

THE ALKALINE HYDROLYSIS
OF
SOME ETHYL BROMO - 1 - NAPHTHOATES

A THESIS
PRESENTED FOR
THE DEGREE OF MASTER OF SCIENCE
AND HONOURS

UNIVERSITY OF NEW ZEALAND
1957.

G.S. OGILVIE.

V QD
501
.034

C O N T E N T S

	Page
ABSTRACT	1
I INTRODUCTION	2
II EXPERIMENTAL SECTION	
A. Preparation of Esters	7
B. Preparation of Reagents	16
C. Determination of Rate Constants... . .	18
III RESULTS	21
IV DISCUSSION	
A. Method for Determining Rate Constants	27
B. Mechanism of the Reaction	28
C. Relative Free Energies, Heats, and Entropies of Activation... . .	29
D. Hammett Substituent Constants... . .	35
REFERENCES	39

ABSTRACT

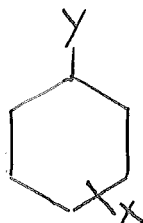
3 Bromo - 1 - naphthoic acid, 4 - bromo - 1 - naphthoic acid, 5 - bromo - 1 - naphthoic acid, and their ethyl esters have been prepared. The kinetics of alkaline hydrolysis in ethanol - water (85:15 W/W) of these esters, together with the unsubstituted ester, have been studied, using stainless steel reaction vessels, over the temperature range 25-65°C. Arrhenius frequency factors and energies of activation have been determined. The frequency factors have been shown to be constant within a small experimental error. Relative free energies, heats, and entropies of activation for these hydrolyses have been evaluated and their significance discussed. Hammett substituent constants for the bromo - substituent in the 3, 4, and 5 positions of naphthalene have been calculated and discussed.

I.

INTRODUCTION

An increasing amount of critical evidence within the last few years indicates that the effect of structure on the reactivity of organic compounds may be approximately treated as the sum of independent polar, resonance, and steric contributions. An approximately quantitative separation of these three effects of structure on reactivity would permit the unambiguous study of each effect, which, in turn, would yield results of considerable importance to both practical and theoretical organic chemistry.

The most successful such relationship connecting reactivity with structure is undoubtedly the Hammett equation. Hammett¹ found that for meta - and para - substituted side-chain derivatives of benzene (Type I), the



Type I

effect of structure on reaction rates and equilibria is usually determined solely by the polar effect of the substituent. In these compounds, substituents are held rigidly at large distances from the functional group and thus no change in steric interactions occurs between the reactant and transition state (rate case), or between reactant and final state (equilibrium case). The mathematical expression of this relationship is the now well-known Hammett Equation².

$$\frac{-\Delta\Delta G^\ddagger}{2.303RT} = \log \left(\frac{k}{k_0} \right) = \sigma \rho$$

In this equation:-

(a) k and k_0 are rate or equilibrium constants for the reactions of substituted and unsubstituted compounds respectively.

(b) σ is the "substituent constant", which is dependent only on the nature and position of the substituent (i.e. independent of the nature of the reaction).

(c) ρ is the "reaction constant" which depends upon the reaction and upon the reaction conditions.

The assumption has been made that the Hammett equation applies to both rate and equilibrium data. This is supported by the transition state theory of reaction rates, which states that the rate of reaction is determined by an "equilibrium" between the reactant and the transition states. Thus, in terms of this theory, a reaction may be regarded as a special type of equilibrium.

Hammett² selected the well studied ionization of benzoic acids in water at 25°C as the standard reaction. By assigning $\rho = 1$ for this reaction, then from equation (1), $\sigma = \log \left(\frac{k}{k_0} \right)$ is obtained. By plotting values of σ , obtained for a number of substituents by this method, against $\log \frac{k}{k_0}$ for any particular reaction, then ρ may be obtained for that reaction. Definition of σ and ρ constants by this method suffers from the fact that, as general values, they are based upon a particular reaction series with its concomitant errors. Accordingly Jaffe⁴ has redefined σ as that value best fitting all the available data.

Jaffe⁴ has found that the equation is followed, with a precision of $\pm 15\%$, by 3180 experimentally determined rate and equilibrium constants. From these he has confirmed the suggestion of Hammett² that the polar effects of meta- and para-substituents of benzene, as represented by σ constants, are additive.

Roberts and Moreland⁵, and Taft⁶, by two entirely different approaches have shown that the Hammett σ constant is the sum of

separable inductive polar and resonance polar effects on reactivity.

Studies on the Hammett equation have been concentrated mainly on benzene and its derivatives. It requires to be shown whether the Hammett equation can be extended to all aromatic systems and what modifications, if any, may be required. In contrast to the situation pertaining to the benzene series, little information is available on other aromatic compounds.

As a start in the obtaining of information on the effects of substituents on reactions of given groups in these systems, research has been undertaken at this College on the fused ring system of naphthalene. In particular, the alkaline hydrolysis of a series of substituted ethyl 1 - naphthoates has been studied.

For the naphthalene series, in the absence of steric effects of the substituent group on the functional group, the effect of the substituent on reactivity should be determined solely by its polar effect. The Hammett equation should therefore apply. Comparison of the polar effect of corresponding substituents in the naphthalene and benzene series may thus be made in terms of the Hammett constants.

The reaction constant should be the same for both series. This is because the reaction, the reaction conditions and the reaction mechanism are the same. The only likely difference, that could alter the reaction constant, is that the transmission of the polar effect of the substituent may be altered by steric inhibition of resonance of the functional group in naphthalene series by the ortho fused benzene ring. However, except in the case of direct resonance interaction, the polar effect of the substituent and the resonance effect of the functional group appear to be independent variables⁷. Thus such a difference would not alter the polar effect of the substituent on the reaction and hence would not alter the reaction constant.

Comparison of substituent constants of 3- and 4- substituted 1- naphthyl compounds with those of meta- and para- benzene compounds can also be made. Difference in bond length and bond character between naphthalene and benzene may alter the substituent constants. For 4- substituted naphthalene derivatives a steric effect on the substituent caused by the adjacent fused ring is also possible, and has been confirmed⁸ for the 4- nitro - substituent.

Unfortunately, in contrast to the benzene series where a considerable fund of information concerning the effects of substituents on reactions of given groups is available, little information on similar effects in the naphthalene series is to hand. Eberbach⁹ (1893) determined the dissociation constants of the ten available amino - naphthalene - sulphonic acids. Bryson^{10,11} (1949) had determined the pKa values of the fourteen nitro-naphthylammonium ions and the dissociation constants of thirteen amino - naphthalene - sulphonic acids. Price^{12,13} (1952) has studied the rate constants for the alkaline hydrolysis of the ethyl esters of substituted 1- and 2- naphthoic acids in dioxan - water (70:30 W/W) and the dissociation constants of substituted 1- naphthoic acids in ethanol - water. Schreiber and Kennedy¹⁴ (1956) have studied dissociation constants for a number of nitro - 1 - naphthols. Berliner (private communication) is measuring the dissociation constants of various nitro - naphthoic acids.

Work from this department was begun with a study¹⁵ of the kinetics of alkaline hydrolysis of esters and amides of 1- and 2- naphthoic acids, followed by work⁸ on the kinetics of alkaline hydrolysis of ethyl 2- nitro-, 3- nitro-, 4- nitro-, 5- nitro-, 6- nitro-, 8- nitro-, and 4:5 dinitro- 1- naphthoates in ethanol - water (85:15 W/W). J.E. Packer¹⁶ studied ethyl 3- methyl and 4- methyl - 1- naphthoates and the unsubstituted compound. Mitchell²² studied ethyl 3- chloro and 4- chloro - 1 - naphthoates along with the unsubstituted ethyl 1- naphthoate.

The present work was undertaken to widen the field of study to include a series of bromo-derivatives, namely, ethyl 3- bromo, 4- bromo, and 5- bromo- 1 - naphthoates. This should enable a comparison of the results for the bromo substituents $(-I,+M)$ with each other, with corresponding benzene compounds, and with the chloro - $(-I,+M)$ methyl - $(+I,+M)$ and nitro $(-I,-M)$ substituents previously studied.

In this project the kinetics were followed by a titration method. The hydrolysis reaction of the esters was studied in ethanol water (85:15 W/W). Caldin and Long¹⁸ point out that in this medium most of the base is present as ethoxide ion. It appears¹⁹ that the concentration of ethoxide ion is independent of temperature. Since only relative rates are required in the present work, it is not necessary to evaluate the true rate constants.

II

EXPERIMENTAL SECTION

A. Preparation of Esters.

(a) General.

(1) Melting points are uncorrected.

(2) Reference melting points are given in brackets after the measured figures. Unless otherwise stated they are the highest given in "Elsevier's Encyclopedia of Organic Chemistry".

(3) All microanalyses were carried out at the University of Otago.

(b) Preparation of Esters.

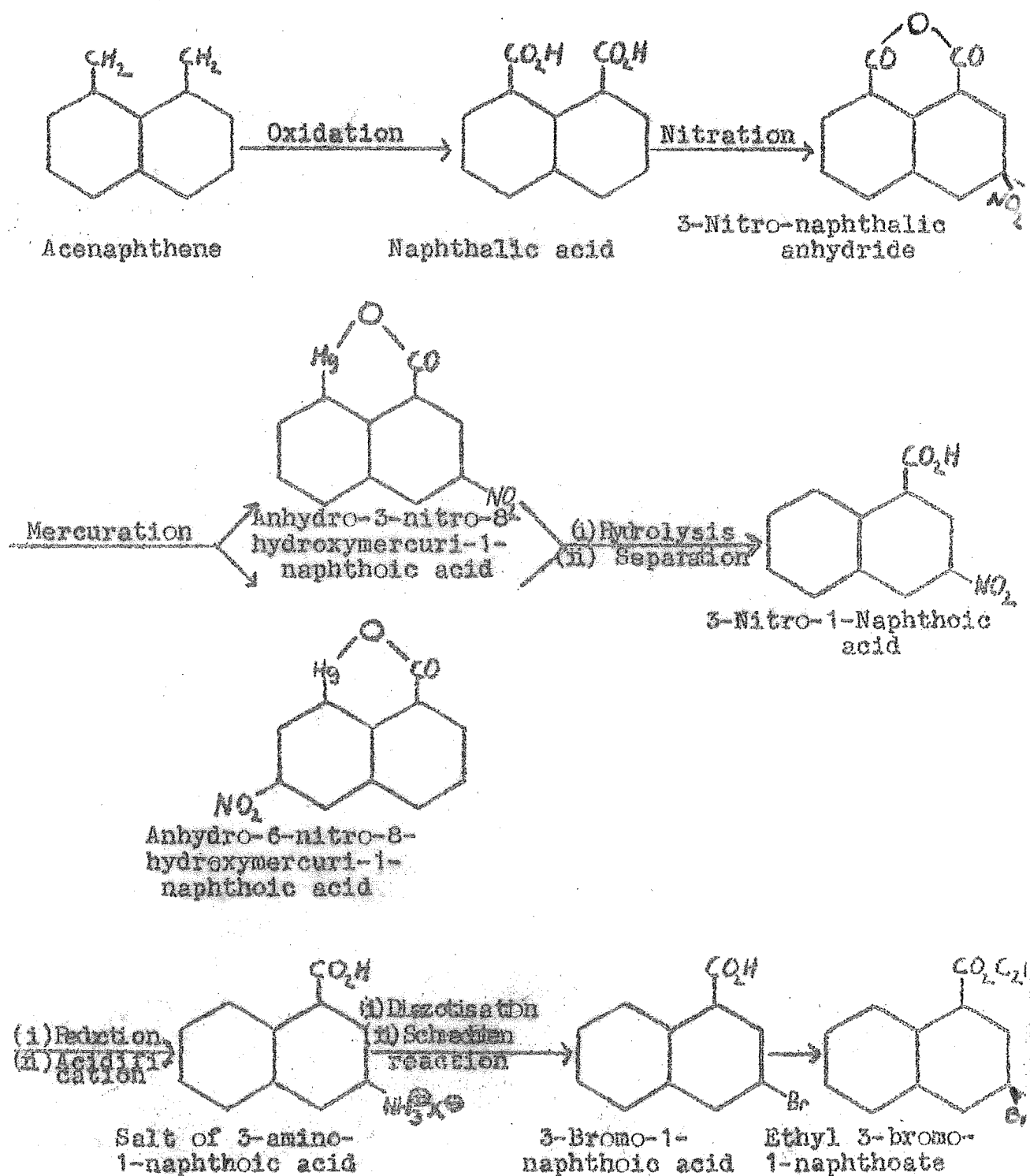
Likely methods for the preparation of the acids are:-

(1) 3 - Bromo - 1 - naphthoic acid

The preparation of 3 - nitro - 1 - naphthoic acid from acenaphthene, followed by diazotisation and a Sandmeyer reaction to give 3 - bromo - 1 - naphthoic acid. 3 - Nitro - 1 - naphthoic acid had already been prepared²⁰. 3 - Bromo - 1 - naphthoic acid has been prepared from this²¹, in low yield (13%) by reduction to the amine salt, followed, without isolation of the amine salt, by a Sandmeyer reaction. The amine has been prepared by Leuck²⁰, who found it to be unstable, but who succeeded in obtaining its hydrochloride in good yield (90%), by reduction of 3 - nitro - 1 - naphthoic acid with sodium hyposulphite. The amine sulphate has been also prepared, in almost theoretical yield, by reduction of 3 - nitro - 1 - naphthoic acid with ferrous sulphate with ammonia²².

Newman and Wise²³ state that most bromo-naphthalene derivatives formed by the Sandmeyer reaction are obtained in poor yield. They recommend the Schwechten modification of the Sandmeyer reaction. In this procedure, a mercuric complex of the diazo-salt is formed and thermally decomposed with sodium bromide as a diluent. Using this method they increased their yield of 2 - bromo - naphthalene obtained from 2 - naphthylamine from 2% to 65%. Similarly, in the phenanthrene series yields

FIGURE I
Preparation of Ethyl 3-bromo-1-naphthoate



of 40 - 60% have been obtained using the Schwechten modification, whereas the compounds are apparently unobtainable by the normal Sandmeyer procedure ²⁵.

