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THE ALKALINE HYDROLYSIS OF THE
ETHYL AND METHYL ESTERS
OF
1-NAPHTHOIC ACID AND 2-NAPHTHOIC ACID.

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SUMMARY

Samples of the ethyl and methyl esters of 1-naphthoic acid and 2-naphthoic acid have been prepared and the kinetics of hydrolysis of these esters have been studied in alkaline solutions over the temperature range 30°C - 60°C. Aqueous methanol was employed as solvent for the methyl esters, and aqueous ethanol for the ethyl esters. Relative reactivities at the 1- and 2- positions as measured by this work are in line with theoretical prediction, and the relative rates of the methyl and ethyl esters have been discussed. Comments have been made on an earlier investigation by Bergmann and Hirshberg of the methyl compounds, the results of which appear to be anomalous. A value for the Hammett $\sigma$ constant for the fused benzene ring has been derived and has been compared with values calculated by other investigators.
I. INTRODUCTION

In recent work on the chemistry of naphthalene, considerable interest has been taken in the relative reactivities of the 1- and 2- positions. Experimental evidence and the theoretical work of Jaffe\(^1\), have indicated that the electron density at the 1- position is higher than that at the 2- position. With but two exceptions, viz. sulphonation, and Friedel-Crafts reactions, attack by an electrophilic reagent occurs predominantly in the 1- position\(^2\). In these two exceptions, however, temperature and solvent conditions are the governing factors upon which depends the relative ease of substitution at the two positions.

The available evidence regarding the relative susceptibilities of the 1- and 2- positions towards nucleophilic substitution and displacement is, however, neither extensive nor clear-cut. Reactions involving the replacement of groups at either the 1- or 2- positions have been carried out,\(^2,3,4\) and in every case the rate constant for the 2-naphthyl compound was found to exceed that for the 1-naphthyl compound. The mechanisms proposed involve a rate-determining bimolecular nucleophilic step, which is facilitated by electronegative groups attached to the site of the attack. The higher rate of reaction for the 2- position, is in line with the evidence that the electron density at the 2- position is lower than that at the 1- position.

The difference in electron density at the 1- and 2- positions is reflected in the relative reactivities of side-chains attached to these positions. Comparison of side-chain reactivities of 1- and 2- naphthalene derivatives in reactions where the reaction site is directly linked to the ring-carbon atoms are therefore of interest. Furthermore, such reactions are much more amenable to experimental study than are reactions involving direct substitution in the ring. In many such reactions involving nucleophilic replacement on the side-chain, the rate of reaction of the 1-naphthyl
compound has been observed to be higher than the rate for the corresponding 2-naphthyl compound. Ingold and Patel\textsuperscript{5}, for example, studied the neutral hydrolysis of 1- and 2-bromomethyl-naphthalene in 90% aqueous alcohol at 25° and measured the following first order rate constants.

\[
\begin{align*}
1\text{-bromomethyl-naphthalene} & \quad 220 \times 10^{-6} \text{ sec}^{-1} \\
2\text{-bromomethyl-naphthalene} & \quad 185 \times 10^{-5} \text{ sec}^{-1}
\end{align*}
\]

The following mechanism, in which preliminary ionization is considered to be the rate-determining step, may be assumed to apply, on the basis of the unimolecular mechanism proposed by Hughes, Ingold and Scott\textsuperscript{6} for the corresponding hydrolysis of phenyl-ethyl-chloride.

\[
\begin{align*}
C_{10}H_{7}CH_{2}Br & \rightleftharpoons C_{10}H_{7}CH_{2}^{+} + Br^{-} \\
+H_{2}O & \rightarrow C_{10}H_{7}CH_{2}^{+}O_{2}H \\
-H & \rightarrow C_{10}H_{7}CH_{2}OH
\end{align*}
\]

Electron-donating groups aid the preliminary ionization, and the reaction will therefore be faster in the case of the 1-naphthyl compound. In all cases where the 1-naphthyl rate constant exceeds that of the corresponding 2-naphthyl compound, a unimolecular mechanism has been proposed.

