.$^{-1}$
59	0.0510	0.4013	1.0031	1.03	10.51
60	0.0545	0.4013	1.0031	1.03	11.45
61	0.0506	0.2006	1.0031	1.03	5.57
62	0.0503	0.1003	1.0031	1.03	2.46
63	0.0517	0.4013	1.0014	4.14	7.70
64	0.0508	0.4013	1.0014	0.83	13.72

Run No.	$[HNO_3]$(M)	[Anisole](M)	[AcOH](M)	$[LiClO_4]$(M) x10^3	Rate x10^5 mole 1^{-1} sec.$^{-1}$
65	0.0521	0.4014	1.0010	1.21	13.23
66	0.0521	0.4014	1.0010	1.21	13.03

Run No.	$[HNO_3]$(M)	[o-Xylene](M)	Rate x10^6 1.mole^{-1}sec.$^{-1}$	k x10^2 1^2mole^{-2}sec.$^{-1}$
67	0.0506	0.414	2.07	1.60
68	0.0514	0.414	1.70	1.25
69	0.0527	0.414	5.80	3.96
70	0.0537	0.414	6.87	4.44

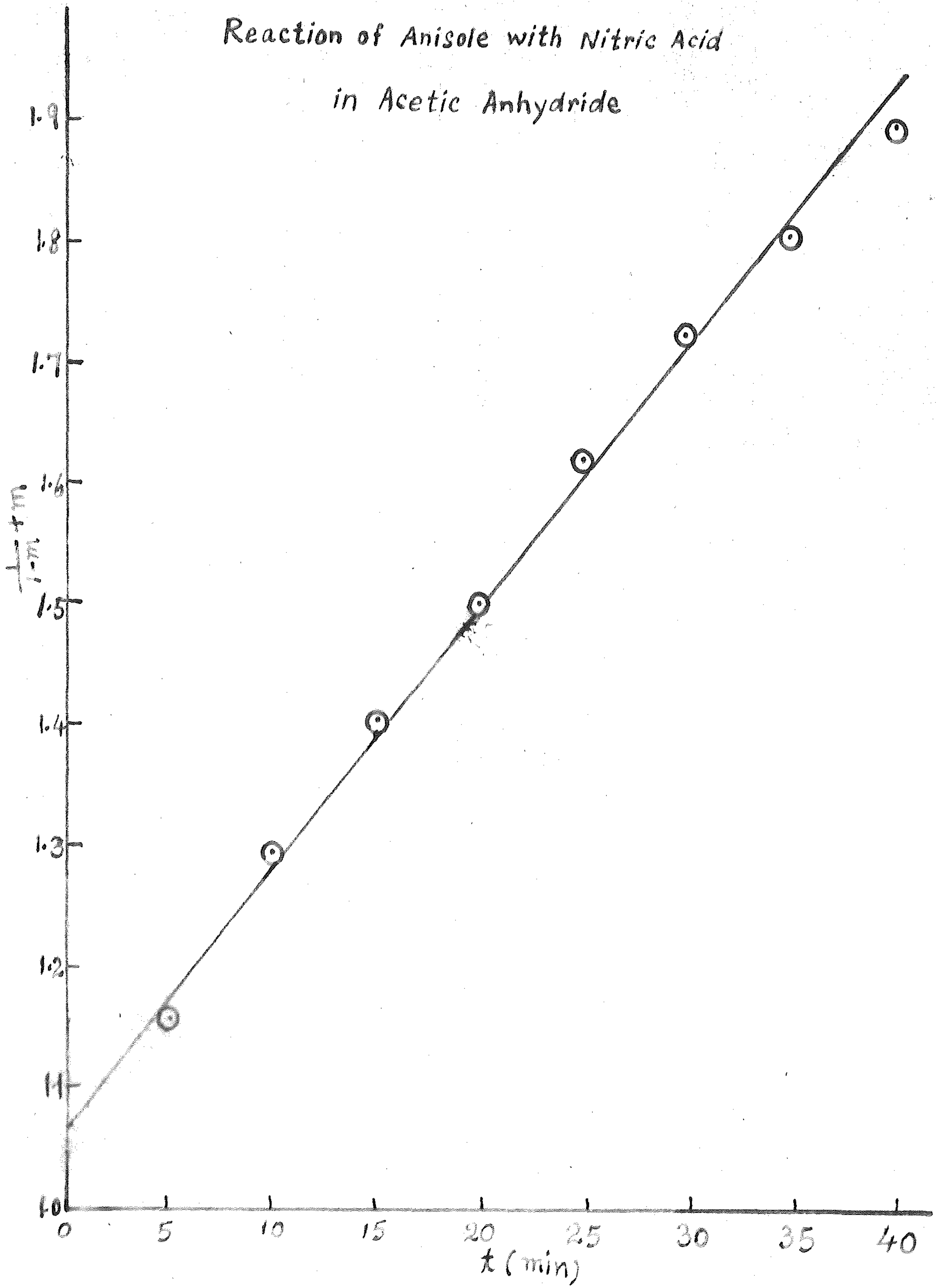
GRAPH I

Reaction of Anisole with Nitric Acid
in pure Acetic Anhydride



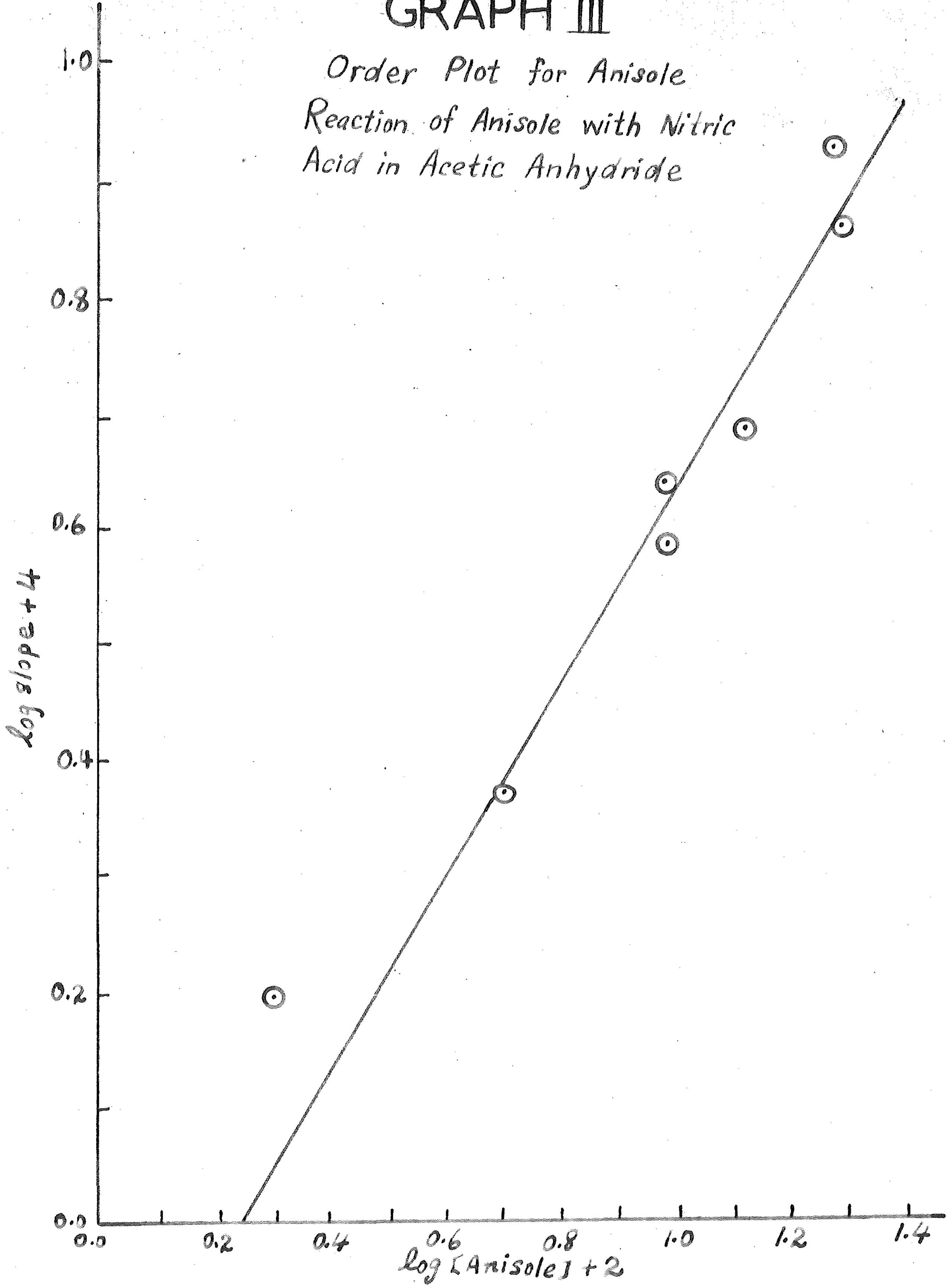
GRAPH II

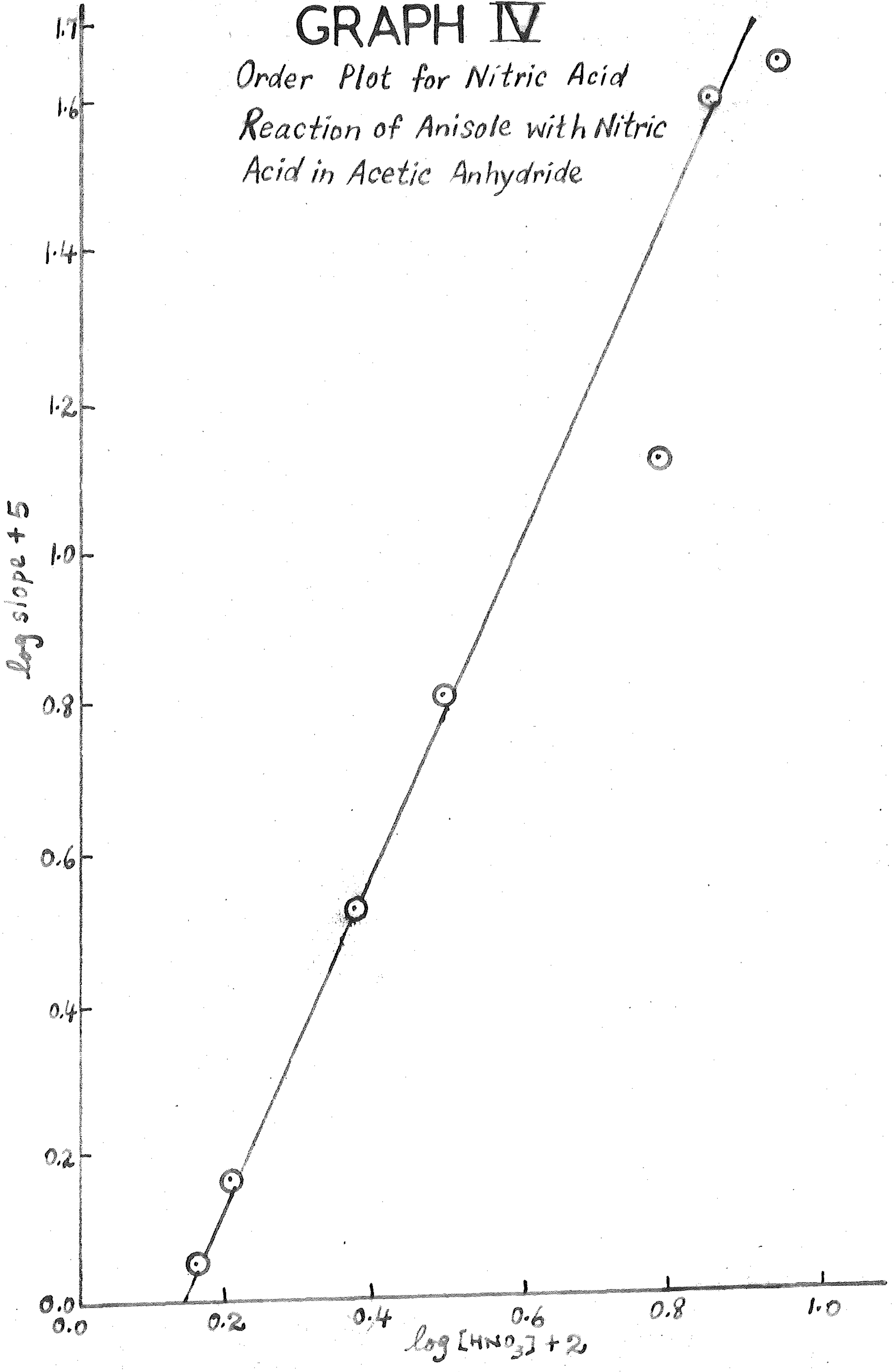
Reaction of Anisole with Nitric Acid in Acetic Anhydride



GRAPH III

Order Plot for Anisole
Reaction of Anisole with Nitric
Acid in Acetic Anhydride



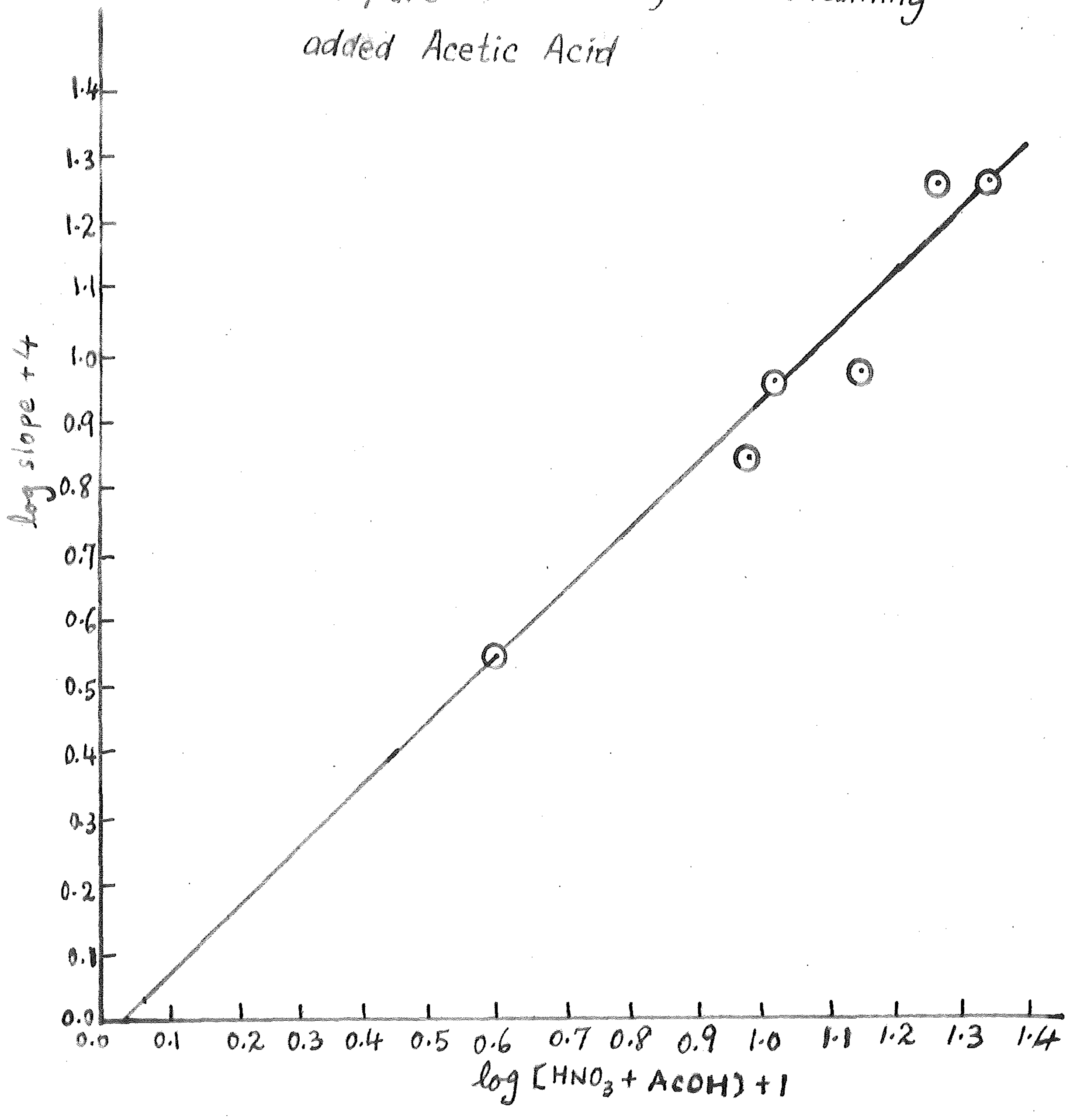


GRAPH IV

Order Plot for Nitric Acid
Reaction of Anisole with Nitric
Acid in Acetic Anhydride