(2) 4 - Bromo - 1 - naphthoic acid.

The preparation of 1:4 - dibromo - naphthalene and its conversion to 4 - bromo - 1 - naphthoic acid, by the formation of an organo - metallic derivative and its subsequent carboxylation. The advantage of this method is that only three steps are involved from naphthalene. 1:4-Di - bromo - naphthalene has been obtained in low yield²⁶, by bromination of naphthalene. The Grignard solution obtained from 1:4-dibromo - naphthalene gave 4 - bromo - 1 - naphthoic acid in good yield.²⁷

(3) 5 - Bromo - 1 - naphthoic acid.

The bromination of 1 - naphthoic acid, followed by separation of the isomers obtained. This bromination has been carried out in acetic acid ³⁸, the isomers being separated by fractional recrystallisation.

(1) Ethyl 3 - bromo - 1 - naphthoate.

3 - Bromo - 1 - naphthoic acid was synthesised following the route shown in Figure I.

Naphthalic Acid²⁰.

A solution of acenaphthene (200g.) in glacial acetic acid (2400 ml.) was placed in a 4 l. beaker, while sodium dichromate (1320 g), was slowly added, with vigorous mechanical stirring, so that the temperature stayed in the range 60 - 70°C. Cooling in an ice-bath was necessary at the start of the addition. Addition was completed in one hour. The solution was then heated under reflux for five hours, after which it was poured into 2.5 l. of warm water and left to stand overnight. The resulting solid was filtered off and then washed with water, before being warmed with 3.5 l. of 2½% sodium hydroxide solution. The solution obtained was filtered and the remaining solid was warmed with more 2½% sodium hydroxide (2 l.) before farther filtration. Naphthalic acid was precipitated from the combined filtrates by acidifying with concentrated hydrochloric acid.

The creamy-white solid was filtered at the pump, washed well with water, and dried in a vacuum oven at 70°C. The residues (those solids undissolved by the two alkaline extractions) were heated under reflux with two parts of glacial acetic acid for a further three hours, after which the above extraction process was repeated. Yield, 230 g. (85%); m.p. 273°C (274°C).

3 - Nitro - naphthalic anhydride. 20

Concentrated sulphuric acid (1 l.) was placed in a 3 l. beaker surrounded by an ice-salt cooling mixture. Naphthalic acid (200 g.) was dissolved in the sulphuric acid and the solution cooled to 10°C. Dry A.R. potassium nitrate (100 g.) was then added, with vigorous mechanical stirring, to the solution at a rate sufficient to keep the temperature between 10 - 15°C. Addition was completed in forty-five minutes. The solution was stirred at room temperature for one hour, then at 100°C for fifteen minutes, poured onto ice, stirred well, and left to stand for an hour. The fawn solid formed was filtered at the pump washed twice with cold water and twice with hot water, and dried in a vacuum oven at 90°C. The yield of crude nitro-anhydride (m.p. 242°C) was 220 g.

Impurities were extracted by washing with hot toluene (4 ml./g.). Further purification was obtained by a series of extractions with hot glacial acetic acid, (4 ml./g.). Since the anhydride was more soluble than the impurities, the solid which crystallised on cooling the extract was enriched in anhydride.

In this manner 183 g. (81%), mp 248°C (251 - 252°C), were obtained.

Anhydro 3 - nitro - and 6 - nitro - 8 - hydroxy - mercuric - 1 - naphthoic acids 20.

3 - Nitro - naphthalic anhydride (119 g.) was dissolved in a solution of sodium hydroxide (65 g.) in water (2340 ml.). This solution was filtered and added to a solution of mercuric oxide (107 g.) in acetic acid (75.5 ml.) and water (293 ml.). A cream-coloured precipitate was formed immediately. The solution was then acidified with glacial acetic acid until it reacted acid to

litmus. (This is important as was illustrated in trial runs when the respective yields for acidified and non - acidified solution were 72% and 63%). The mixture was heated continuously under reflux for seven days, after which time it gave no test for mercury when a clean copper strip was suspended in it. The fawn-coloured precipitate was filtered at the pump, washed with water, and dried.

Yield, 165 g. (80%).

3 - Nitro - 1 - naphthoic acid ²⁵.

The mixture of hydroxy - mercuri - compounds (165 g.) was heated under reflux with concentrated hydrochloric acid (470 ml.) and water (960 ml.) for four hours. A brown solid was formed which was filtered at the pump, washed with water, and dried. Yield 72 g. (68%). This was a mixture of 3 - nitro - and 6 - nitro - 1 - naphthoic acids.

The mixed acids (62 g) were treated with glacial acetic acid (250 ml.), boiled for a few minutes, filtered whilst hot, and the filtrate left to stand. The residue was treated once more as above with the same sample of solvent. After four such steps most of the mixed acids had been dissolved. The 6 - isomer was concentrated in the glacial acetic acid solution. All samples of the crystals obtained on cooling were recrystallised several times from glacial acetic acid and the mother liquors systematically worked up. The yield of 3 - nitro - 1 - naphthoic acid so obtained was 45 g. (54%), m.p. 269°C (271.5°C).

Sulphate of 3 - amino - 1 - naphthoic acid ²².

3 - Nitro - 1 - naphthoic acid (5.5 g.) was dissolved in 15% ammonia (75 ml.) and a solution of ferrous sulphate (45 g.) in water (75 ml.) was added. The mixture was boiled for fifteen minutes, during which time the ammonia content was kept approximately constant by the addition of more ammonia at frequent intervals. The clear, light yellow, filtrate on acidification with 50% sulphuric acid, gave a light yellow precipitate of amine sulphate. Because of the rather high solubility of

this salt, much of it remains in solution and hence no attempt at isolation of the salt was made.

3 - Bromo - 1 - naphthoic acid.

(Following a method similar to that used by Newman and Wise²³ for the preparation of 2 - bromo - naphthalene).

The solution of the amine salt was cooled to 3°C in an ice bath. A solution of sodium nitrate in water (1:20 W/W) was slowly added with vigorous mechanical stirring. The end point of the reaction was obtained by using starch - iodide paper. The solution was stirred for forty minutes before a cold suspension of mercuric bromide, formed by treating mercuric nitrate (8.6 g) with sodium bromide (12.5 g) in a total volume of 38 ml. of water, was added with stirring. The yellow, insoluble, complex which separated immediately was collected by filtration, washed with water, and air dried in a vacuum desiccator. For decomposition the complex (14 g) was well mixed with finely ground sodium bromide (28 g) and placed in an Erlenmeyer flask fitted with a ground-glass joint. The Erlenmeyer flask was connected to a two - necked 250 ml. flask which was also fitted with a reflux condenser. This 250 ml. flask was heated to 100 - 110°C in a glycerol bath and the mixture slowly transferred to it by rotation of the Erlenmeyer flask. After each addition of complex, a vigorous gas evolution occurred. After decomposition was complete, the organic acids were extracted with 15% ammonia solution. The solution so obtained was acidified with 20% hydrochloric acid and the precipitate formed was filtered, washed free of mineral acid, and dried. Crude 3 - bromo - 1 - naphthoic acid (4.0 g), m.p. 220°C, was obtained.

The crude compound was purified by dissolving in alcohol, passing through an alumina column, eluting with more alcohol, and boiling down the light pink solution obtained from the first coloured band. This gave 3.1 g. of 3 - bromo - 1 - naphthoic acid, m.p. 236°C (236-237°C). The yield from 3 - nitro - 1 - naphthoic acid is 50% as compared to 13%

obtained by Rule and Thompson ²¹ using the normal Sandmeyer technique.

Ethyl 3-bromo-1-naphthoate.

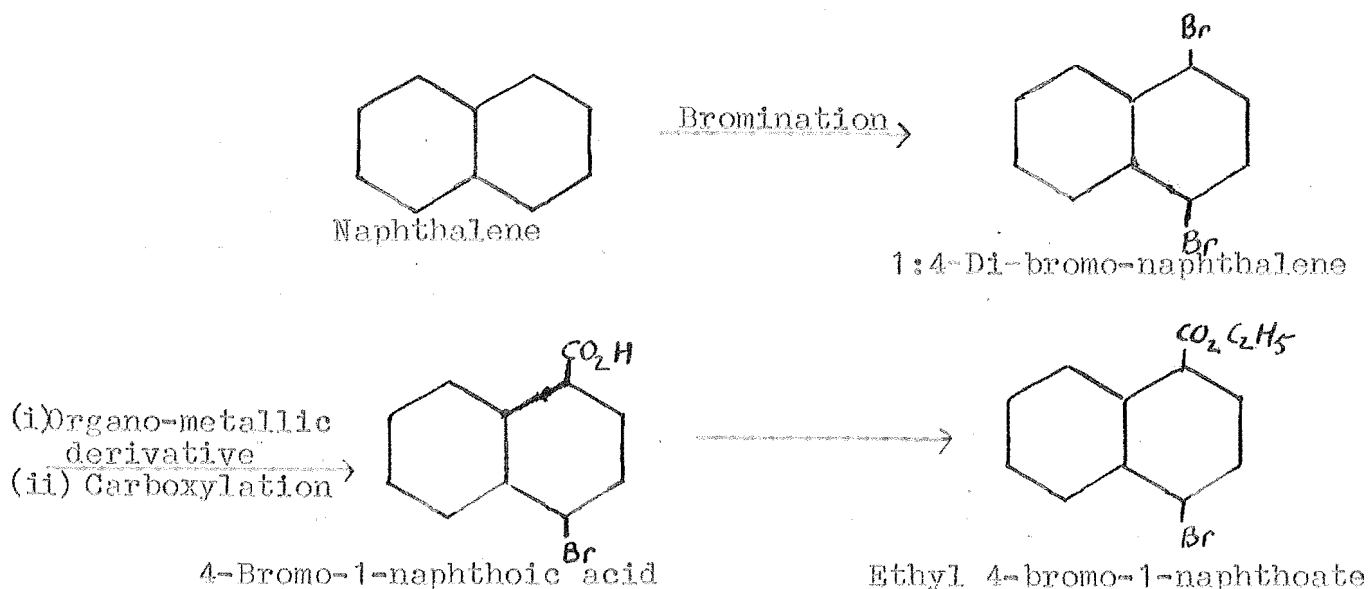
3-Bromo-1-naphthoic acid (3 g.), dissolved in ethanol (70 ml.), was heated under reflux for four hours while dry hydrogen chloride was passed over the surface. The volume was reduced to approximately 30 ml. and the solution then washed into a separating funnel with 100 ml. of ether. The solution was washed twice with water, then with 10% sodium carbonate solution until the washings gave no precipitate on acidification. On evaporation of the ether and cooling in an acetone - "dry ice" bath, solid ester was obtained. This was recrystallised three times from petroleum ether (b.p. 50°C-70°C) (charcoal), and once from aqueous alcohol (charcoal). 1.3 G. of colourless needles, m.p. 28°C, together with 0.6 g. of ester, m.p. 27°C, were obtained. This compound has not previously been reported.

Analysis:

	C	H	Br
% calculated	55.94	3.97	28.63
% found	56.82	4.00	28.12

(2) Ethyl 4-bromo-1-naphthoate.

Ethyl 4-bromo-1-naphthoate was prepared from naphthalene by the following route:- 26,27.



1 : 4 - Dibromo - naphthalene.²⁶

Naphthalene (32 g) in chloroform (150 ml.) was placed in a 500 ml. three necked flask fitted with a mechanical stirrer and a thermometer. A small excess of bromine (95 g) in chloroform was slowly added, the temperature being kept below -5°C with an ice - salt cooling mixture. Addition was completed in three hours. The solution was allowed to come to room temperature and then left for three hours. Excess bromine and chloroform were then distilled off until the volume was about 100 ml. Ethanol (300 ml.) was added and a white solid precipitated. This was fractionally recrystallised from alcohol to give 26.5 g. (37%) of 1:4 dibromo - naphthalene, m.p. $81-82^{\circ}\text{C}$ ($81-82^{\circ}\text{C}$), and 32 g. of eutectic mixture (m.p. 68°C) of 1:4 - and 1:5 - dibromo - naphthalene. Zalkind²⁶ reports yields of up to 10% of the pure 1:4 dibromo - naphthalene but mentions that mild conditions give greater yields.

4 - Bromo - 1 - naphthoic acid.

n - Butyl lithium in ether appears to be particularly effective for the replacement of a single halogen atom by lithium in dihalogeno - benzenes. Higher yields of mono-halogeno - benzoic acids are obtained using this reagent than when the normal Grignard reagent is used²⁹. Work in the naphthalene series indicates a similar trend¹⁷.

(1) Preparation of n - butyl lithium³⁰

Anhydrous ether (100 ml.) was placed in a 250 ml. three necked flask fitted with a stirrer, thermometer, and a dropping funnel. After flushing the apparatus with dry nitrogen, 4.3 g. of lithium ribbon, cut into small pieces, were placed in the flask under a stream of nitrogen. With the stirrer started, about fifteen drops of a solution of dry n - butyl bromide (34 g.) in anhydrous ether (50 ml.) were added from the dropping funnel. The reaction mixture was cooled to -10°C . by immersing the flask in a "dry-ice"- acetone bath. The solution became slightly cloudy and bright spots developed on the lithium. The remainder of the n - butyl bromide was then

added, over thirty minutes, at an even rate. After the addition was completed the mixture was allowed to warm up to 10°C , with stirring, for two hours. The reaction mixture was then filtered, under nitrogen, through a narrow tube loosely plugged with glass wool. The solution was standardised by hydrolysing, with distilled water, aliquots containing reacted and unreacted *n* - butyl lithium solution. By titration of the hydrolysed aliquots with standard acid, the amount of alkali due to the hydrolysis of *n* - butyl lithium was obtained and hence the normality of the *n* - butyl lithium solution was obtained.