The greater reactivity of certain 2-naphthyl compounds over the corresponding 1-naphthyl compound is observed when the rate-determining step involves a bimolecular nucleophilic attack on the side-chain. Linetskaya and Sapezhnikova\textsuperscript{7} found that the rates of acid hydrolysis of 1- and 2-naphthylsulphonyl chlorides in 50% aqueous acetone at 30° were in the ratio of 0.131 : 0.219. The reaction was observed to be facilitated by substituent groups which removed electrons from the site of the reaction, and retarded by those which donated electrons. They proposed a mechanism involving a rate-determining attack by a water molecule on the protonated sulphonyl chloride. It follows that the more electronegative 2-naphthyl group will facilitate reaction by such a mechanism.

Of special interest, however, are the results of Bergmann
and Hirshberg who studied the alkaline hydrolysis of methyl 1- and 2-naphthoates in 85% methanol-water at 60°C, and determined second order rate constants for these two esters.

methyl 1-naphthoate $2.06 \times 10^{-2}$ litre g.-mol.$^{-1}$ min.$^{-1}$
methyl 2-naphthoate $1.53 \times 10^{-2}$ litre g.-mol.$^{-1}$ min.$^{-1}$

Now, the mechanism of the alkaline hydrolysis of carboxylic esters may be represented on the model of carbonyl addition and its retrogression as:

\[
\begin{align*}
\text{HO} + \text{C}-\text{OR} & \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} \text{HO} - \text{C}-\text{OR} \\
& \underset{\text{slow}}{\overset{\text{fast}}{\rightleftharpoons}} \text{HO} - \text{C} + \text{OR}
\end{align*}
\]

or alternatively by using the model of nucleophilic substitution thus:

\[
\begin{align*}
\text{HO} + \text{C}-\text{OH} & \underset{\text{slow}}{\overset{\text{fast}}{\rightleftharpoons}} \text{HO} - \text{C}-\text{OR} \\
& \underset{\text{slow}}{\overset{\text{fast}}{\rightleftharpoons}} \text{HO} - \text{C} + \text{OR}
\end{align*}
\]

The real complex will be mesomeric between the above two representations and as a result will possess a greater stability than that possessed by either complex. The existence of the most condensed intermediate state as a molecule having a life which is long in comparison with a collision period, as opposed to a transition state, has been demonstrated by Bender. As the intermediate complex is negatively charged, electropositive substituents should retard, and electronegative substituents accelerate, the hydrolysis by this mechanism. A large amount of experimental evidence supports these postulates.

In view of the greater electron-donating tendency of the 1-naphthyl group, methyl 2-naphthoate would be expected to undergo hydrolysis more quickly than methyl 1-naphthoate, i.e. the reverse of Bergmann's order. Support for this view has been given by Fitzgerald who carried out the alkaline hydrolysis of 1- and 2-naphthamides in dioxane-water. The mechanism of this reaction is very similar to that of ester hydrolysis and, on the basis
of electron densities, 2-naphthamide should hydrolyse at a rate higher than 1-naphthamide. The results show good correlation with this principle, 2-naphthamide hydrolysing over ten times as fast as 1-naphthamide. In order to provide a quick check on Bergmann's ester work, Fitzgerald carried out the alkaline hydrolysis of ethyl 1- and 2-naphthoates in 85% ethanol-water at two temperatures and found that ethyl 2-naphthoate had a higher rate constant than ethyl 1-naphthoate.

Because of the conflict between Bergmann's results and those expected from theory, and because Fitzgerald's brief examination indicated the possibility of error in Bergmann's results, it was decided to examine in detail the alkaline hydrolysis of the methyl and ethyl esters of 1- and 2-naphthoic acids. The ethyl esters were to be hydrolysed in 85% ethanol-water and the methyl esters in 85% methanol-water, in which solvent the experiments of Bergmann and Hirshberg were carried out. In addition, the derived rate constant for ethyl 2-naphthoate at four temperatures was used to determine the Hammett substituent constant ($\sigma$) for the 2-naphthyl fused ring. The calculation of the constant for this system is of interest in that the two values recorded in the literature differ appreciably.
2. PREPARATION OF MATERIALS

PREPARATION OF THE ESTERS.