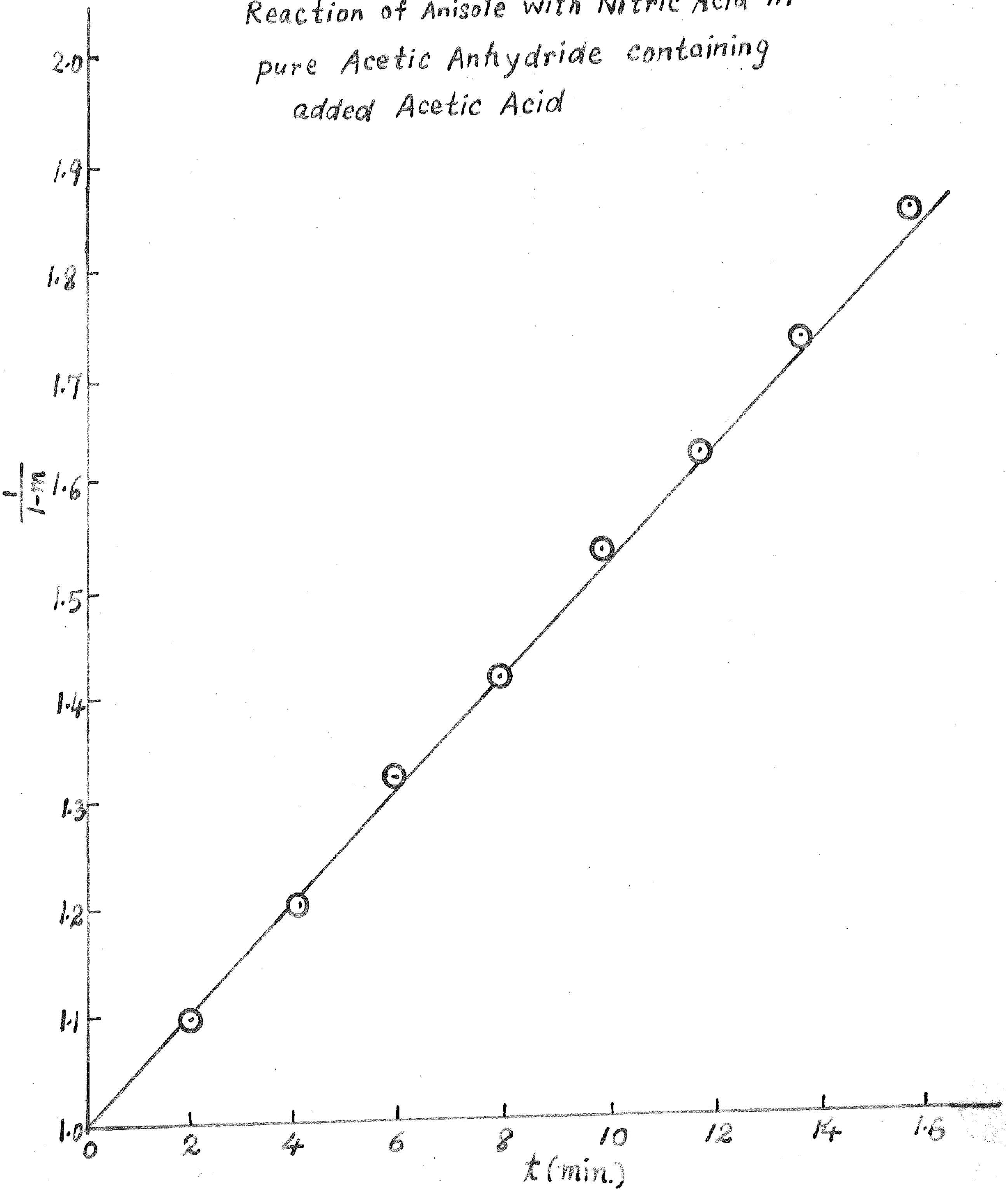
GRAPH V

Order Plot for Acetic Acid
Reaction of Anisole with Nitric Acid
in pure Acetic Anhydride containing
added Acetic Acid



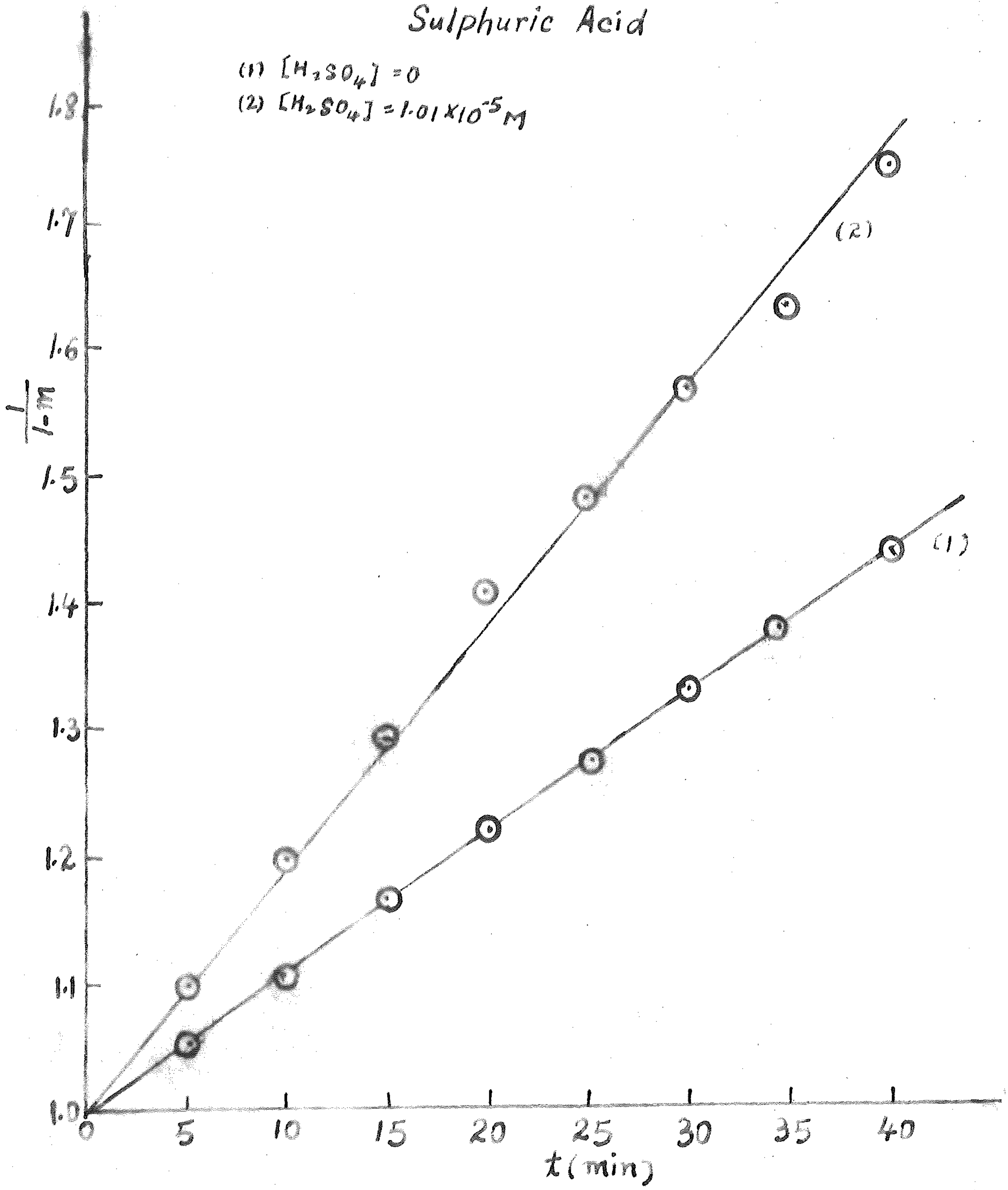
GRAPH VI

Reaction of Anisole with Nitric Acid in pure Acetic Anhydride containing added Acetic Acid