(11) Preparation of 4 - bromo - 1 - naphthoic acid.

(Following a method used by Gilman and Moore³¹ for the preparation of 1 - naphthoic acid).

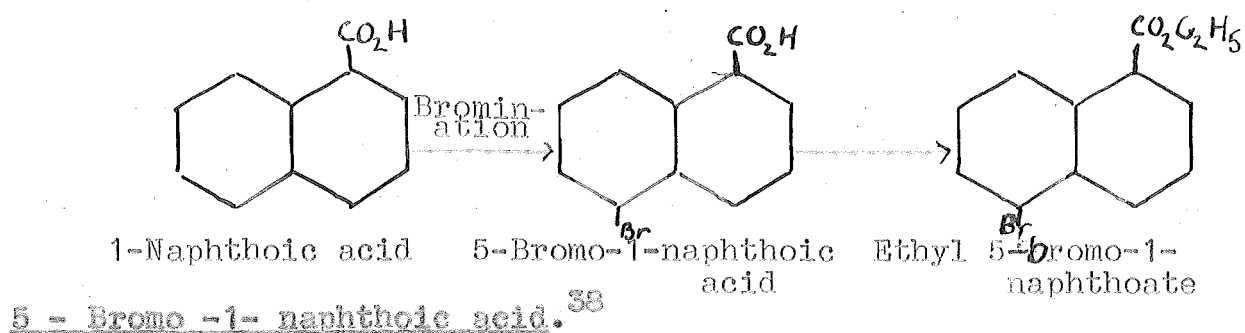
Dry 1:4 - dibromo - naphthalene (.05 moles) was added to *n* - butyl lithium (.07 moles) in ether (70 ml.) in a flask previously flushed with nitrogen. The mixture was shaken at room temperature for five minutes. The contents were then poured into a slurry of solid carbon dioxide (ca. 40g.) and ether. After stirring for a few minutes the mixture was left until all the carbon dioxide had disappeared. The ether layer was extracted with three aliquots of equal volume (approx. 140 ml.) of 8% ammonia and the extractions acidified with 20% hydrochloric acid. The precipitated, crude product was filtered, washed with water, and dried. After recrystallisation from 1:1 alcohol-water 10 g. (80%) of 4 - bromo - 1 - naphthoic acid, m.p. 221°C (220°C), was obtained.

Ethyl 4 - bromo - 1 - naphthoate.

The method of preparation of this ester was similar to that for the 3 - isomer. The yield, after recrystallisation from ethanol, was 6 g. from 6.5 g. of acid. (83%), m.p. 42°C . ($42-43^{\circ}\text{C}$). Further purification through a short alumina column, followed by three recrystallisations (charcoal) removed the persistent, fawn colour and resulted in 4.0 g of white needles, m.p. 43.5°C .

(3) Ethyl 5 - bromo - 1 - naphthoate.

This was prepared by the following route ²⁸:-



1 - Naphthoic acid 4.5 g.), bromine (3.75 g.) and acetic acid (50 ml.) were heated under reflux in a 100 ml. flask for three and a half hours, after which time evolution of hydrogen bromide had ceased. Water was added to precipitate the acid which was then filtered at the pump. One recrystallisation gave 2.7 g. (43%), m.p. 260°C (262°C). Further purification was not attempted as the likely impurity, 8 - bromo - 1- naphthoic acid, being sterically hindered, is not esterified by dry hydrogen chloride in ethanol ³².

Ethyl 5 - bromo - 1- naphthoate.

The method of preparation of ethyl 5 - bromo - 1 - naphthoate was similar to that used for the 3- isomer. The yield from 4.9 g. was 4.8 g. (88%) of colourless needles, m.p. 48-49°C (48-49°C), after two recrystallisations from 1:1 alcohol - water (charcoal).

(4) Ethyl 1 - naphthoate.

Ethyl 1 - naphthoate was prepared from recrystallised 1- naphthoic acid in a similar manner to that described for ethyl 3 - bromo - 1 - naphthoate. The ester was purified by two vacuum distillations. Only a relatively small middle fraction, b.p. 138°C at 3-4 mm. was collected for use.

B. Preparation of Reagents.

Volumetric Ware.

With one exception the volumetric ware was calibrated according to the methods given by Vogel ³³. These consist in determining the weight of water occupied by the volume which is to be calibrated and calculating the true volume from the weight of water and its density at the calibration temperature. All weighings were corrected for buoyancy. The pipette used for delivery of aliquots from the reaction flask was calibrated by determining the weight of the actual reaction solution delivered.

Water.

The water used for making up solutions was from the laboratory distilled water supply. Where necessary the water was freed from carbon dioxide by boiling it under reduced pressure for about fifteen minutes at 40°C. It was then saturated with nitrogen, cooled, and used immediately for the purpose required.

Ethanol.

The ethanol used for kinetics was obtained as the middle fraction of a distillation of fifteen litres of commercial absolute alcohol through a 5 ft. column packed with glass helices. The column was run under reflux, as close as possible to flooding, for 144 hours. Two litres were run off at a reflux ratio of 1 to 30. Most of the aldehyde present in the alcohol should be in these initial fractions. The next ten litres of distillate were collected at the same reflux ratio. An estimate of the amount of aldehyde in the sample was made by comparative tests with Schiff's reagent. Less than .001% aldehyde was present.

The ethanol was stored under nitrogen in a flask fitted with a siphon and stopcock. The density was determined at 25°C using a pycnometer of approximately 15 ml. capacity, which was first standardised with distilled water. Fifteen determinations were obtained for the ethanol. The values, in good agreement with each other, gave an average density corresponding to a composition 99.64% $\pm$.02% of ethanol, by weight. This value

was obtained from the density-composition data from the International Critical Tables.

Hydrochloric acid solution.

A solution of approximate normality 0.01 was prepared. It was standardised against samples from a solution of freshly recrystallised A.R. borax, using methyl red as indicator. It had normality of 0.01011 ± 0.00002 . A second standardisation, in which different borax was used, gave a value agreeing to one part in a thousand.

Sodium hydroxide solutions.

Two solutions of sodium hydroxide were prepared from A.R. sodium hydroxide. They were made carbonate free by preparing a saturated solution and separating the insoluble carbonate by filtration (pump) through a sintered glass funnel, using an apparatus designed to exclude carbon dioxide during the filtration³⁴. The approximate amount required for each solution was shaken up in a 4 litre polythene bottle with carbonate-free distilled water. Each bottle was fitted with a soda-lime guard tube and a polythene tube leading to a burette, the whole apparatus being designed so that the solution could be transferred to the burette without being brought into contact with carbon dioxide in the air.

The stronger of the two solutions was standardised against A.R. potassium hydrogen phthalate using phenolphthalein as an indicator. The normality was found to be 0.2571 ± 0.0002 . The weaker solution standardised against the standard hydrochloric acid, using bromothymol blue as indicator, had a normality of $0.00714 \pm 0.1\%$. Since the burette used for this solution had a calibration factor of 1.003, the normality was taken as .00716, as delivered by the burette.

Indicator.

Thymol blue was used as the indicator for following kinetics. It was prepared by triturating 0.25 g. of the solid indicator with 2 ml. of 0.25N sodium hydroxide, before diluting to 250 ml. with water.

"Alkaline Reagent".

Approximately 800 g. of 99.64% ethanol solution were weighed into a Winchester bottle. The amount of .2571 M sodium hydroxide required to make the ethanol - water composition 85:15 (W/W) and the molality approximately 0.015, was added. The Winchester was then fitted with a stopcock and siphon so that the solution could be run out under nitrogen. The molality was determined by withdrawing aliquots with a calibrated 5 ml pipette and adding them to an excess of acid solution. The excess acid was then titrated with .00716 N sodium hydroxide solution using bromothymol blue as indicator. An atmosphere of nitrogen was maintained in the Erlenmeyer flask during titration. This stock solution of alkaline reagent was restandardised at frequent intervals. The concentration of alkali decreased less than 1% per fortnight. Thus at room temperature and with the concentration of alkali used, alkaline attack on the glass container is very slight. This enables such a stock solution to be stored for reasonable periods of time, thus avoiding lengthy preparation of solutions for individual runs.

C. Determination of Rate Constants.

Temperature control and Measurement.

The heating of the water-filled thermostatted bath was controlled by two heating elements, one of which was in series with a Variac, a Sunvic hot wire vacuum switch, and a Simmerstat; the other element was in series with a Variac and maintained a constant supply of heat, not quite sufficient to hold the bath at the required temperature. By appropriate adjustment of the Variac and Simmerstat in series with the regulator the temperature of the bath could be kept constant to $\pm 0.01^{\circ}\text{C}$. Bath temperatures were determined with thermometers checked against thermometers standardised by the National Physical Laboratory.

Time Measurement.

Times were measured using a stop-watch previously checked against the N.Z.B.S. time signals.

Method:

The analytical procedure used for the determination of rate constants was similar to that used by previous workers in this laboratory.^{8,12} The method is based on the procedure of Evans, Gordon and Watson³⁵. Current modifications will be discussed later.

A sample of ester was weighed into a small, glass boat. The alkaline ethanol solution required to contain an equivalent number of moles was then exactly weighed out into a stainless steel cylindrical reaction vessel of 75 ml. capacity. The weight of ester was so chosen that the quantity of solution required would be approximately 40 g. The glass boat containing the ester was dropped into the reaction vessel, which was then stoppered and shaken. The vessel was placed in the bath, left for approximately ten minutes for temperature equilibrium to be reached, and the first aliquot (5 ml) removed with the pipette. The aliquot was run into a flask containing excess acid which stops the hydrolysis reaction. The amount of alkali in the aliquot was then determined by back - titration. Using this method it was possible to follow three runs simultaneously.

By keeping the molar concentrations of alkali and ester equal, it was possible to calculate the rate constants, using the simplified form of the second order rate equation.

$$\frac{dx}{dt} = k(a - x)^2 \quad (3)$$

where a = initial concentration of ester and alkali in moles per kilogram.

x = concentration of product in moles per kilogram.

$a - x$ = concentration of unreacted ester in moles per kilogram.

t = time in seconds.

k = rate constant in kilogram mole⁻¹seconds⁻¹.

Integrating and rearranging (3).

$$\frac{1}{a-x} = kt + \frac{1}{a} \quad (4)$$

Thus if $\frac{1}{a-x}$ is plotted against t , the bimolecular rate constant is obtained from the slope. This rate constant was converted to the normal units of litre mole⁻¹ seconds⁻¹.

Blank runs (that is, with no ester) over a period of 36 hours at 55°C and 65°C showed no change in alkali concentration. Thus both attack of alkali on the vessel and evaporation of ethanol and absorption of carbon dioxide when the aliquots were withdrawn, are shown to be negligible.

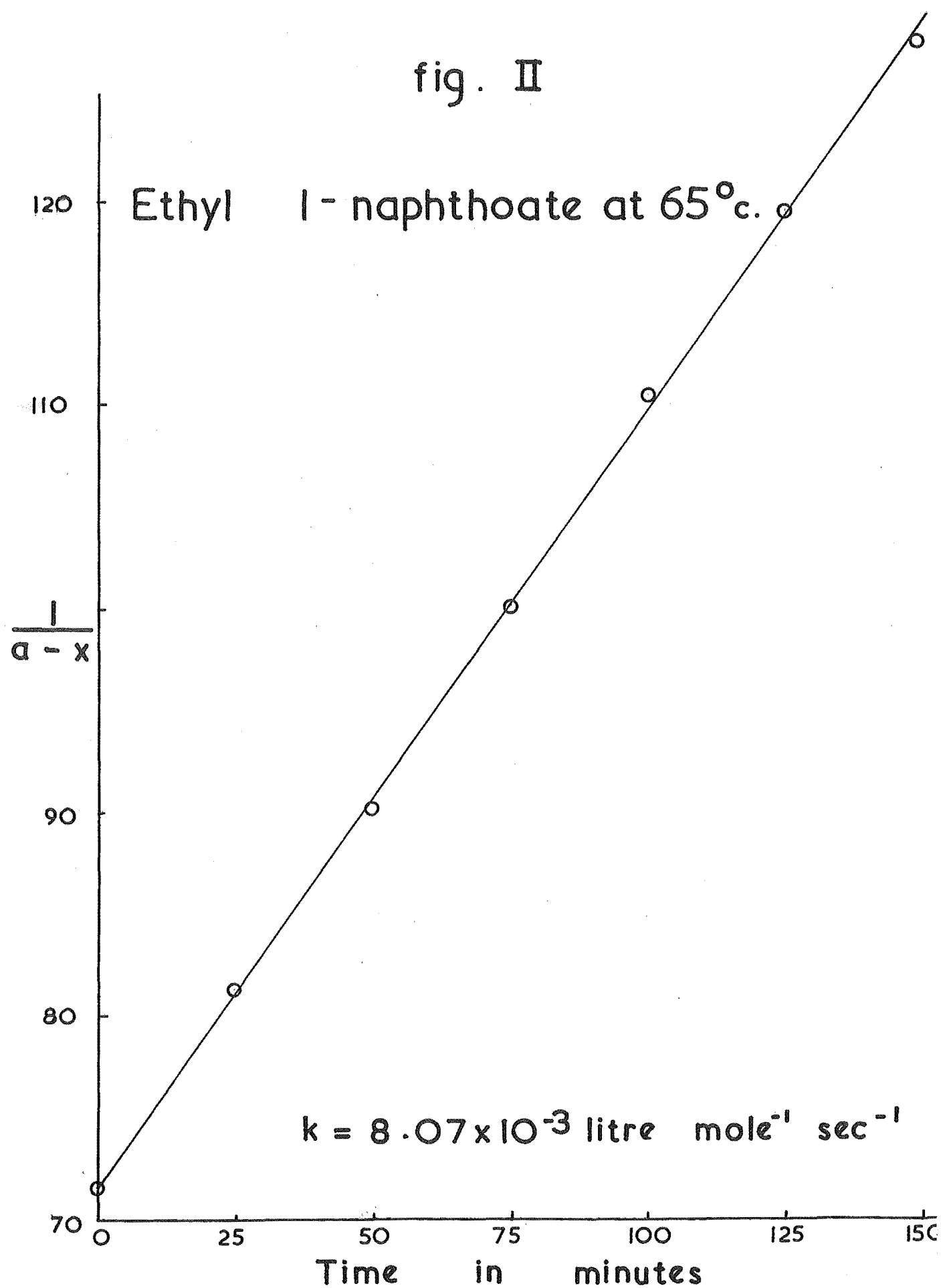
Densities of 85% ethanol at 65°C, 55°C and 45°C were obtained by solving the equation¹⁶.

$$d_T = 0.84770 - 0.00814T - 0.0000012T^2 \quad (5)$$

where d_T is the density at T°C.