The four esters, methyl and ethyl, 1- and 2-naphthoates, have been prepared by the esterification of the parent acid with the appropriate alcohol in the presence of an acid catalyst. Bergmann and Hirshberg\(^8\) (methyl esters), and Price and Michel\(^{13}\) (ethyl 2-naphthoate) obtained quantitative yields when the naphthoic acid and alcohol were heated under reflux in a stream of hydrogen chloride. In the present work this method was adopted for the preparation of all the esters.

1-Naphthoic acid was recrystallised from a dilute acetic acid solution and, on drying in a vacuum oven, was observed to have a melting point of 160\(^\circ\). (Beilstein 160\(^\circ\) - 161\(^\circ\)). The melting point of 2-naphthoic acid, recrystallised from ethyl alcohol and dried in a vacuum oven, was 182\(^\circ\). (Beilstein 182\(^\circ\) - 182.5\(^\circ\)). 25g. of 1-naphthoic acid were heated under reflux with 200 ml. of pure distilled ethanol in a two-necked 500 ml. flask. A condenser was fitted to one neck, and through the other neck a stream of hydrogen chloride was admitted from a simple generator. After three hours about two-thirds of the excess alcohol was distilled off and the residue allowed to stand. On cooling, the contents of the flask were transferred to a separating funnel, 30 ml. of ether were added and three washings with 50 ml. portions of water carried out. The ether layer was then washed with 50 ml. portions of 10% sodium bicarbonate solution to separate any unreacted acid from the ester, and the process repeated until neutralisation of the bicarbonate washings with an acid gave no further precipitate of 1-naphthoic acid.

The above preparation and extraction were repeated using 2-naphthoic acid and ethanol to prepare ethyl 2-naphthoate. By using methanol with each naphthoic acid the methyl esters were prepared in a similar manner. On evaporating off the excess methanol, methyl 2-naphthoate precipitated on cooling. After washing with bicarbonate solution the ether was evaporated
off and the solid ester recrystallised three times from methanol and dried in a vacuum oven. The observed melting point was 76.2° (Bergmann and Hirshberg 76°). The ethereal solutions containing the other three esters were dried for some hours with anhydrous potassium carbonate, filtered and then distilled under reduced pressure. A second vacuum distillation was carried out, the middle 50% collected and the following boiling points observed:

- Ethyl 1-naphthoate 194° - 196° at 45 mm. Hg (184° - 186° at 24 mm. Hg; 188° - 186° at 20 mm. Hg; 220.5° at 74 mm.)
- Ethyl 2-naphthoate 194° - 195° at 37 mm. Hg (146° - 147° at 1 - 2 mm. Hg; 224.0° at 74 mm. Hg)
- Methyl 1-naphthoate 165° - 166° at 17 mm. Hg (165° at 17 mm. Hg)

The three esters were dried thoroughly in a vacuum oven to constant weight and ethyl 2-naphthoate, which is a solid at room temperatures, was found to have a melting point of 36.0° (35.5° - 36.2°, 34.5° - 35°, 32°). Immediately after distillation the melting point of this ester was 26°, which suggests that the somewhat low values quoted by earlier workers are probably the result of incomplete drying of the ester.

The amount of unreacted acid was in each case approximately 2 g., the yields of once distilled ester, or, in the case of the solid methyl 2-naphthoate, of crude solid were of the order of 80%.

PURIFICATION OF ETHANOL FOR USE AS SOLVENT.

Commercial ethanol was purified by the method suggested by Danner and Hildebrand. The amine and other basic impurities were first removed by distilling 95% commercial ethanol with 5 ml. of concentrated sulphuric acid and 20 ml. of water per litre. About 10 l. of distillate were collected and, on testing with Schiff's solution, a high proportion of aldehyde was found to be present. For the removal of the aldehyde, the alcohol was heated under reflux for about six hours with 10 g. of silver nitrate and 1 g. of potassium
hydroxide per litre. An intense silver mirror was formed on the flask, and the alcohol was distilled from the solution and again heated under reflux over silver nitrate and potassium hydroxide. This was repeated three times, and deposits of silver continued to come down. Comparisons of Schiff's tests with the alcohol and standard solutions of aldehyde in alcohol, showed approximately 0.1% of aldehyde to be present.