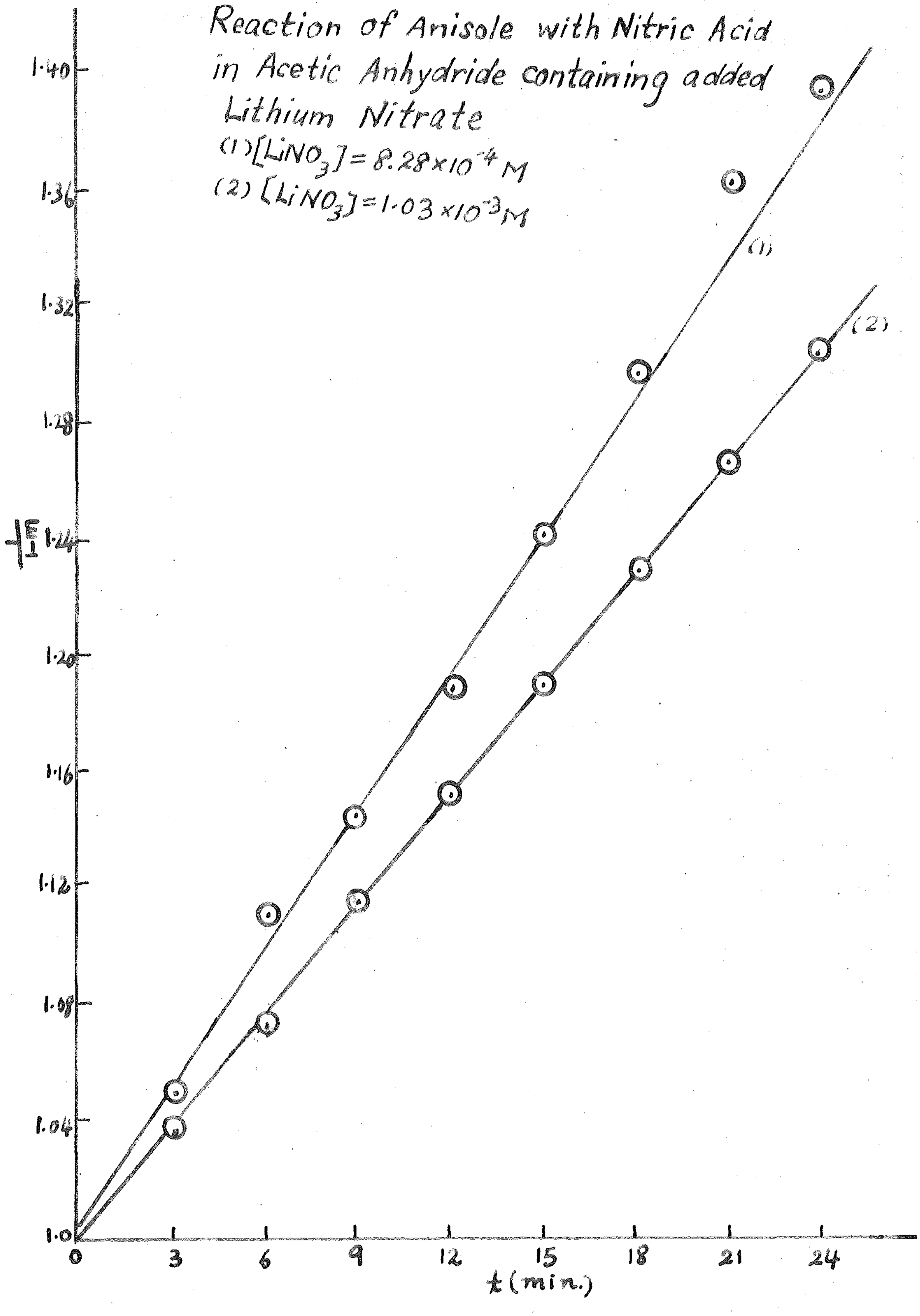


GRAPH VII

Reaction of Anisole with Nitric Acid in pure Acetic Anhydride containing added Sulphuric Acid



GRAPH VIII



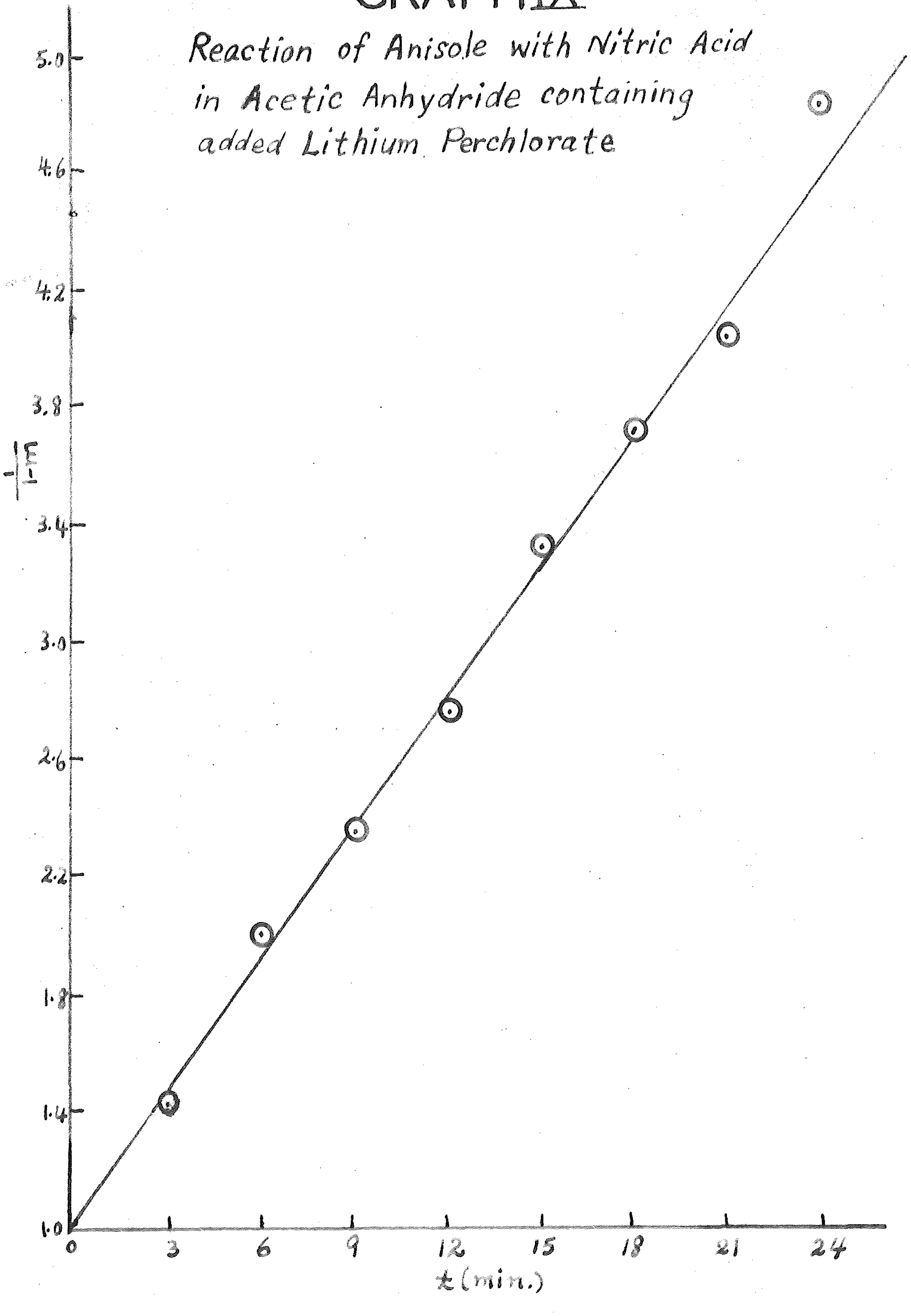
Reaction of Anisole with Nitric Acid in Acetic Anhydride containing added Lithium Nitrate