In all cases runs were followed to approximately 50% hydrolysis.

fig. II



III RESULTS.

Details of one typical run and the accompanying graph are given for each ester studied.

(1) Ethyl 1 - naphthoate at 65°C.

Wt. ester = .16040 g.

Alkaline reagent contains .01511 moles base per 1000 g.

∴ Wt. alkaline ethanol reagent required for equimolecular concentrations

$$= \frac{.16040 \times 1000}{.01511 \times 200.24} \text{ g.}$$

$$= 53.01 \text{ g.}$$

Wt. alkaline reagent delivered by pipette at 65°C = 4.02 g.

Density 85% ethanol at 65°C = .78972

∴ $\left(\frac{1}{\text{Density}} \right)_{65^\circ\text{C}}$ = 1.266

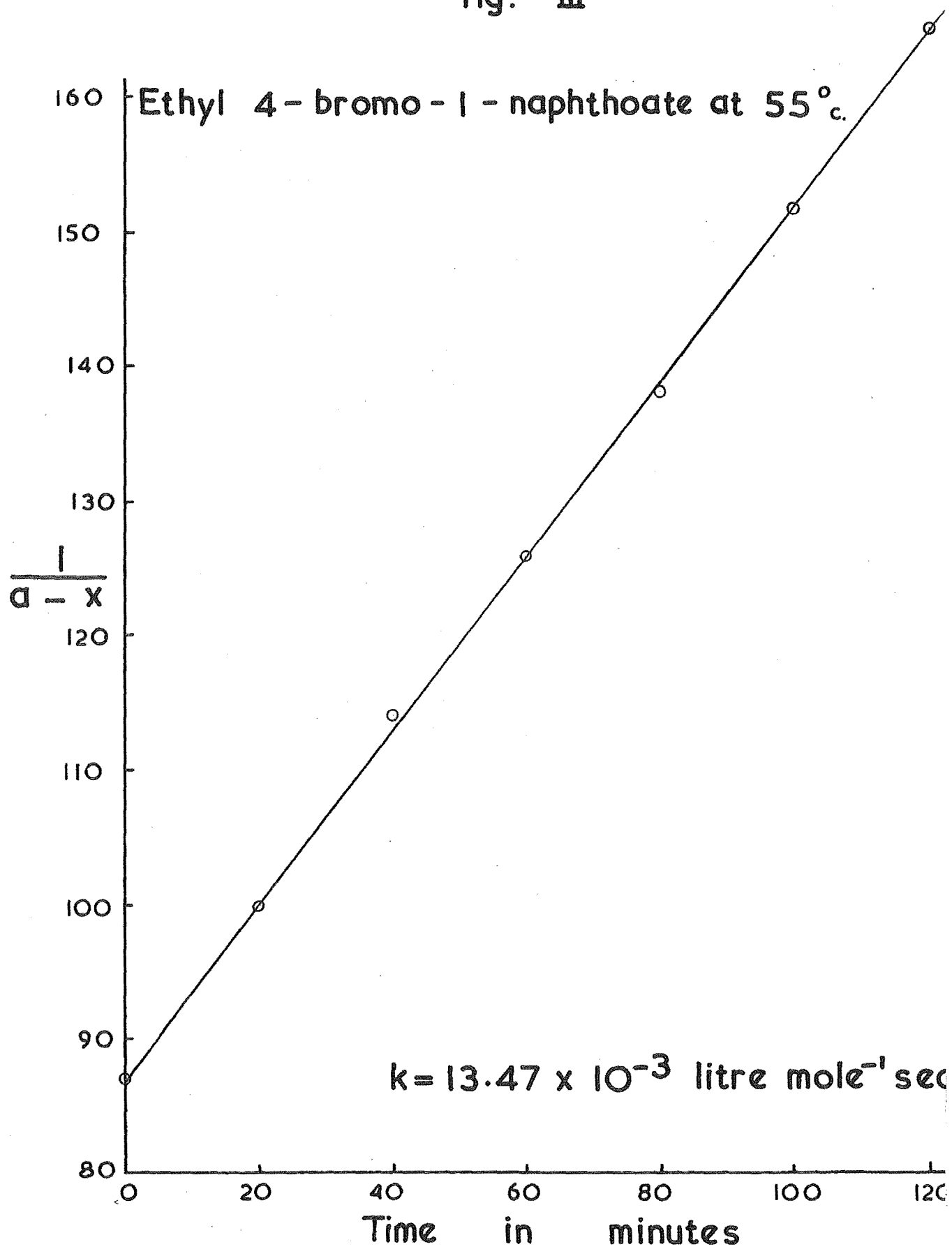
Titration Results

Time in mins.	Vol. NaOH used (ml.)	Moles $\times 10^5$ NaOH used	Moles $\times 10^5$ HCl used	Moles $\times 10^5$ NaOH in aliquot	$\frac{1}{a - x}$ (moles per 1000 g.) ⁻¹
0	2.04	1.461	7.077	5.616	71.6
45	2.99	2.141	7.077	4.936	81.4
50	2.25	1.611	6.066	4.455	90.2
75	2.87	2.055	6.066	4.011	100.2
100	3.40	2.434	6.066	3.632	111.7
125	3.79	2.714	6.066	3.352	119.9
150	4.11	2.943	6.066	3.123	128.7

Result: $k = 2.07 \times 10^{-3} \text{ litre mole}^{-1} \text{ sec}^{-1}$

A plot of time against $\frac{1}{a - x}$ is shown in Figure II

fig. III



(2) Ethyl 4 - bromo - 1 - naphthoate at 55°C.

Wt. ester = .13305 g.

Alkaline reagent contains .01242 moles base per 1000 g.

∴ Wt alkaline reagent required for
equimolecular concentrations = $\frac{.13305 \times 1000}{279.15 \times .01242}$ g.

= 38.38 g.

Wt. alkaline reagent delivered by pipette
at 55°C = 4.055 g.

Density 85% ethanol at 55°C = .79929

∴ ($\frac{1}{\text{density}}$) 55°C = 1.251

Titration Results

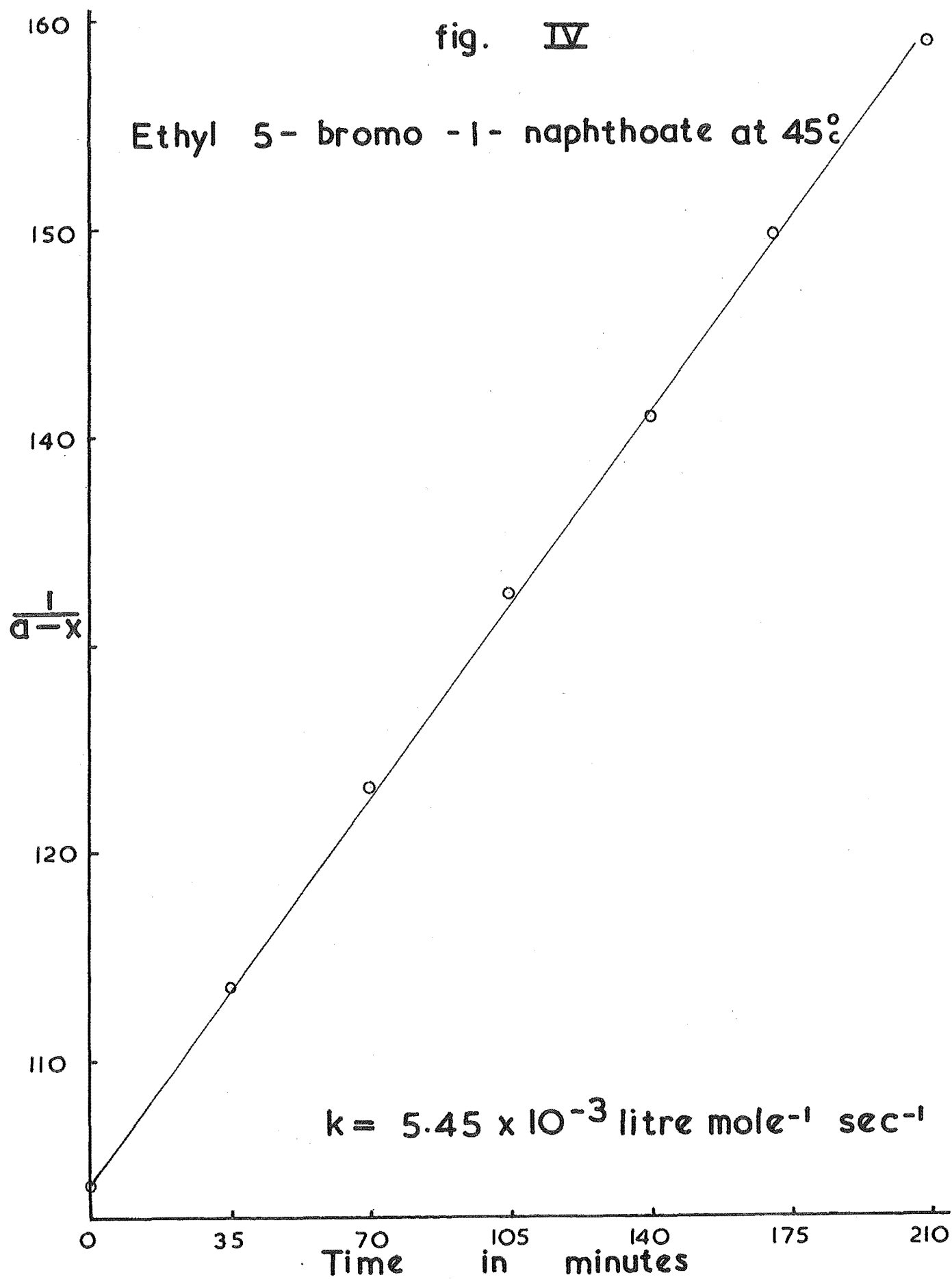
Time in mins.	Vol NaOH used(ml)	Moles x 10 ⁵ NaOH used	Moles x 10 ⁵ HCl used	Moles x 10 ⁵ NaOH in aliquot	$\frac{1}{a-x}$ (moles per 1000 g.) ⁻¹
0	1.96	1.403	6.066	4.663	87.0
20	2.79	1.998	6.066	4.068	99.7
40	3.55	2.542	6.066	3.524	115.1
60	3.97	2.843	6.066	3.223	125.8
80	4.37	3.129	6.066	2.937	138.1
100	4.74	3.394	6.066	2.672	151.8
120	5.04	3.609	6.066	2.457	165.0

Result: $k = 13.47 \times 10^{-5}$ litre mole⁻¹ sec⁻¹.

A plot of t against $\frac{1}{a-x}$ is shown in Figure III.

fig. IV

Ethyl 5-bromo-1-naphthoate at 45°



(3) Ethyl 5 - bromo - 1 - naphthoate at 45°C.

Wt. ester = .11150 g.

Alkaline reagent contains .01015 moles base per 1000 g.

∴ Wt. alkaline reagent required for
equimolecular concentration

$$= \frac{.11150 \times 1000}{279.15 \times .01015} \text{ g.}$$

$$= 39.35 \text{ g.}$$

Wt. alkaline reagent delivered by pipette
at 45°C = 4.085 g.