The method of Dunlap for the removal of aldehyde from ethanol was carried out on the original alcohol, and after three treatments the percentage of aldehyde present was found to be slightly lower than that obtained for the previous method. In this method 1.5 g. of silver nitrate, dissolved in about 5 ml. of water, were added (per litre) to base-free alcohol, and the alcohol shaken thoroughly. 3 g. of potassium hydroxide were dissolved in about 20 ml. of warm alcohol and, after cooling, added slowly to the alcoholic silver nitrate solution. The silver oxide thrown down in the alcohol is, according to Dunlap, in a better condition to effect a rapid and complete oxidation of the aldehyde than silver oxide added directly to the alcohol. After two days the silver oxide, which had settled completely, was filtered off and the alcohol was subjected to the same treatment again.

The claims of the authors of the above methods, of complete aldehyde removal, were not supported, although both methods were found useful for the removal of a large portion of the aldehyde present. Complete removal of the aldehyde was effected by efficient distillation of the alcohol after subjecting it to the above treatments. Five litres of the alcohol were heated under reflux in a flask fitted with a 5 ft. distillation column, packed with Dixon gauze rings. After allowing about 24 hours for the concentration of the lower boiling aldehydes at the top of the still, 500 ml. of alcohol were distilled off at the rate of about 20 ml. per hour. 3½ litres of aldehyde-free alcohol were then collected slowly and 6 l. of alcohol so purified were stored in a flask of the type shown in diagram I. Sufficient distilled water was
Diagram 1
Alcohol container
added to bring the alcohol to 95% - 96% ethanol-water by weight and the exact percentage then found by use of a calibrated pycnometer and suitable tables.

PURIFICATION OF METHANOL FOR USE AS SOLVENT.

The commercial methanol had been prepared synthetically; it was found to be free from acetone and to contain a relatively low percentage (less than 0.001%) of aldehyde, by a comparative Schiff's test. Three litres were distilled through a 5 ft. column and after concentrating the aldehyde fraction by continuous reflux the first 300 ml. were distilled off slowly, and 2 l. of pure methanol then collected. About 6 l. of methanol were prepared in this way and stored in a flask similar to that used for the ethanol. The alcohol was made about 96% methanol-water by weight and its density determined by use of a calibrated pycnometer.

PREPARATION OF STANDARD SODIUM HYDROXIDE SOLUTIONS.

For titrations at the concentrations of hydrochloric acid and sodium hydroxide used by previous workers (Fitzgerald\textsuperscript{11} 0.005 N acid and alkali; Evans, Gordon and Watson\textsuperscript{16} 0.01 N acid and alkali), the best available indicator is bromothymol blue. This indicator however gives variable results when carbonate is present in the alkali. It was accordingly necessary to prepare carbonate-free sodium hydroxide and, during the titrations, to restrict carbon dioxide absorption by the weak alkaline solutions. A carbonate-free sodium hydroxide solution was prepared by dissolving 50 g. of sodium hydroxide in 50 ml. of distilled water from which solution the carbonate settled out on centrifuging\textsuperscript{19}. From the clear solution above the precipitated carbonate, 10.4 ml., 1.3 ml. and 0.65 ml. were pipetted out and added to a 1 l., a 2 l. and another 2 l. polythene container respectively, each containing distilled water. This distilled water had been prepared free from carbon dioxide by heating to about 40° and boiling the water under reduced pressure for about 10 minutes. Nitrogen was then admitted to the
evacuated flask to restore the pressure to 1 atmosphere.
On the addition of the alkali to the water nitrogen was
freely introduced into the polythene container above the
water level further to ensure that the atmosphere above the
standard alkaline solutions was free of carbon dioxide. The
apparatus shown in the diagram was then set up to facilitate
titrations with alkali and to prevent absorption of carbon
dioxide during titrations.