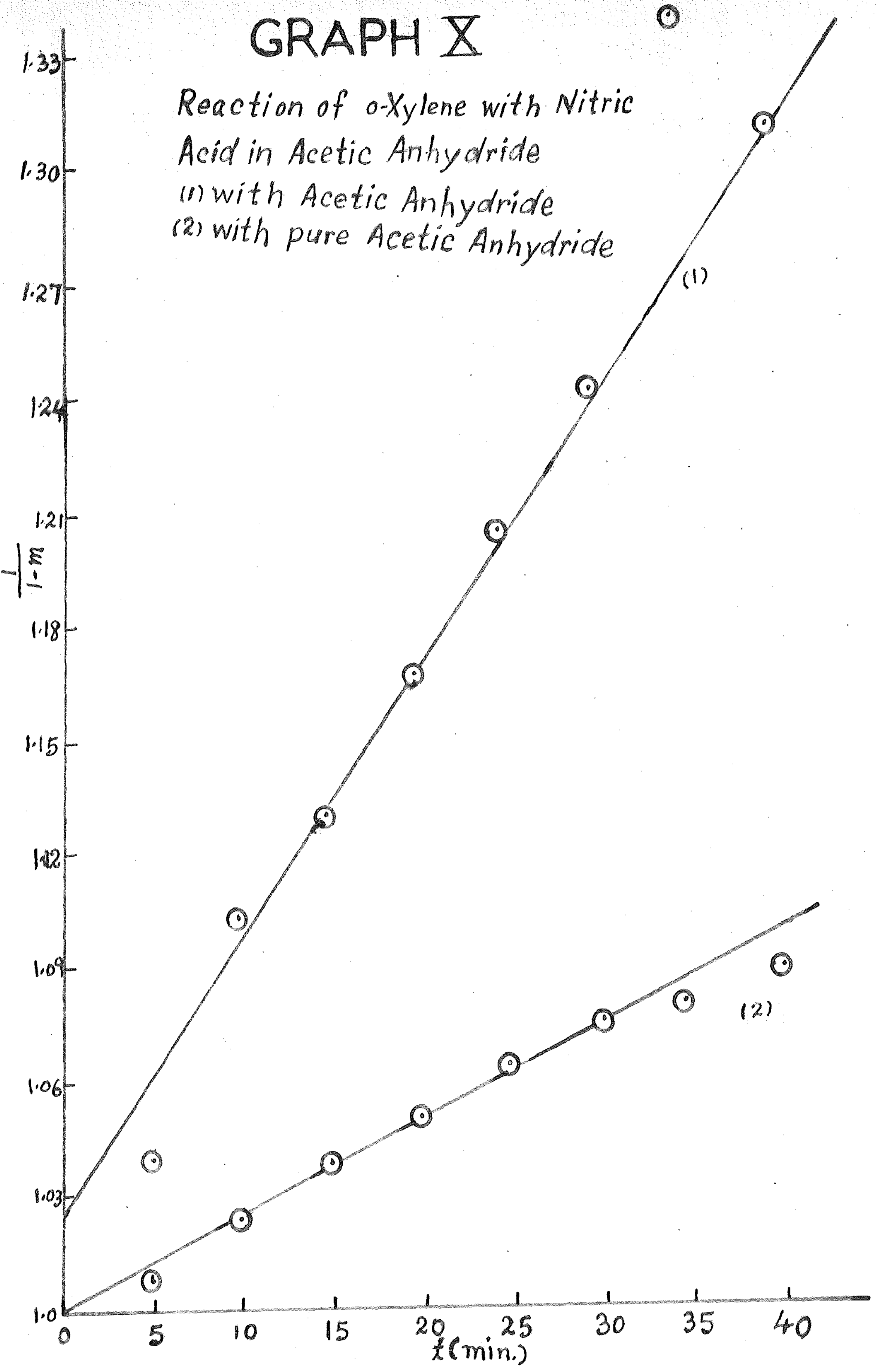
(1) $[LiNO_3] = 8.28 \times 10^{-4}$ M

(2) $[LiNO_3] = 1.03 \times 10^{-3}$ M

GRAPH IX

Reaction of Anisole with Nitric Acid in Acetic Anhydride containing added Lithium Perchlorate