Density 85% ethanol at 45°C = .80864

∴ $\left(\frac{1}{\text{Density}} \right)_{45^\circ\text{C}}$ = 1.237

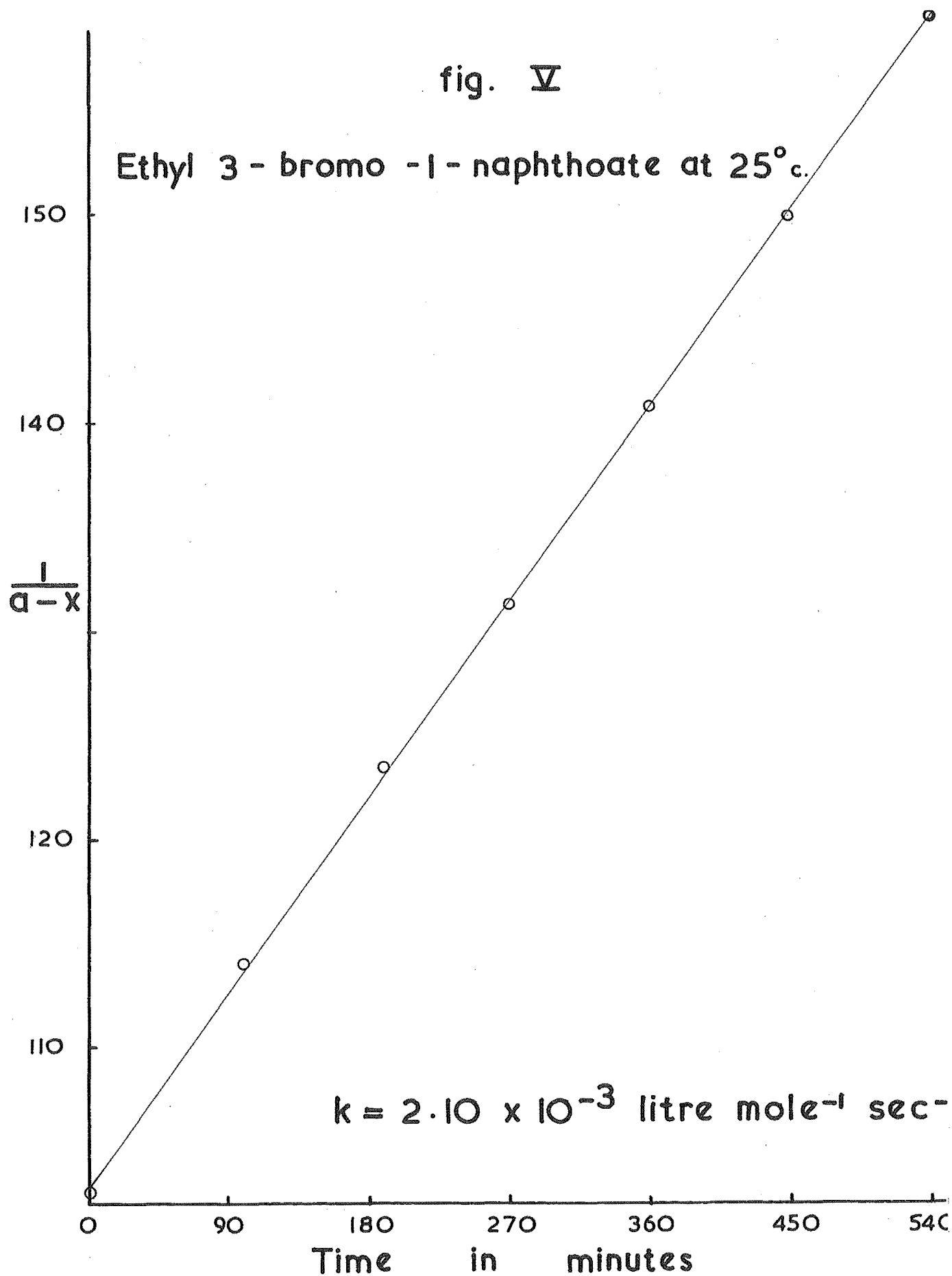
Titration Results

Time in mins.	Vol. NaOH used (ml)	Moles $\times 10^5$ NaOH used	Moles $\times 10^5$ HCl used	Moles $\times 10^5$ NaOH in aliquot	$\frac{1}{a-x}$ (moles per 1000 g.) ⁻¹
0	1.58	1.131	5.055	3.924	104.0
35	2.04	1.461	5.055	3.594	113.5
70	2.44	1.747	5.055	3.308	123.3
105	2.76	1.976	5.055	3.079	132.5
140	3.02	2.162	5.055	2.893	141.0
175	3.25	2.327	5.055	2.728	149.5
210	3.48	2.492	5.055	2.563	159.2

Result: $k = 5.45 \times 10^{-3}$ litre mole⁻¹ sec⁻¹.A plot of t against $\frac{1}{a-x}$ is shown in Figure IV.

fig. V

Ethyl 3 - bromo - 1 - naphthoate at 25°c.



(4) Ethyl 3 - bromo - 1 - naphthoate at 25°C.

Wt. ester = .10800 g.

Alkaline reagent contains .00980 moles base per 1000 g.

∴ Wt. alkaline reagent required for

equimolecular concentrations

$$= \frac{.10800 \times 1000}{.0098 \times 279.15} \text{ g.}$$

$$= 39.47 \text{ g.}$$

Wt. alkaline reagent delivered by
pipette at 25°C

$$= 4.120 \text{ g.}$$

Density 85% ethanol at 25°C

$$= .82660$$

$$\therefore \left(\frac{1}{\text{density}} \right)_{25^\circ\text{C}}$$

$$= 1.210$$

Time in mins.	Vol. NaOH used (mL)	Moles $\times 10^5$ NaOH used	Moles $\times 10^5$ HCl used	Moles $\times 10^5$ NaOH in aliquot	$\frac{1}{a-x}$ (moles per 1000 g.) ⁻¹
0	1.48	1.050	5.055	3.995	103.1
100	2.14	1.529	5.055	3.526	114.0
190	2.51	1.800	5.055	3.255	123.5
270	2.78	1.991	5.055	3.064	131.2
360	3.07	2.198	5.055	2.857	140.7
450	3.31	2.371	5.055	2.684	149.8
540	3.54	2.535	5.055	2.520	159.5

Result: $k = 2.10 \times 10^{-5}$ litre mole sec⁻¹.A plot of t against $\frac{1}{a-x}$ is shown in Figure V.

The complete list of rate constants for the four esters is given in Table I. These values were fitted to the Arrhenius rate equation.

$$k = A e^{\frac{-E}{RT}} \quad (6)$$

$$\text{or } \log_{10} k = \log_{10} A - \frac{E}{RT} \ln 10 \quad (7)$$

where E is the activation energy and $\log_{10} A$ is the frequency factor. Plots of $\log_{10} k$ against $\frac{1}{RT \ln 10}$ for each of the esters are given in Figures VI, VII, VIII, and IX. The points shown are those for the mean experimental values of the rate

TABLE IRate constants $\times 10^3$ in Litre Mole⁻¹ sec⁻¹.

Temperature	Substituted Ethyl 1 - naphthoate.			
	<u>H</u>	<u>3-Br</u>	<u>4-Br</u>	<u>5-Br</u>
25°C [±] .01°C	.241	2.16	1.050	1.040
	.242	2.13	1.040	1.047
	.240	2.10		1.037
<u>Mean</u>	<u>.241</u>	<u>2.13</u>	<u>1.045</u>	<u>1.041</u>
35°C [±] .01°C	.716		2.72	
	.719		2.77	
			2.83	
<u>Mean</u>	<u>.717</u>		<u>2.77</u>	
45°C [±] .01°C		11.27		5.57
		11.20		5.45
		11.33		5.57
<u>Mean</u>		<u>11.27</u>		<u>5.53</u>
55°C [±] .01°C	3.43		13.29	12.68
	3.40		13.29	12.59
	3.45		13.20	
	3.45		13.47	
<u>Mean</u>	<u>3.43</u>		<u>13.31</u>	<u>12.64</u>
65°C [±] .01°C	8.12	49.6	31.8	25.93
	8.12	52.0	32.0	25.93
	8.07	52.4	31.6	25.64
	8.07			
<u>Mean</u>	<u>8.10</u>	<u>51.3</u>	<u>31.8</u>	<u>25.83</u>