Standardisation of the alkaline solutions was carried out
with potassium hydrogen phthalate$^{20}$ and the following values
found for the normalities of the three solutions.

\[
\begin{align*}
0.1592 \pm 0.0002 \\
0.01030 \pm 0.00004 \\
0.00500 \pm 0.00002 \\
\end{align*}
\]

PREPARATION OF STANDARD HYDROCHLORIC ACID SOLUTIONS.

47 ml. of "Analar" hydrochloric acid were diluted to
one litre with distilled water and the solution standardised
against freshly recrystallised borax$^{21}$. By using calibrated
pipettes and volumetric flasks, further standard solutions of
required normalities were prepared. The normalities of the
standard acids were:

\[
\begin{align*}
0.5237 \\
0.06529 \\
0.01302 \\
0.00651 \\
\end{align*}
\]

These values were checked by direct titration of these
solutions with the standard alkali solutions, and the percent-
age deviation error was found in each case to lie within
the error involved in the titration. This latter error is a
maximum for the weaker solutions, where the difficulty in
estimating the end point is greatest, but is nevertheless
smaller than 0.5%.

PREPARATION OF INDICATOR

0.5 g. of bromothymol blue were dissolved in 250 ml. of
50% ethanol-water.
Diagram 2
System for titrations with alkali

soda-lime tube

to draw alkali into burette

polythene container

from nitrogen cylinder
3. EXPERIMENTAL PROCEDURE

The procedure adopted was an adaptation of the method used by Evans, Gordon and Watson\(^1\) to study the rates of hydrolysis of certain benzoic esters.

Approximately 180 g. of 94.86\% ethanol-water (w/w.) were weighed in a 400 ml. round-bottomed flask fitted with a ground-glass stopper. From the weight of the alcohol the weight of water (m) g. required to make an 85\% ethanol-water (w/w.) solution was calculated. A calculated volume (y) ml. of 0.1592 N alkali was then added with the difference (m - y) g. of boiled-out distilled water. The flask was shaken and immersed in a thermostatted bath. After allowing about 30 minutes a 10 ml. pipette calibrated for use at the particular bath temperature was used to withdraw a sample from the solution. This sample was added to a 250 ml. conical flask containing 10 ml. of 0.00651 N hydrochloric acid and about 100 ml. of boiled-out distilled water. During the addition of the aliquot to the conical flask, a constant stream of nitrogen was admitted to the flask above the liquid surface, through a bent glass tube connected by rubber tubing to a nitrogen cylinder. This stream was continued whilst the solution was titrated against the standard 0.005 N sodium hydroxide solution, using 5 drops of bromothymol blue as indicator. Further aliquots were removed from the alkaline solution until the amount of 0.005 N alkali which had to be added, was constant. Three titrations were found to be sufficient in most cases and, from the constant value, the normality of the solution was calculated.

The 10 ml. pipette used to add the hydrochloric acid, delivered 9.98 ml. at 18°c. The 10 ml. pipette used to extract samples delivered 9.93 ml. of 85\% ethanol at 40°.

If (N) is the normality of the alcoholic alkaline solution at 40° and (\(\times\)) ml. is the volume of 0.005 N alkali added it follows that:–
9.98 \times 0.00651 = 9.93 x N + x \times 0.005

i.e. \quad N = \frac{13.06 - x}{9.93} \times 0.005

The normality can also be calculated quite accurately from the amount of 0.1592 \text{N} alkali added as the following example shows.

\text{Weight of 94.86\% ethanol-water (w/w.)} = 184.72 \text{ g.}

\text{\therefore Weight of pure ethanol present} = 175.23 \text{ g.}

\text{\therefore Corresponding weight of 85\% ethanol-water (w/w.)} = 206.14 \text{ g.}

\text{\therefore Weight of water to be added to make 85\% ethanol-water (w/w.)} = 21.42 \text{ g.}

\text{Density of 85\% ethanol at 40^\circ} = 0.81322 \text{ g./ml.}

\text{\therefore Volume of 206.14 g. of 85\% ethanol at 40^\circ} = 255.6 \text{ ml.}

Hence to prepare a 0.006 \text{ N} solution of sodium hydroxide at this temperature if (y) \text{ ml.} of 0.1592 \text{ N} alkali are to be added

\[ y \times 0.1592 = 0.006 \times 255.6 \]

\[ y = 9.63 \]

This calculation assumes that the presence of the weak sodium hydroxide solution in the ethanol does not affect the change in density of the 85\% ethanol with temperature.