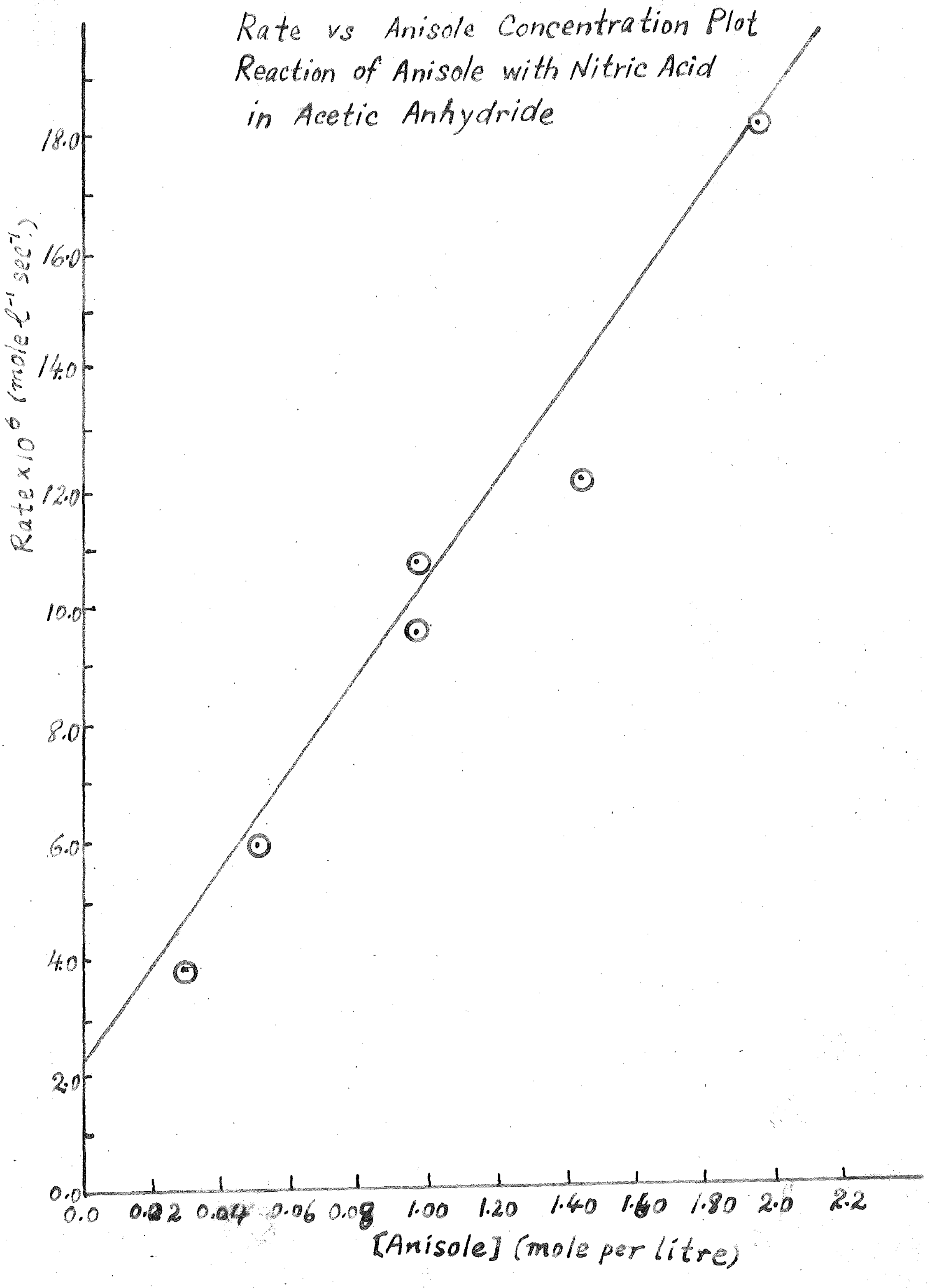
GRAPH X

Reaction of o-Xylene with Nitric Acid in Acetic Anhydride

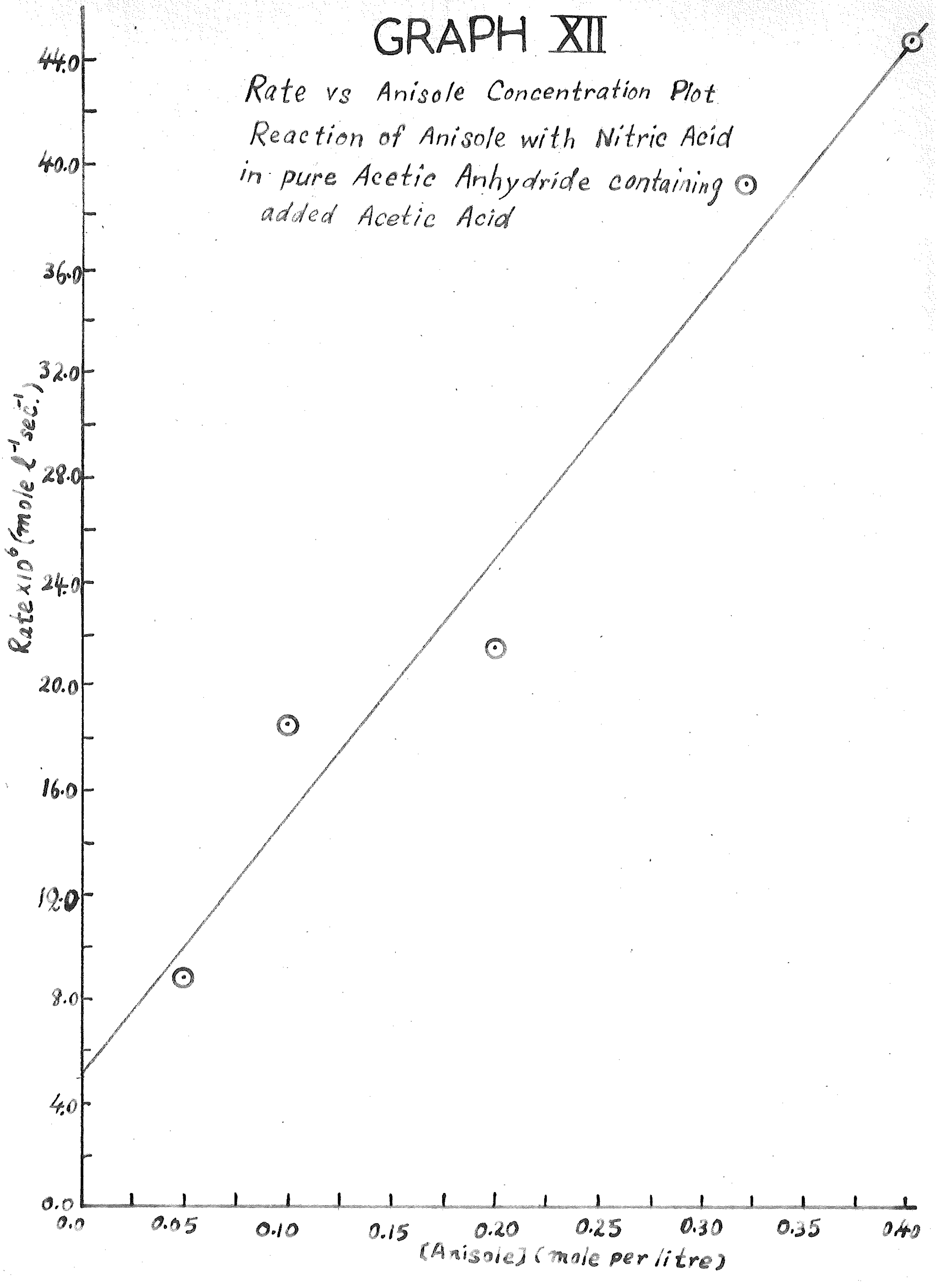
(1) with Acetic Anhydride

(2) with pure Acetic Anhydride

GRAPH XI


Rate vs Anisole Concentration Plot
Reaction of Anisole with Nitric Acid
in Acetic Anhydride

GRAPH XII



Rate vs Anisole Concentration Plot
Reaction of Anisole with Nitric Acid in pure Acetic Anhydride containing ⊙ added Acetic Acid

DISCUSSION

Rate Measurements

Effect of added Acetic Acid

The catalytical effect of acetic acid on the nitration of anisole can be seen from Table X. There are great differences in rate constants obtained from runs which were carried out in ordinary analytical reagent grade acetic anhydride (runs 3-12), fractionated acetic anhydride (runs 1,2,13-23), fractionated acetic anhydride containing added acetic acid (runs 24-47), and ordinary analytical reagent grade acetic anhydride containing added acetic acid (runs 48-52). These differences are attributed to the presence of varying amounts of acetic acid in acetic anhydride.

On the assumption that the reaction has a first order dependence on anisole, a second order dependence on acetic acid (see p. 45), the mean rate constant calculated from runs 24-47, which were carried out in fractionated acetic anhydride containing added acetic acid, was found to be 4.43×10^{-2} $1.^{3}$mole^{-3}sec.$^{-1}$. Employing this mean rate constant and the rates obtained from runs which were carried out in ordinary analytical reagent grade acetic anhydride (runs3-12), the concentrations of acetic acid which would give the observed rates were calculated. Values found lay in the range 0.4-1.5 M and grouped closely about the mean concentration of 0.94 M. This concentration is equivalent to 5% of acetic acid present in the ordinary analytical reagent grade acetic anhydride. This figure seems reasonable since the purity of "AnalaR" acetic anhydride is stated to be "not less than 95%". The concentration of acetic acid present in fractionated acetic anhydride can likewise be calculated from the rates obtained from the runs which were carried out in fractionated acetic anhydride. With the same assumption as before and using the mean rate constant, 4.43×10^{-2} $l.^{3}mole^{-3}sec.^{-1}$, the values for the concentrations of acetic acid in fractionated acetic anhydride were found to range from 0.02-0.2 M with a mean of 0.1 M. This corresponds to 0.5% of acetic acid. Read[9] also found differences in apparent rates in the nitration and acetoxylation of o-xylene when different samples of acetic anhydride were used as solvent. The differences were likewise attributed to differing concentrations of acetic acid present in acetic anhydride.

Effect of added Sulphuric Acid

As shown in runs 53-58 (Table X), it is clear that the addition of a concentration of 10^{-5}M sulphuric acid in the reaction mixture increases the rate by 75% as compared to that in fractionated acetic anhydride and by a factor of five in 4×10^{-5} M sulphuric acid.

Sulphuric acid exists as acetyl sulphuric acid, CH_3COOSO_2OH, in acetic anhydride. Because any small amount of even very weakly basic impurities would markedly affect the very low concentration of the very strong acetyl sulphuric acid, the order dependence of the rate on sulphuric acid concentration was not further investigated. Read[9] obtained a larger increase rate factor (19) in the nitration and acetoxylation of o-xylene with 0.04 M nitric acid and 4.5×10^{-5}M sulphuric acid. The runs on anisole were carried out with 0.05 M nitric acid. It would be expected that the catalytical effect of sulphuric acid would be less marked at higher nitric acid concentrations.

Effects of added Lithium Nitrate and added Lithium Perchlorate

It has been shown in Table X (runs59,60 and 64) that the rates of nitration are decreased by factors of three to six in presence of added lithium nitrate as compared to that without addition of lithium nitrate. It is suggested that lithium nitrate functions as an anticatalyst.

On the other hand, in contrast to the anticatalytic effect of lithium nitrate, lithium perchlorate exhibits a marked accelerating effect. Runs 65 and 66 (Table X) showed that on the addition of 1.21×10^{-3}M lithium perchlorate solution to the reaction mixture, the rate of nitration increases by a factor of three as compared to runs without added lithium perchlorate, and by factors of nine to eighteen as compared to those runs with added lithium nitrate. While this catalytic effect may be due to the fact that a trace of perchloric acid, present in lithium perchlorate solution, would accelerate the reaction substantially, it should be pointed out that some care was taken to ensure that the solution contained (a slight) excess of lithium acetate rather than an excess of perchloric acid. It is suggested that the acceleration represents a true ionic strength effect. Whatever the actual transition state of the reaction, it is almost certainly much more polar than the reactants. Thus a polar solvent with high dielectric constant and/or high ionic strength would be expected to accelerate the reaction. Since addition of lithium perchlorate increases the ionic strength, it therefore causes a marked catalytic effect on the reaction.

Order of Anisole, Nitric Acid and Acetic Acid

In contrast to the concurrent acetoxylation and nitration reactions of o-xylene in nitric acid-acetic anhydride mixture which were zeroth-order in the substrate[9], the rate of nitration of anisole is dependent upon the anisole concentration. As shown in Table IX the experimentally measured order obtained from the order plot of anisole is somewhat less than unity but does approximate to a first order dependence. There is no significant difference in the order determined for runs with added and without added acetic acid. This indicates that the reaction path is similar in both cases.

A plot of rate vs anisole concentration (Graph XI) is linear and has a positive intercept of 2.07 x10^{-6} moles l.$^{-1}$sec.$^{-1}$ for runs without added acetic acid, and of 4.91 x10^{-6} moles l.$^{-1}$sec.$^{-1}$ (Graph XII) for runs with added acetic acid. It appears, therefore, that the non-integral value of the order in anisole arises from the fact that part of the rate is independent of anisole concentration, the remainder of the rate depending on the first power of the anisole concentration.

However, for nitration of anisole the order dependence on nitric acid is comparable to that found by Read[9] for acetoxylation and nitration of o-xylene. In the absence of added acetic acid his order was 3.14, not significantly different from the value of 2.94 determined in this work (Table IX). Thus, nitration of anisole in the absence of added acetic acid, like acetoxylation and nitration of o-xylene, exhibits a third order dependence on nitric acid concentration. It should be noted that the order in nitric acid changes when catalytic reagent such as acetic acid is added in the reaction mixture. Read's mechanism[9] for acetoxylation and nitration of o-xylene, which involves rate determining formation of protonated acetyl nitrate, requires a second order dependence of the rate increase, produced by addition of a constant amount of acetic acid, on the nitric acid concentration. In fact, he obtained order of 2.34 (in 0.34M acetic acid solution) and 2.31 (in 2.2M acetic acid solution) respectively. In the present work the order with respect to nitric acid was found to be 2.49 when acetic acid was added. Again the order determined in this work with anisole is not significantly different from that found by Read using o-xylene. However, all these values appear to be significantly greater than the integral value of 2.