fig. VI

Arrhenius Plot

Ethyl - 1 - naphthoate

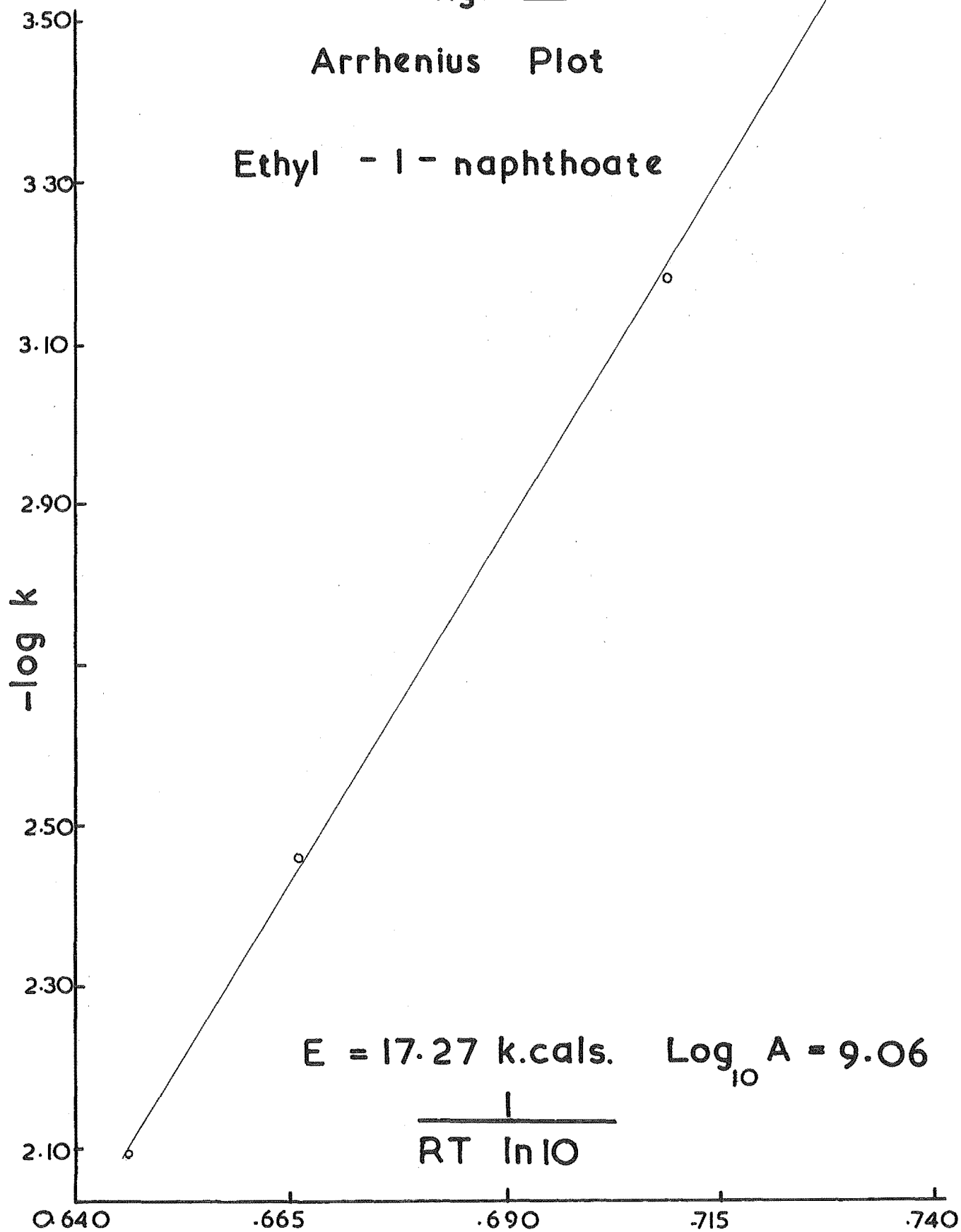


fig. VII

Arrhenius Plot

Ethyl 3-bromo-1-naphthoate

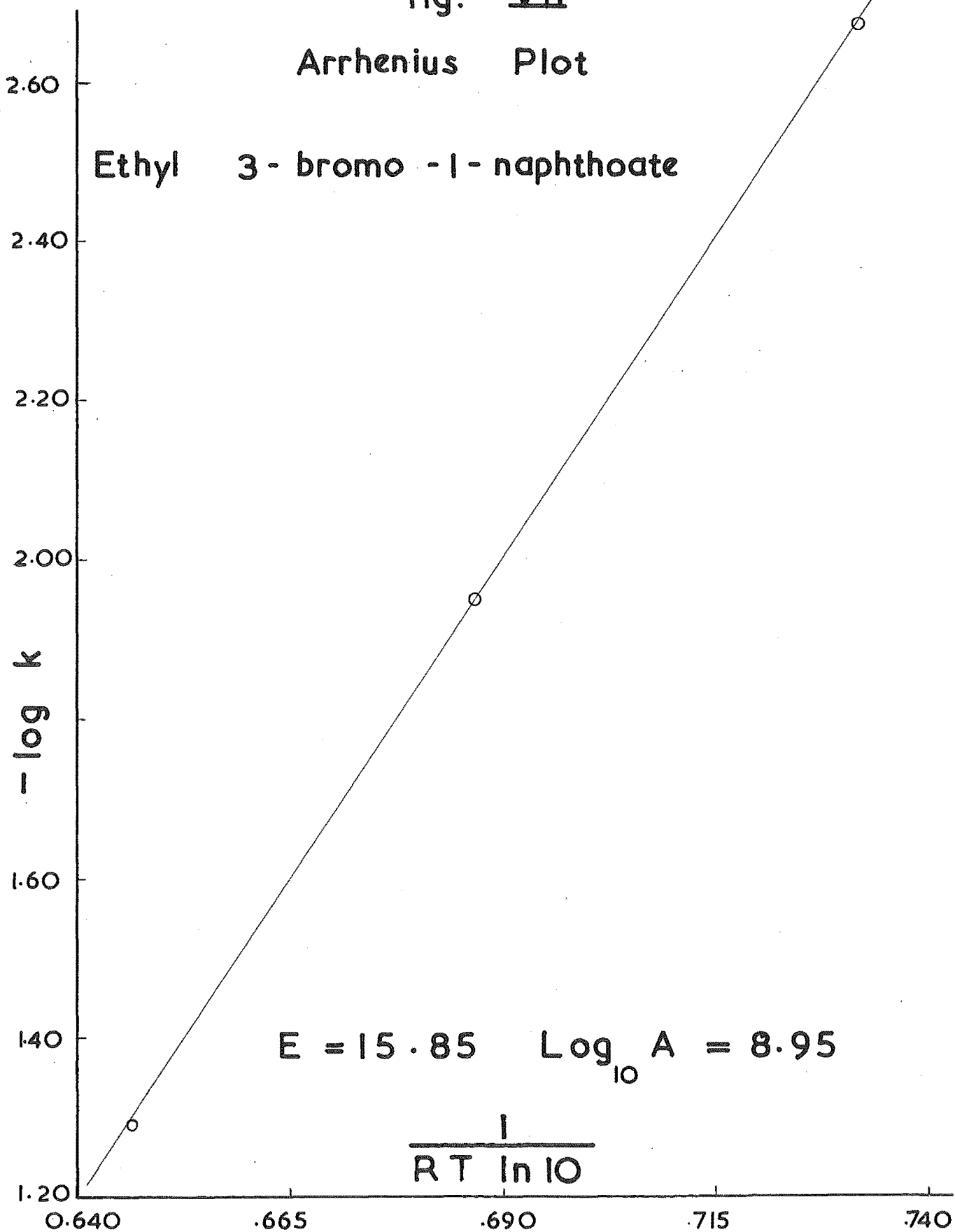


fig. VIII

Arrhenius Plot

Ethyl 4-bromo-1-naphthoate

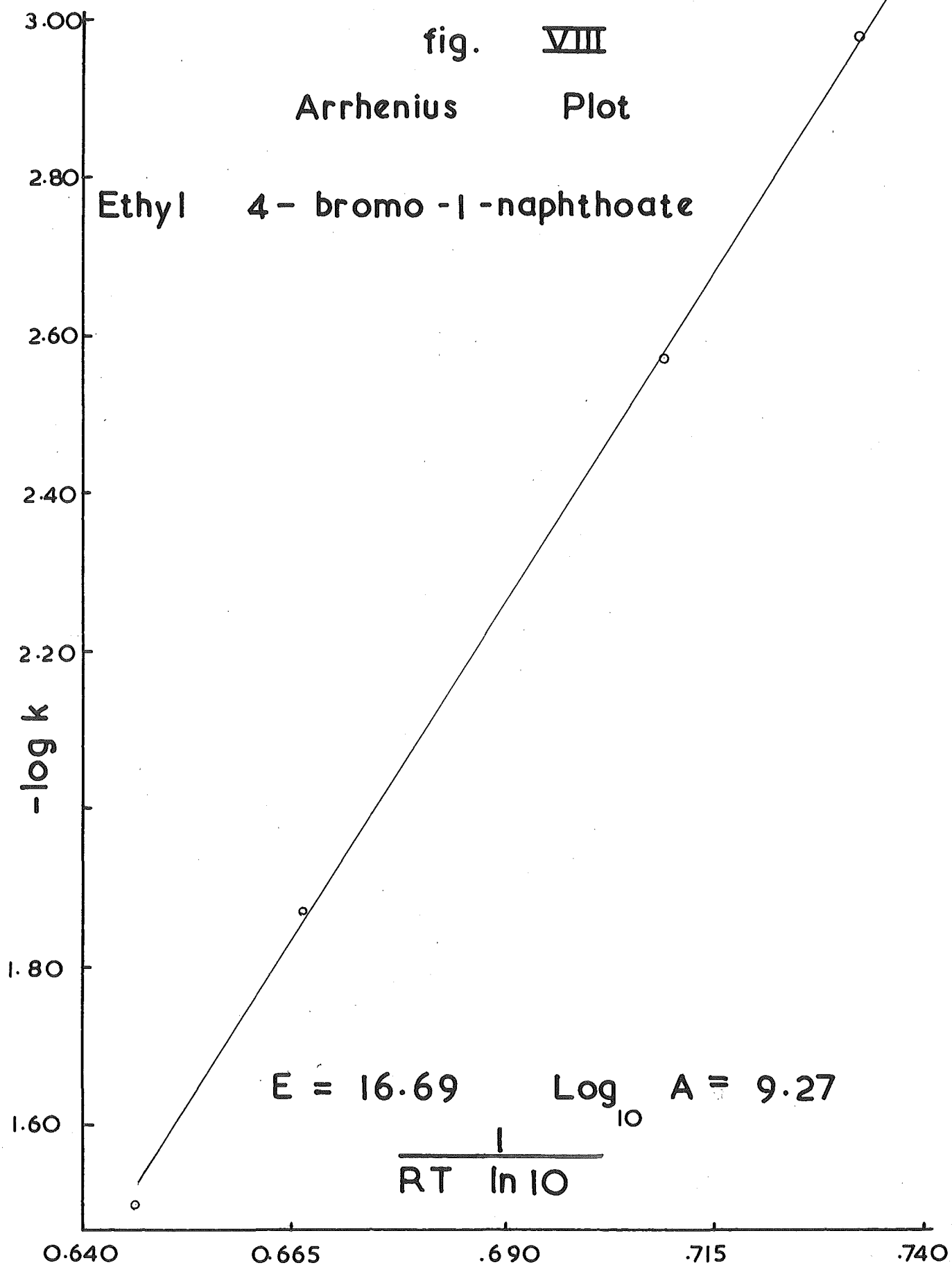
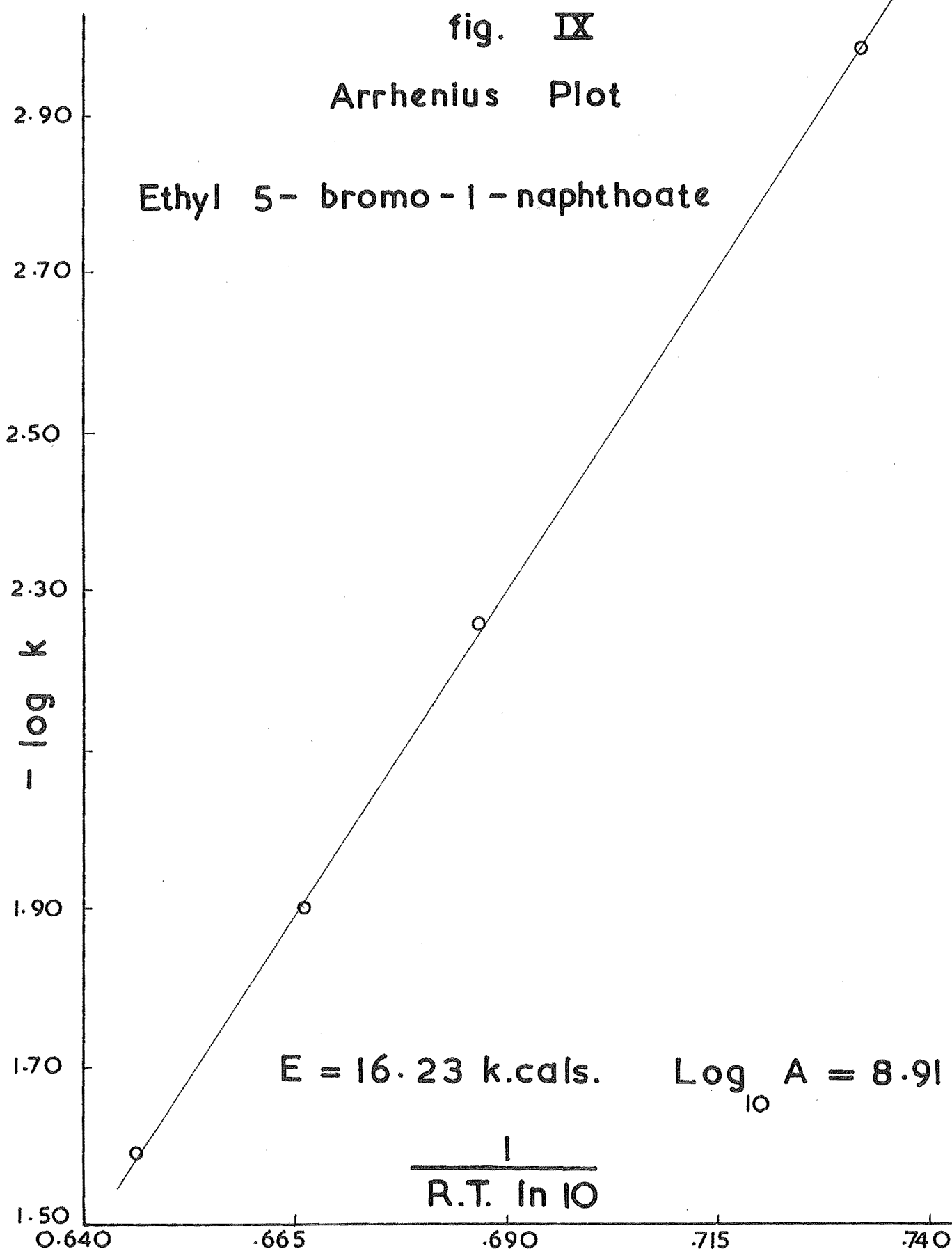


fig. IX

Arrhenius Plot

Ethyl 5-bromo-1-naphthoate



constant at the given temperature, but the lines drawn are those obtained by the method of least squares³⁶, using the individual values that were obtained. From equation (7) the slopes of the graphs give the activation energy E and the intercepts give values for $\log_{10} A$. The errors in slope and intercept were calculated³⁷. It must be emphasised that these errors are only a measure of the error in fitting the regression line to the points obtained and not a measure of the absolute accuracy of E and $\log_{10} A$.

The values of E and $\log_{10} A$ are given in Table II below -

TABLE II
Arrhenius Parameters

<u>Compound</u>	<u>E (k.cal.mole⁻¹)</u>		<u>$\log_{10} A$</u>	
Ethyl 1- naphthoate	17.27 [±]	.14	9.06 [±]	.10
Ethyl 3- bromo -1- naphthoate	15.85 [±]	.06	8.94 [±]	.05
Ethyl 4- bromo -1- naphthoate	16.69 [±]	.14	9.27 [±]	.10
Ethyl 5- bromo -1- naphthoate	16.23 [±]	.07	8.91 [±]	.05

Experimental Accuracy and Probable Errors.

There are experimental errors in the weighing, timing, withdrawing of aliquots, and titrating processes used in the determination of the rate constant. The total such error is estimated to be of the order of $\pm 1\frac{1}{2}$ %. The experimental rate constants can be seen from Table I to have a variance of this order.

IV

DISCUSSIONA. The Method for Determining Rate Constants.

Certain features of the method for determining rate constants are discussed under the following headings.

(1) Blank effects.

Using glass vessels previous workers ^{8,16,17} in this department had noted the consumption of alkali during a blank run without ester. Mitchell ¹⁷ found that such a "blank effect" increased with temperature and that at 65°C the effect was of the order of 3% decrease in alkali concentration per hour. Other workers have also noted such effects. For example, Westheimer and Metcalf ³⁸ found that alkali concentration decreased at 55°C by 0.4% per hour. It is difficult to correct for such an effect because it causes a continuous change in concentration of alkali relative to ester, thus upsetting the original equimolar conditions. In this work blank effects were eliminated by using stainless steel reaction vessels. (see page 20).

(2) Solvent addition.

In measuring the rate constants, the end point of the back titration was obscured by flocculant precipitates. Mitchell (private communication) avoided this precipitation in his work ¹⁷ by adding 5 ml. of neutralised distilled alcohol to the hydrochloric acid into which each aliquot was run. In this work for runs on ethyl 4 - bromo - 1 - naphthoate at 65°C the back titrations were carried out with and without extra solvent.

Without the solvent individual runs were not only erratic, as expected due to the obscured end point, but also the rate constants obtained were about twelve per cent lower than those obtained with the extra solvent. The difference must be because the precipitate contains much of the organic acid to be titrated. Therefore, where such precipitation occurs, the rate constants are in error, and hence in this work extra solvent was always added.

(3) Indicator.

Since, at the end point, the titration was that of sodium hydroxide against an organic acid, thymol blue indicator (pH change 8.0 - 9.5) was used.

B. Mechanism of Reaction.

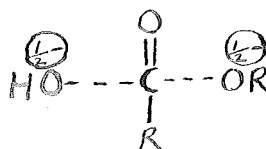
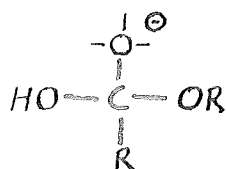
Ingold³⁹ has classified the possible mechanisms of ester hydrolysis. This classification is based on (a) the nature of the reagent, (b) the position of fission of the ester, and (c) the order of reaction.

In this work the attacking reagent was the hydroxyl ion. The order of reaction has been conclusively shown to be first order with respect to hydroxyl ion and to ester and second order overall⁸. According to Ingold's classification, the mechanism is thus determined except for knowledge of the position of fission of the ester. The two possibilities are "acyl-oxygen fission"⁷, or "alkyl-oxygen fission", which, in Ingold's terminology are the $B_{Ac}2$ and $B_{Al}2$ mechanisms respectively.

"Acyl - oxygen" fission has been proved by O¹⁸ studies⁴⁰ for ethyl benzoates in 85% ethanol and thus the $B_{Ac}2$ mechanism is expected for ethyl naphthoate alkaline hydrolysis in this solvent. Furthermore, it has recently been shown by similar studies⁴¹ that both sterically hindered methyl 2:6-dimethyl benzoates and normal methyl benzoates undergo alkaline hydrolysis in dioxan-water by the "acyl-oxygen fission" mechanism. The steric influence of the fused benzene ring in the naphthalene series can be assumed therefore to cause no change in mechanism

from that of the "acyl-oxygen fission" of the benzene series.

"Acyl-oxygen fission" may be represented by two mechanisms, one involving an addition intermediate and the other a transition state intermediate. These are represented by I and II respectively.



These differ only in electron distribution and therefore may be regarded as canonical forms of a mesomeric system. The mesomeric intermediate will, by resonance theory, be more stable than either of the two contributing canonical forms.

C. Relative Free Energies, Heats and Entropies of Activation.

The thermodynamic quantities in terms of which the effect of structures on reaction can be discussed are given by the relative free energy, heat, and entropy changes for the hypothetical equilibrium ⁴².