9.63 \text{ ml.} of alkali are required then to be added to the 184.72 \text{ g.} of ethanol with \((21.42 - 9.63) = 11.79 \text{ g.}\) of distilled water and, on bringing the solution up to 40^\circ and withdrawing samples as above, the volumes of 0.005 \text{ N} alkali added were found to be 1.03, 0.99, 1.02, 1.00 \text{ ml.} The mean value of 1.01 corresponds to a normality of 0.00607.

On completion of the "blank" titrations a 100 \text{ ml.} calibrated pipette was used to withdraw two 100 \text{ ml.} portions from the sodium hydroxide in ethanol solution, which were run into two clean, dry, 300 \text{ ml.} flasks. These flasks were stoppered with ground-glass stoppers placed in the bath and allowed to approach temperature equilibrium for at least half an hour. In the meantime, the equivalent weight of ester corresponding to the known volume and concentration of alkali pipetted into the reaction flasks, was calculated and weighed out into a small glass weighing boat. The ester was then
added to the alkaline solution in the reaction vessel and thoroughly shaken in the bath until it had dissolved. Then at convenient time intervals 10 ml. aliquots were removed from the flasks, added to 10 ml. of excess acid as in the "blank" titrations, and titrated with the standard 0.005 M alkali in the presence of nitrogen.

The purpose in adding the samples to excess acid was to reduce the reaction speed as much as possible during the titration, ester hydrolysis proceeding at a much slower rate in acid than in alkaline solutions. The conical flasks containing the acid and distilled water were kept some 30 minutes before use in an ice-bath further to reduce the speed of the reaction and hence allow a sharp end-point to be reached in the titration. In view of these precautions, the 10 ml. of solution contained by the pipette were assumed to have stopped reacting when transference to the excess acid was complete. The concentration measurements were then assumed to hold at the instant of half-delivery of the pipette. After the first measurement of concentration was made it was found practicable to run into the excess acid a volume of standard alkali such that in the next titration only about 0.2 ml. of alkali were required to be further added. This precaution enabled a constant time interval between half-delivery of the pipette contents and the end-point of the titration to be kept. It follows that this step compensates for any continued reaction during the titration and furthermore means that carbon dioxide absorption, which slightly affects the end point even with nitrogen present, is kept down to a minimum. From the amount of alkali required to neutralise the excess acid, the concentration of the solution was determined and hence at specific time intervals the mass of ester reacted could be determined. As the concentrations of ester and sodium hydroxide were kept equivalent, second order rate constants were calculated using the simplified form of the second order rate equation.
where \( a \) is the initial concentration of each reactant, and 
\( x \) the concentration of the product at a time \( t \).

Integrating and rearranging, we get:

\[
\frac{dx}{dt} = k(a - x)^2
\]

Thus if \( \frac{x}{a(a - x)} \) is plotted against the time \( t \) the bimolecular rate constant \( k \) is obtained. By weighing out about 180 g. of 94.86% ethanol-water (w/w.) to which the required amounts of water and alkali had been added to make 85% ethanol, two 100 ml. portions were obtained and the reaction therefore carried out in duplicate. The slower reactions, where the time intervals between measurements were made larger, were carried out sometimes three or four at a time by suitably adjusting the weight of ethanol and the volume of 0.1592 N alkali required. This volume of alkali was so adjusted that the concentration of the alkaline solution did not exceed that of the standard acid. In some cases the hydrolysis of the less reactive esters at the lower temperatures was speeded up by doubling the concentration of ester and alkaline solutions and using standard 0.01302 N acid in excess.