Read's mechanism[9] also requires a first order dependence of the rate increase on the acetic acid concentration. For o-xylene the experimental order was 0.91 and for anisole a value of 1.03 was found. Neither of the values differ significantly from the integral value of 1.

The comparison of the orders in the substrate, nitric acid and acetic acid between the nitration of anisole and o-xylene is quite similar except that the former is dependent on the substrate concentration and the latter is independent of the substrate concentration. It is thus obvious that nitration of anisole in acetic anhydride has a similar mechanism as that of o-xylene and perhaps differs in the rate determining step.

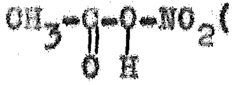
The Mechanism

It was concluded in the previous section that a similar mechanism to that for o-xylene (p.5) would serve to explain the kinetic results for anisole with the rate determining step being the reaction of the protonated acetyl nitrate with the substrate. However, it should be pointed out that the same protonated acetyl nitrate which is the active entity in the acetoxylation and nitration of o-xylene cannot be the major nitrating species when anisole is the substrate. This follows because formation of protonated acetyl nitrate is the rate determining step in the o-xylene reaction and as shown in Table X nitration of anisole is three to four times as fast as acetoxylation and nitration of o-xylene under similar conditions.

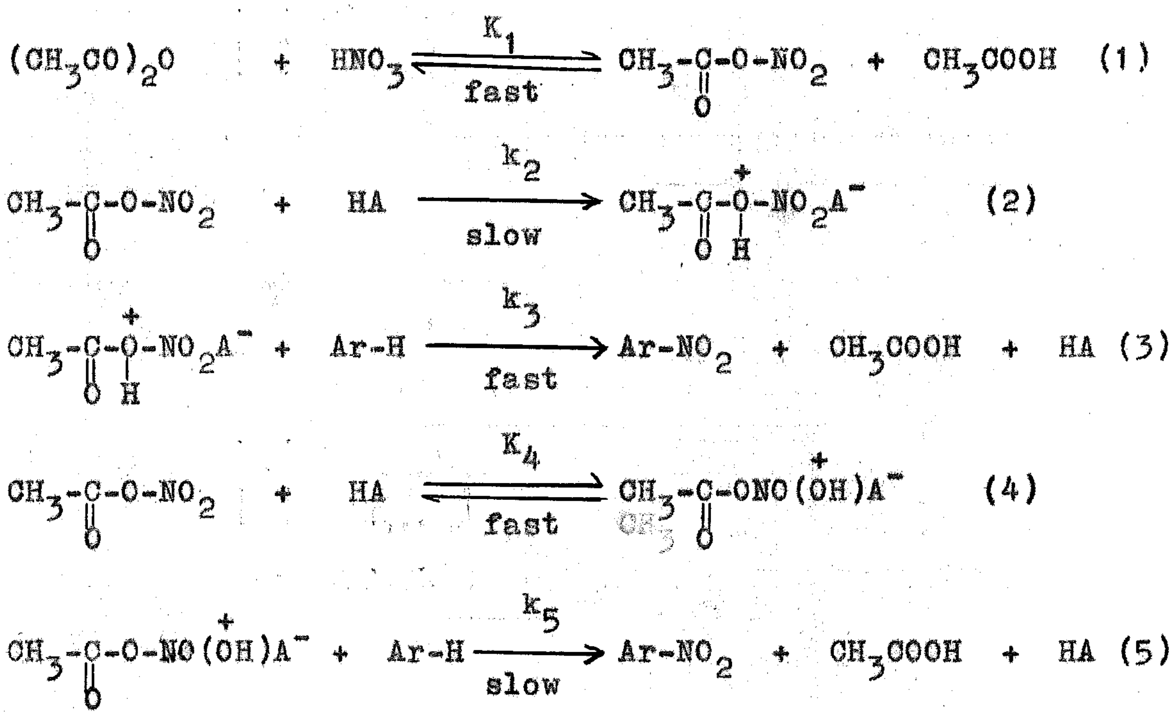
It might be suggested that the protonated acetyl nitrate which is responsible for nitration and acetoxylation of o-xylene is also involved in the anisole independent reaction. If this were so then the rates of the o-xylene reaction and those of anisole independent reaction would be identical under the same conditions since in each case formation of the (same) protonated acetyl nitrate would be the rate determining step. Unfortunately it is impossible to compare exactly the rates of the two reactions because the rates were not obtained under identical conditions and, moreover, the amount of acetic acid impurity in the acetic anhydride used for the runs with o-xylene is unknown. Therefore the precise rate constants cannot be evaluated from the data. However estimates of the amount of acetic acid impurity in acetic anhydride lead to rate constants for the o-xylene reaction which appear to be about 2.1 times greater than the rate constants evaluated for the anisole independent reaction. Apparently further work is required to settle this discrepancy.

Since anisole is more reactive than o-xylene it must be sufficiently reactive to react immediately with any of the "Read" protonated acetyl nitrate (p.5). From Wright's finding[8] it might be expected that anisole would react with one of the "Read" protonated acetyl nitrate to give a high yield of acetoxylated product. The most favourable conditions for the formation of acetoxylated derivatives are at low anisole concentrations for then the rate of the anisole dependent reaction, presumably leading to nitro-derivatives only, is at a minimum. A single gas chromatographic examination of the reaction product did not reveal any acetoxy compound and further study of the reaction products obtained at very low anisole concentrations would be warranted.

Until the points discussed above are decided, the mechanism of the nitration of anisole in acetic anhydride will remain in doubt. However it is tentatively suggested that the anisole independent reaction is brought about by the "Read" protonated acetyl nitrate, probably



$CH_3-\underset{\underset{O}{\|}}{C}-\overset{+}{\underset{\underset{H}{|}}{O}}-NO_2$ (I) and the anisole dependent reaction involves a less reactive protonated acetyl nitrate, perhaps, $CH_3-\underset{\underset{O}{\|}}{C}-ONO(\overset{+}{O}H)$(II). The mechanism of the reaction would then be



$$(CH_3CO)_2O + HNO_3 \underset{fast}{\overset{K_1}{\rightleftharpoons}} CH_3-\underset{\underset{O}{\|}}{C}-O-NO_2 + CH_3COOH \quad (1)$$

$$CH_3-\underset{\underset{O}{\|}}{C}-O-NO_2 + HA \xrightarrow[slow]{k_2} CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{\overset{+}{O}}-NO_2A^- \quad (2)$$

$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{\overset{+}{O}}-NO_2A^- + Ar-H \xrightarrow[fast]{k_3} Ar-NO_2 + CH_3COOH + HA \quad (3)$$

$$CH_3-\underset{\underset{O}{\|}}{C}-O-NO_2 + HA \underset{fast}{\overset{K_4}{\rightleftharpoons}} CH_3-\underset{\underset{O}{\|}}{C}-ONO(\overset{+}{O}H)A^- \quad (4)$$

$$CH_3-\underset{\underset{O}{\|}}{C}-O-NO(\overset{+}{O}H)A^- + Ar-H \xrightarrow[slow]{k_5} Ar-NO_2 + CH_3COOH + HA \quad (5)$$

The rate equation derived from the above mechanism is

$$rate = k_2[CH_3COONO_2][HA] + k_5[CH_3COONO(\overset{+}{O}H)A^-][Ar-H] \quad (6)$$

Since equilibrium in (1) lies to the right, $[CH_3COONO_2]$= stoichiometric $[HNO_3]$. Substituting $[CH_3COONO_2]$ in (6), we obtain

$$rate = k_2[HNO_3]_{st}[HA] + k_5K_4[HNO_3]_{st}[HA][Ar-H] \quad (7)$$

In absence of added strong acid, HA is nitric acid, and it follows that

$$[HA] = [HNO_3] = \frac{[HNO_3]_{st}[CH_3COOH]}{K_1[(CH_3CO)_2O]}$$

Substituting HA in (7), the rate equation becomes

$$\text{rate} = \frac{k_2 [HNO_3]^2_{st} [CH_3COOH]}{K_1 [(CH_3CO)_2O]} + \frac{k_5 K_4 [HNO_3]^2_{st} [CH_3COOH] [Ar\text{-}H]}{K_1 [(CH_3CO)_2O]}$$

Putting

$$k' = \frac{k_2}{K_1 [(CH_3CO)_2O]} \quad \text{and} \quad k'' = \frac{k_5 K_4}{K_1 [(CH_3CO)_2O]}$$

and on substitution the above equation then becomes

$$\text{rate} = [HNO_3]^2_{st} [CH_3COOH] (k' + k'' [Ar\text{-}H]) \qquad (8)$$

Equation (8) thus predicts a less than first order dependence of the rate of reaction on anisole, a second order dependence on nitric acid and a first order dependence on acetic acid. The order found were 0.75 with respect to anisole, 2.49 in nitric acid in the presence of added acetic acid, and 1.03 in acetic acid (cf. Table IX). In the absence of added acetic acid, $[CH_3COOH] = [CH_3COONO_2]$ and a third order dependence on nitric acid should be observed. The value found was 2.94. The agreement between the predicted order of the reactants and those found is about as good as that obtained by Read[9] in his study on the acetoxylation and nitration of o-xylene.