X is a general reactant of a reaction series and X_o is the reactant selected as the standard of comparison. The starred terms throughout this discussion refer to corresponding reaction transition states. The following thermodynamic relationships apply for this equilibrium ⁴⁴.

$$\Delta\Delta G^{\ddagger} = -RT \ln \frac{k}{k_o} \quad (8)$$

$$\Delta\Delta H^{\ddagger} = E - E_o \quad (9)$$

$$\Delta\Delta S^{\ddagger} = \ln 10 R (\log_{10} A - \log_{10} A_o) \quad (10)$$

$\Delta\Delta G^{\ddagger}$, $\Delta\Delta H^{\ddagger}$, and $\Delta\Delta S^{\ddagger}$ are the relative free energy, heat, and entropy of activation and k, E, and A are as previously defined. Using equations (8), (9), and (10), and with ethyl naphthoate as the standard ester, relative free energies, heats,

and entropies of activation have been calculated. These values are shown in Table III together with values obtained by earlier workers. Also included in Table III are the values obtained for ethyl 1-naphthoate under similar conditions by Fierens⁴⁶. Where workers have studied both substituted and unsubstituted esters, then values given are those obtained from their particular values for the standard ester. Where workers have not studied the unsubstituted ester, the values given are those obtained using values of ethyl 1-naphthoate as found in the present project. In this way variations due to individual workers will be reduced. Corresponding values for the benzene series^{35,45} are given in Table IV.

Conditions for the Hammett equation to hold⁴ are either (a) $\Delta\Delta S^\ddagger = 0$ or (b) if $\Delta\Delta S^\ddagger \neq 0$, then $\frac{\Delta\Delta S^\ddagger}{\Delta\Delta H^\ddagger} = \text{constant}$. From Table III it is seen that values of $T\Delta\Delta S^\ddagger$ obtained in the present work are 0 ± 0.30 k.cals., and no significant trend is observable. From Table IV it is seen that such values for ethyl benzoates (excepting the sterically hindered 2-nitro-benzoate) under similar conditions are 0 ± 0.20 k.cals. It is concluded that in both series $T\Delta\Delta S^\ddagger$ is equal to zero within experimental error and hence a sufficient condition for the Hammett equation to apply is obeyed.

Values of $T\Delta\Delta S^\ddagger$ for esters, unhindered by the substituent, obtained outside this work are slightly larger, as is shown in Table III. Fischer, Murdoch, et.al.²³, point out that Arrhenius log A values (upon the constancy of which zero values of $T\Delta\Delta S^\ddagger$ depend) vary markedly for small changes in ethanol-water composition. On this basis, they suggest that slight variations in the composition of the batches of ethanol-water used are sufficient to cause the deviation from zero obtained for the values of $T\Delta\Delta S^\ddagger$.

Since Mitchell¹⁷, using one batch of ethanol obtained values of log A which varied from 8.73 to 9.62 and since care was taken by all workers both in obtaining an accurate determination of the ethanol-water composition and also in avoiding changes in this composition during storage, the explanation

TABLE III

Substituted Ethyl 1- naphthoate	Reference	$k_{25^\circ\text{C}} \times 10^3$	E	$\log 10^4$	$\Delta\Delta G^\ddagger_{(25^\circ\text{C})}$	$\Delta\Delta H^\ddagger_{(25^\circ\text{C})}$	$T\Delta\Delta S^\ddagger_{(25^\circ\text{C})}$
H	* a.	.250	17.27	9.06	-	-	-
H	17 a.	.286	16.74	8.73	-	-	-
H	16 a.	.251	17.22	9.01	-	-	-
H	46 a.	.335	16.93	8.94	-	-	-
3-Br	* a.	2.13	15.85	9.27	-1.27	-1.42	-.15
4-Br	* a.	1.08	16.69	8.95	-0.86	-0.58	+.28
5-Br	* a.	1.021	16.23	8.91	-0.83	-1.04	-.18
3-Cl	17 a.	2.08	16.13	9.14	-1.17	-0.61	+.56
4-Cl	17 a.	.954	17.25	9.62	-0.71	+0.51	1.23
3-Me	16 a.	.176	17.78	9.27	+0.21	+0.56	+.35
4-Me	16 a.	.109	18.05	9.26	+0.50	+0.83	+.34
2-NO ₂	8 b.	.031	16.62	7.67	+1.26	-0.65	-1.89
3-NO ₂	8 b.	11.00	16.39	10.03	-2.27	-0.88	+1.37
4-NO ₂	8 b.	12.00	16.29	10.02	-2.32	-0.98	+1.35
5-NO ₂	8 a.	4.17	16.19	9.49	-1.68	-1.06	+.58
6-NO ₂	8 a.	3.89	15.84	9.20	-1.63	-1.43	+.19
8-NO ₂	8 a.	.0017	19.71	8.66	+3.00	+2.44	-.55
4:5-di-NO ₂	8 a.	.246	18.32	10.62	-4.14	-1.95	+2.12

* From the present work.

(a) Titration method.

(b) Conductivity Method.

Units: k is in litre mole⁻¹ sec.⁻¹; E , $\Delta\Delta G^\ddagger$, $\Delta\Delta H^\ddagger$, and $T\Delta\Delta S^\ddagger$ are in k cal. mole⁻¹.

TABLE IV							
Substituted Ethyl 1- benzoate	Reference	$10^3 k (25^\circ\text{C})$	E	$\log_{10} A$	$\Delta\Delta G^\ddagger (25^\circ\text{C})$	$\Delta\Delta H^\ddagger (25^\circ\text{C})$	$T\Delta\Delta S^\ddagger (25^\circ\text{C})$
H	45	0.550	17.7	9.78	-	-	-
H	35	0.621	17.7	9.73	-	-	-
4-Br	45	2.89	16.8	9.77	-0.98	-0.90	0.06
3-Cl	35	4.77	16.4	9.71	-1.22	-1.3	-0.10
4-Cl	45	2.37	16.8	9.69	-0.86	-0.9	-0.06
3-Me	35	0.433	17.9	9.77	0.20	0.2	-0.01
4-Me	45	0.251	18.2	9.76	0.47	0.5	0.04
3-NO ₂	35	42.9	15.4	9.94	-2.50	-2.3	0.20
4-NO ₂	35	72.0	14.8	9.72	-2.81	-2.9	-0.10
2-NO ₂	35	5.41	15.1	8.84	-1.09	-2.6	-1.30.

The values for this substituent have been recalculated from the rate constants given by Evans, Gordon and Watson⁵⁰, who appear to have made an error in their calculations from their own rate constants.

Units: k is in litre mole⁻¹sec.⁻¹; E , $\Delta\Delta G^\ddagger$, $\Delta\Delta H^\ddagger$, and $T\Delta\Delta S^\ddagger$ are in kcal. mole⁻¹.

given appears inadequate for the deviations observed. By using the experimental modifications of method, as discussed in Section (A) of this discussion such deviations have been reduced and values of $T\Delta\Delta S^\ddagger$ have only small random deviations from zero. The mean value obtained for $\log_{10} A$ in this work is 9.06 ± 0.20 .

For the 4- bromo ester studied, the value of $\Delta\Delta G^\ddagger$ was similar, within experimental error, to that of the corresponding benzene ester. Unfortunately the hydrolysis of ethyl 3- bromo - benzoate has not been studied in 85% ethanol. For Hydrolysis under other conditions^{48,49} ethyl 3 - chloro and 3 - bromo - benzoates have similar relative free energies of activation. As the relative free energies of activation of ethyl 3 - bromo - and ethyl 3 - chloro - 1 - naphthoates are also similar (Table III) it may be assumed that similar relationships between the series will hold generally for both substituents. For all substituted ethyl 1 - naphthoates where the substituent is not affected by steric requirements of other groups, the $\Delta\Delta G^\ddagger$ values for the two series (Tables III and IV) agree within experimental error. This implies that the polar effect of the substituent is independent of any effects caused by differences between the series. In particular this confirms the principle (see page 4) of independence of the polar effect of the substituent and the resonance effect of the functional group in these cases.

On the other hand, the mean values for the Arrhenius parameter $\log_{10} A$ are different for the two series. The values are 9.06 and 9.76 for the naphthalene and the benzene series respectively. This difference is caused by a steric effect of the adjacent fused benzene ring in 1 - naphthyl derivatives. This is discussed below in a consideration of steric effects of this substituent.

The transition state for the reaction studied has greater steric requirements than the reactant state. In the presence of adjacent groups this causes:-

- (1) Increasing steric strain because of repulsions between

non-bonded atoms ⁴⁸. This is a potential energy effect and increases the relative heat of activation.

(2) Interference of adjacent groups with the internal motions of one another ⁴². This is a kinetic energy effect and increases the energy of activation by decreasing the entropy of activation.

Taft ⁴⁹ shows that, for the ester hydrolysis reaction, decrease in the entropy of activation in a reaction series is caused solely by the steric hindrance to motions term as in (2) above and that this term is thus equal to the $T\Delta\Delta S^\ddagger$ value. Thus regarding naphthalene as a member of the benzene series with a fused benzene ring substituent, the steric hindrance to motions effect of this substituent for the reaction series studied can be measured by the value of $T\Delta\Delta S^\ddagger$ obtained by substituting the respective $\log_{10} A$ values in equation (10). The value so obtained is 0.9 k. cal. This value compares with that of 0.6 k cal. obtained by Wong ⁵⁰ for the same substituent in a similar reaction with dioxan-water as solvent. Values for this effect (calculated from the results of Evans, Gordon and Watson ³⁵) for ortho methyl and nitro groups, when these substituents are members of the same reaction series as studied in this work, are 0.9 k cal. and 1.1 k. cal. respectively.

The relative heat of activation for the fused benzene substituent may be obtained using corresponding energy of activation values of Tables III and IV in equation (9). In those cases, as discussed above, where the $\Delta\Delta G^\ddagger$ values for the two series are similar, then $\Delta\Delta H^\ddagger$ values for the fused benzene substituent are zero. Taft ⁴⁹ has shown that this term may be subdivided as below:-

$$\Delta\Delta H^\ddagger = \Delta\Delta E_\sigma^\ddagger + \Delta\Delta E_\psi^\ddagger + \Delta\Delta E_R^\ddagger \quad (11)$$

where $\Delta\Delta E_\sigma^\ddagger$ is the potential energy polar effect of the substituent, $\Delta\Delta E_\psi^\ddagger$ is the potential energy resonance effect of the substituent, and $\Delta\Delta E_R^\ddagger$ is the steric strain effect as in (1) above. For the fused ring substituent Wong ⁵⁰ has shown, using the Ingold-Taft relationship ⁶, that $\Delta\Delta E_\sigma^\ddagger$ is essentially zero. For the hydrolysis reaction studied an adjacent group, by decreasing the resonance stabilisation of the reactant state relative to the transition state, will lower the energy of

activation. The $\Delta\Delta E^\ddagger_\psi$ term which measures this effect will thus be negative. The effect due to steric strain will be to raise the energy of activation and thus $\Delta\Delta E^\ddagger_R$ will be positive. Thus, although it is shown that -

$$\Delta\Delta E^\ddagger_R + \Delta\Delta E^\ddagger_\psi = 0$$

all that can be said of the individual terms is that they must be equal in magnitude and opposite in sign.

D. Hammett Substituent Constants.

The Hammett equation applies to those reaction series where the influence of the substituent on the free energy of activation is dependent solely on its polar effect. This is so when the relative entropy of activation is zero or proportional to the relative heat of activation. It was shown in the preceding section of this discussion that the relative entropy of activation can be taken as zero for the alkaline hydrolysis of all except 2- and 8- substituted ethyl 1- naphthoates. Substituent constants for the bromo substituent in the 3-, 4-, and 5- position of naphthalene have been calculated from the rate constants at 50°C obtained from Figures VI, VII, VIII, and IX using the value of ρ (2.322) given by Jaffe.⁴ These values, along with values similarly obtained by the earlier workers are shown in Table V. Corresponding values for the benzene series are also given⁴.

TABLE V
Substituent Constants.

Substituent	3-Br	4-Br	5-Br	3-Cl	4-Cl	3-CH ₃	4-CH ₃	3-NO ₂	4-NO ₂	5-NO ₂	7-NO ₂
Naphthalene	.364	.257	.236	.356	.238	-.043	-.126	.68	.70	.50	.48
Benzene	.391	.232		.373	.227	-.069	-.170	.71	.78		

The standard deviation of σ is given by Jaffe⁴ as 0.06. The values for the two series above are within this limit, with the exception of the 4- nitro - substituent. For the 3- position in naphthalene and benzene the effect of the substituent is almost entirely on inductive polar effect. Since for the 3 -

position in the two series the substituent and functional groups are similarly placed with respect to each other this effect should be comparable and hence the σ constants should be similar for both series. Roberts and co-workers (for example, reference 51) have shown that the inductive effect is not transferred through the π bond system and hence the difference in π bond system of naphthalene does not affect the validity of the above conclusion. For the 4 - position the comparison is complicated by the fact that a resonance contribution from the substituent group to the ring affects the electron density at the 1- position and hence becomes an important polar effect of the substituent. Possible steric inhibition of this resonance effect by the adjacent fused benzene ring must be considered for the naphthalene series. This accounts for the lowering of the σ value for the 4- nitro substituent in naphthalene relative to benzene⁸. Further work is at present being done in this field.

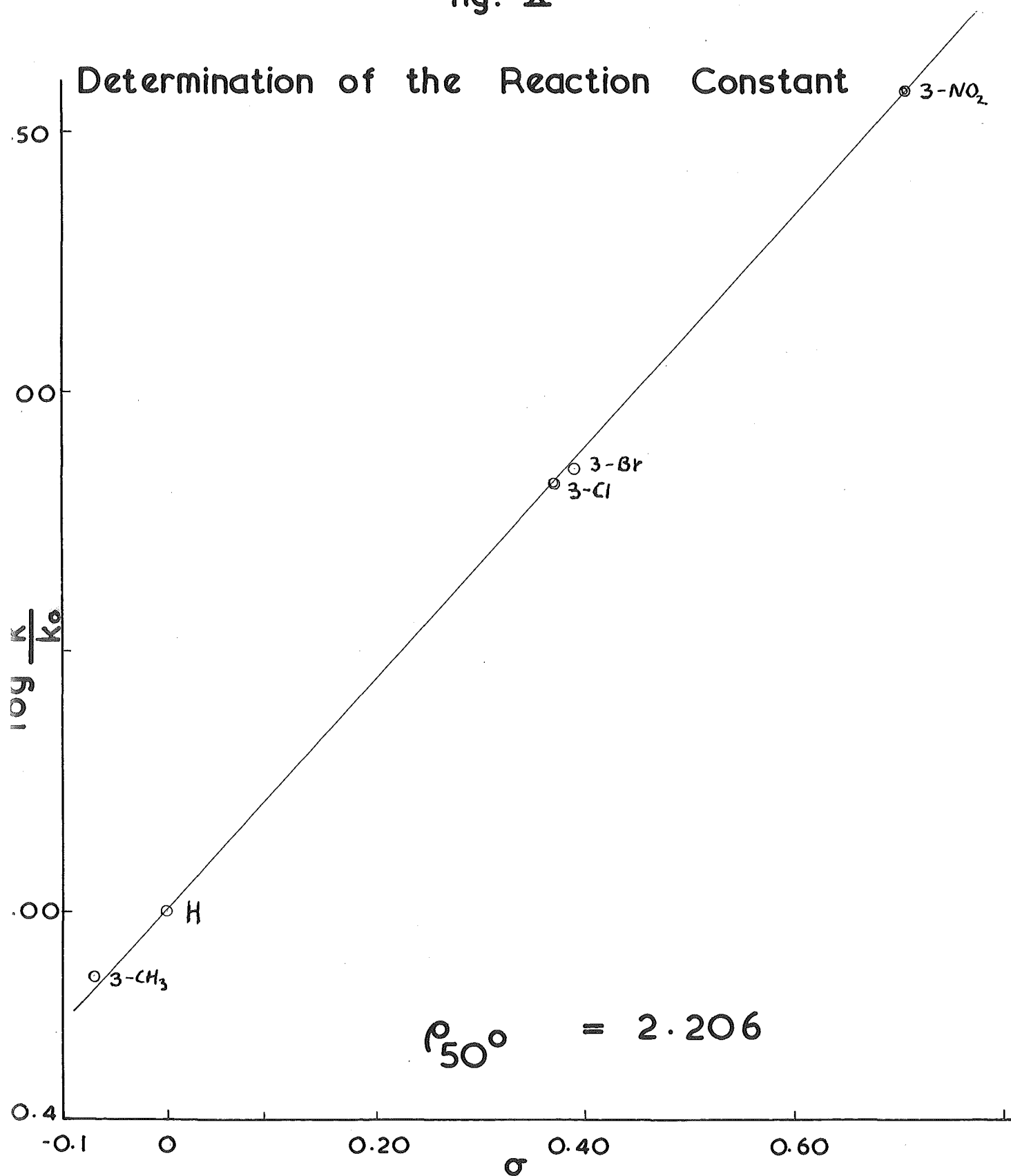
Slight differences between the ρ constant for the two series could be caused by :-

(a) Resonance effect of the functional group not being completely independent of the polar effect of the substituent. As was stated in the Introduction such an effect is usually well within the inherent inaccuracy of the Hammett equation.

(b) Stabilisation of either the reactant or the transition state by solvation effects which are affected by the steric requirements of the adjacent fused benzene ring. Taft⁵² has shown that for the ester hydrolysis reaction studied ρ is similar for various solvents and hence solvation effects on ρ must be negligible.

It is expected, therefore, that the ρ constant should be similar for both series. This is shown in Figure X where standard σ values for the 3 - position in the benzene series are plotted against $\log \left(\frac{k}{k_0} \right)_{50^\circ\text{C}}$ for 3 - substituted ethyl 1- naphthoates. Considering^o that the number of such substituents is few an excellent Hammett plot is obtained. The ρ value of 2.206 so obtained resembles so closely the value of 2.322 given by Jaffe⁴ that no significance may be attached to the difference.

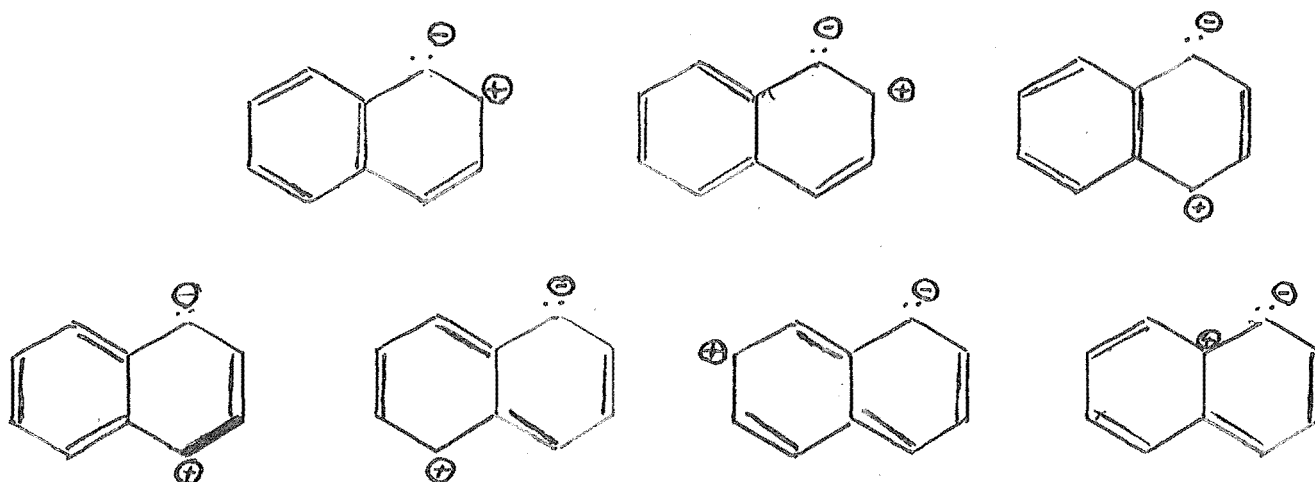
fig. X



This confirms the statements made in (a) and (b) above.

For the reaction studied, the higher the value of the σ constant the higher is the rate of reaction. Comparison of the effects of substituents on reactivity can thus be made by comparison of σ constants.

In order that such substituents effects for 1- naphthyl derivatives may be discussed in terms of inductive effects (I) and resonance effects (M), the contributing ionic structures for naphthalene, with an unshared pair of electrons in the 1- position, must be considered⁵³. These are shown below.



Qualitatively it is assumed that each canonical structure has an equal contribution to the actual structure.

For substituents in the 3-, 4-, and 5- positions the resonance effect on the 1- position, on the qualitative basis of proportionality to the number of canonical forms representing such resonance, would follow the order $4 > 5 > 3$. On the other hand the inductive effect (due to distance and orientation) would be expected to follow the order $3- > 4- > 5-$. Roberts and Moreland⁵ have shown that the difference in the inductive effects for the 3- and 4- positions is very small and propose that this is due to cancelling differences for the distance and orientation effects in the 3- and 4- positions.

On such a basis of inductive and mesomeric effects, results

may be qualitatively explained. Thus for the bromo substituents (-I,+M) studied, the electron-accepting inductive effect accelerates the reaction in the increasing order 5-, 4-, 3- and the electron-donating resonance effect slows the reaction in the increasing order 3-, 5-, 4-. Thus qualitatively the 3- bromo- substituent would be expected to be most effective in accelerating the reaction. This is in agreement with the quantitative result in Table V which shows that $\sigma_{3-\text{Br}}$ is more positive than $\sigma_{4-\text{Br}}$ and $\sigma_{5-\text{Br}}$. The qualitative effects for the 3- bromo- and 4- bromo- substituents are cancelling and from Table V it is seen that values of $\sigma_{4-\text{Br}}$ and $\sigma_{5-\text{Br}}$ are very nearly identical. This means that the decrease in the inductive effect and the decrease in the resonance effect for the 5- position relative to the 4- position are equally important contributions to reactivity. It is to be noted that the σ values for this substituent are all positive. This indicates that the inductive effect in all cases has a more important influence on reactivity than the resonance effect.

The nitro- group (-I,-M) has also been studied⁸ in the 3-, 4-, and 5- positions. For the nitro group both effects are accelerating and hence the reaction is accelerated in the increasing orders 3-, 5-, 4- (-M effect) and 5-, 4-, 3- (-I effect). Thus in this case both effects accelerate the reaction in the 4- position relative to the 5- position. Consequently $\sigma_{5-\text{NO}_2}$ is markedly lower than $\sigma_{4-\text{NO}_2}$. Due to the steric inhibition² of the resonance effect of this substituent in the 4- and 5- positions⁸ the inductive effect is the major effect to be considered in such a comparison of the σ constants for the two positions.

REFERENCES

1. L.P. Hammett, J. Am. Chem. Soc., 59, 96 (1937).
2. L.P. Hammett, "Physical Organic Chemistry", McGraw-Hill Book Company, New York (1940), p. 184.
3. H. Eyring, J. Chem. Phys., 3, 107 (1935).
4. H.H. Jaffe, Chem. Revs., 53, 191 (1953)
5. J.D. Roberts and W.T. Moreland Jr., J. Am. Chem. Soc., 75, 2167 (1953)
6. R.W. Taft Jr., J. Am. Chem. Soc., 75, 4231 (1953).
7. R.W. Taft Jr., in M.S. Newman's "Steric Effects in Organic Chemistry", John Wiley & Sons, New York (1956), p. 581.
8. A. Fischer, J.D. Murdoch, J. Packer, R.D. Topsom, and J. Vaughan, J. Chem. Soc., 1957 (In Press).
9. Eberbach, Z. Physik Chem., II, 608 (1893).
10. A. Bryson, Trans. Faraday Soc., 45, 257 (1949).
11. A. Bryson, Trans. Faraday Soc., 47, 322 (1951).
12. C.C. Price and R.H. Michel, J. Am. Chem. Soc., 74, 3653 (1952)
13. C.C. Price, E.C. Mertz, and J. Wilson, J. Am. Chem. Soc., 76, 153 (1954).
14. K.C. Schreiber and M.C. Kennedy, J. Am. Chem., Soc., 78, 153 (1956).
15. P. Fitzgerald, J. Packer, J. Vaughan and A.F. Wilson J. Chem. Soc., 159, 170 (1956).
16. J.E. Packer, Thesis, University of New Zealand (1956).
17. W.J. Mitchell, Thesis, University of New Zealand (1957).
18. E.F. Caldin and G. Long, J. Chem. Soc., 157, 3737 (1954).
19. E.F. Caldin and G. Long, Private communication.
20. G.J. Louck, R.P. Perkins, and F.C. Whitmore, J. Am. Chem. Soc., 51, 1831 (1929).
21. H.G. Rule and S.B. Thompson, J. Chem. Soc., 140, 1760 (1937).
22. R.G. Gould and W.A. Jacobs, J. Biol. Chem., 120, 146 (1937).
23. M.S. Newman and P.H. Wise, J. Am. Chem. Soc., 63, 2847 (1941).
24. H.W. Schwechten, Ber., 65B, 1605 (1932).
25. W.E. Bachmann and C.H. Boatner, J. Am. Chem. Soc., 58, 2194 (1936).

26. Y.S. Zalkind and S.B. Faerman, J. Russ. Phys. Chem. Soc., 62, 1021 (1930).
27. Y.S. Zalkind, Ber., 67, 1031 (1934).
28. Hausmann, Ber., 9, 1513 (1876).
29. I.T. Millar and H. Heaney, Quart. Rev., XI, 115 (1957).
30. "Organic Reactions", John Wiley & Sons, New York (1951), Vol. VI, p. 352.
31. H. Gilman and F.W. Moore, J. Am. Chem. Soc., 62, 1843 (1940).
32. H.G. Rule, W. Purcell, and R.R.H. Brown, J. Chem. Soc., 137, 169 (1934).
33. A.I. Vogel, "A Text Book of Quantitative Inorganic Analysis", 1st Edn., Longmans, Green & Co., London (1939), p. 238-255.
34. Reference 33, p. 289.
35. D.P. Evans, J.J. Gordon, and H.B. Watson, J. Chem. Soc., 140, 1430 (1937).
36. I.B. Crumpler and J.H. Yoe, "Chemical Computations and Errors", John Wiley & Sons, New York (1940), p. 217.
37. L.P. Hammett, "Introduction to the Study of Physical Chemistry", 1st Edn., McGraw-Hill Book Company, New York (1952) p. 410.
38. F.H. Westheimer and R.P. Metcalf, J. Am. Chem. Soc., 63, 1339 (1941).
39. C.K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, New York (1953), Chapter XIV.
40. M.L. Bender, J. Am. Chem. Soc., 73, 1626 (1951).
41. M.L. Bender and R.S. Dewey, J. Am. Chem. Soc., 78, 317 (1956).
42. F.P. Price Jr. and L.P. Hammett, J. Am. Chem. Soc., 63, 2387 (1941).
43. Reference 7, p. 556.
44. M. Adams - Briers, P.J.C. Fierens, and R.H. Martin, Helv. Chim. Acta, 38, 239 (1955).
45. C.K. Ingold and W.S. Nathan, J. Chem. Soc., 139, 222 (1936).

46. E. Tommila Ann. Acad. Sci. Fennicae, A57, No.13. (1941).
47. E. Tommila and L. Ketonen, Suomen Kemistilehti, 18B, 24
(1945).
48. H.C. Brown and G.K. Barbaras, J. Am. Chem. Soc., 69, 1137
(1947).
49. R.W. Taft. Jr. J. Am. Chem. Soc., 75, 4534 (1953).
50. E. Wang, Thesis, University of New Zealand (1957).
51. J.D. Roberts and R.A. Carboni, J. Am. Chem. Soc., 77,
5554 (1955).
52. R.W. Taft Jr., J. Am. Chem. Soc., 74, 2729 (1952).
53. L. Pauling, "Nature of the Chemical Bond", 2nd Edn.,
Oxford University Press, London (1940), p.152.