Now writing N = initial $[HNO_3]_{st}$; $C + N$ = initial added $[CH_3COOH]$, X = initial $[Ar\text{-}H]$; $\frac{x}{N} = m$ where x is the concentration of reaction product formed in time t;

$b = \frac{k''N}{k' + k''X}$ and $a = \frac{N}{N + C}$, and substituting these values in (8), we obtain

$$N\frac{dm}{dt} = (1-m)^2(1+am)(1-bm)N^2(C+N)(k' + k''X)$$

On rearrangement and integration, we then have

$$\int\frac{dm}{(1-m)^2(1+am)(1-bm)} \doteq \text{constant} = N(C+N)(k' + k''X)t$$

Let $F(m) = \int\frac{dm}{(1-m)^2(1+am)(1-bm)} - A$, and on integration this equation becomes

$$F(m) = \frac{A}{1-m} + B\ln(1-m) + E\ln(1+am) + D\ln(1-bm) - A \quad (9)$$

where $A = \frac{-ab + a-b+1}{(a+1)^2(b-1)^2}$, $B = \frac{2ab-a+b}{(a+1)^2(b-1)^2}$,

$E = \frac{a^2}{(a+1)^2(a+b)}$ and $D = \frac{-b^2}{(b-1)^2(a+b)}$

Because the coefficients in F(m) involve rate constants which we wish to determine, equation (9) is a rather difficult rate equation to work with. However, in nearly all the runs m was small, $a<1$ and $b<1$. Hence on expansion of the logarithmic terms in equation (9) and neglecting terms higher than m^2, F(m) is reduced to

$$F(m) = \frac{1}{1-m} + \frac{1}{2}(b-a)m^2 - 1$$

Since a and b are usually small, the second term can be neglected. Thus

$$F(m) = \frac{1}{1-m} - 1$$

The plot of F(m) vs t should have a slope of $N(N+C)(k' + k''X)$

which reduces to $N^2(k'+k''X)$ in the absence of added acetic acid (when $C = 0$). For the plot in Graph I where $X = 0.2$ M and $C = 0$, k' is only about 10% of $k''X$ and k' may be neglected in comparison with $k''X$. The rate equation thus becomes ($a = 1$ and $b = \frac{N}{X}$)

$$F(m)' = \frac{1}{(1-b)(1-m)} + \frac{\ln(1+m)}{2(1+b)} - \frac{1-3b}{2(1-b)^2}\ln(1-m) - \frac{2b^2}{(1-b^2)(1-b)}\ln(1-bm)$$

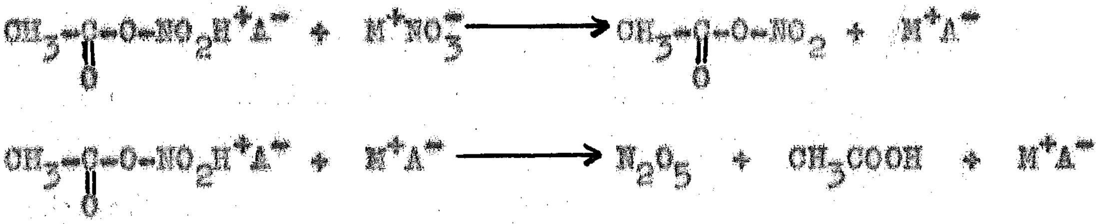
$$= k''N^2Xt + \frac{1}{1-b}$$

This function is used in the F(m) vs t plot for Graph I.

The proposed mechanism is in accord with the kinetic effects of additives. Since addition of acetic acid increases the concentration of free nitric acid by virtue of equilibrium (1), the rate of formation of protonated acetyl nitrate (I) and the equilibrium concentration of protonated acetyl nitrate (II) will increase. Consequently it is expected that rates of anisole independent and dependent reaction and thus the total rate of reaction should be increased by an amount proportional to the amount of added acetic acid (cf. eq.(8)) and this was observed.

Addition of sulphuric acid leads to the formation of the very strong acid, acetyl sulphuric acid, CH_3COOSO_2OH, which acts as HA in the mechanism. Again the rate of formation of (I) and the equilibrium concentration of (II), and hence the overall rate of nitration should be increased. This was also observed.

Lithium nitrate acting as a base reduces the stationary state concentration of (I) through deprotonation of the protonated acetyl nitrate and likewise reduces the equilibrium concentration of (II) by the following two possible reactions[13]:



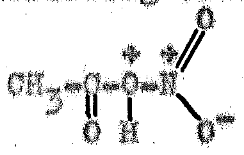
$$CH_3-\underset{\underset{O}{\|}}{C}-O-NO_2H^+A^- + M^+NO_3^- \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-O-NO_2 + M^+A^-$$

$$CH_3-\underset{\underset{O}{\|}}{C}-O-NO_2H^+A^- + M^+A^- \longrightarrow N_2O_5 + CH_3COOH + M^+A^-$$

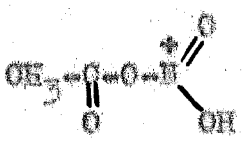
The rates of both reaction paths and the total rates of nitration should be reduced as predicted. The fact that the addition of lithium perchlorate in the reaction mixture increases the total rate of reaction verifies that the effect of lithium nitrate was not a simple rate retarding ionic strength effect.

The Nature of the Reactive Species

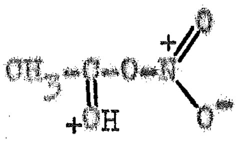
As mentioned on p.5 there are three possible protonated acetyl nitrate. These are in decreasing order of reactivity and increasing order of ease of formation :



(I)



(II)



(III)

The stability order follows from the relative basicities of the three different oxygen atoms. Comparison of the pK values of nitro compounds and acids ($pK\text{-}C_6H_5\overset{+}{N}O_2H = -11.4$[14] ;

$pK\text{-}C_6H_5C\overset{+}{O}_2H_2 = -7.3$[15]) indicates that nitro compounds are considerably less basic than acids and hence (II) would be expected to be much less stable than (III). Furthermore the oxygen atom which is bonded to nitrogen and carbon in acetyl nitrate should be less basic than the other oxygen atoms of the nitrate group since each of these oxygen atoms carries one-half of a formal negative charge. Thus (I) should be less stable than (II). It is suggested that the central oxygen atom in protonated acetyl nitrate is so weakly basic that it is protonated only slowly and formation of (I) then becomes rate determining provided that the substrate with which it reacts, is itself quite reactive. Protonation to form (II) should clearly be much more faster than formation of (I) and it is therefore reasonable to suggest that while formation of (I) is slower than subsequent reaction of (I) with the substrate, formation of (II) is faster than reaction of (II) with the substrate. Hence the reaction of anisole with (I) is a zeroth order reaction while the reaction of anisole with (II) is first order in anisole.

Finally, we may obtain values of k' and k" from the plot of rate vs anisole concentration (see Graphs XI and XII). From equation (8) the intercept of such a plot is N^2Ak' and the slope is N^2Ak'' where A is acetic acid concentration. For runs containing added acetic acid the intercept is 4.91×10^{-6} mole $l.^{-1}$ sec.$^{-1}$ and the slope is 1.02×10^{-4} sec.$^{-1}$. Since

N = 0.05 M and A = 1.0 M, k' is calculated to be 1.96 x 10^{-3} $l.^2 mole^{-2} sec.^{-1}$ and k" is 4.08 x 10^{-2} $l.^3 mole^{-3} sec.^{-1}$. The rate constants ($k_{obs.}$) listed in Table X are related to k' and k" by the expression

$$k_{obs.} = \frac{k'}{X} + k''$$

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