Before carrying out any runs with ester present 85% ethanolic and methanolic solutions were made up and brought up to the bath temperature at which the reactions were to be carried out, in order to standardise the pipettes for use at that particular temperature. The 10 ml. pipette was standardised by removing a sample from the 85% ethanol solution and adding it to a weighing bottle to find the weight of 85% alcohol delivered. From this weight and the known density of 85% ethanol at the particular temperature, the volume of 85% ethanol delivered at this temperature was calculated. Because the densities of both methanol and ethanol change appreciably with variation in temperature, the loss of heat by the contents of the pipette, during filling to the mark, affects the mass of alcohol contained by the pipette. The calibration will therefore depend on the initial temperature
of the pipette and on the time taken to fill the pipette. By using the pipette initially at room temperature and keeping the time for filling fairly constant, the error involved was kept negligibly small.

Extraction of the 100 ml. samples from the standardised stock solutions was made as quickly as possible to prevent any evaporation of alcohol and a consequent increase in concentration of the stock solution. After delivering the first 100 ml., the temperature of the pipette was not far below that of the bath and the heat lost whilst filling successive portions is therefore less. The weights of alcohol delivered from the pipette warmed after one filling differed, however, from the weight delivered on first filling by less than 0.3%. The volume of 85% alcohol delivered by the pipette was calculated from the weight delivered from the second filling and, by preliminary heating of the pipette with a hot air drier before the first extraction, this error was reduced to a negligible value. In the large number of runs carried out in duplicate and triplicate, no constant error between the rate constants calculated from the first and successive solutions was observed.

At every temperature one 100 ml. portion, delivered by the pipette from a previously standardised stock solution, was brought back to the temperature of the bath and therefore to its original concentration. This solution was then subjected to a "blank" run with no ester added, whilst aliquots were removed and the normality of the solution measured at various time intervals comparable with the time intervals during actual runs with ester present. At all temperatures for both ethanol and methanol no change in concentration with time was observed. However, as the glass stopper was removed for each sample extraction, the loss of alcohol through evaporation eventually produced a noticeable increase in concentration after about seven removals at 30° and 40°, and about six removals at 50° and 60°. The number of samples
removed from reacting solutions was accordingly kept below these values for the low and high temperatures. It was furthermore found necessary to grease the stoppers at 60° to prevent alcohol evaporation in between normality measurements.
4. RESULTS

For each of the four esters studied, details and an accompanying graph are given for one typical run. These details are followed by a table of the rate constants for all runs carried out. Included in this table are the rate constants for some reactions carried out with unequal concentrations of ester and alkali as a check on the order of the reaction. Temperature control of the thermostat was effected to ±0.02.

**Ethyl 2-naphthoate in 85% ethanol at 60°.**

Weight of 90.74% ethanol-water mixture = 282.31 g.

```
\cdot \cdot \cdot \text{Weight of pure ethanol present} = 256.17 \text{ g.}
\cdot \cdot \cdot \text{Weight of 85\% ethanol-water by weight on dilution} = 301.37 \text{ g.}
```

Hence mass of water to be added = 19.06 g.

In order to prepare a solution of concentration about 0.006 N, 7.2 ml. of 0.3204 N alkali were added, and the difference, 11.86 g. of distilled water. Using 9.98 ml. of 0.00651 N acid in excess, the titrations were carried out with 0.0050 N alkali. The 10 ml. pipette was calibrated to deliver 9.87 ml. and the 100 ml. pipette 99.94 ml. of alcohol at 60°.

Blank titration values: 1.16, 1.01, 1.03 ml.

Probable mean value 1.02 ml.

Hence $N = \frac{9.98 \times 0.00651 - 0.005 \times 1.02}{9.87}$

$= 0.00606 \text{ N}$

Hence weight of ethyl ester required $= 0.00606 \times 99.94 \times \frac{200}{1000}$

$= 0.1211 \text{ g.}$
### Time

<table>
<thead>
<tr>
<th>Time (secs.)</th>
<th>Volume of alkali required to neutralise excess acid (ml.)</th>
<th>Amount of unreacted ester (a) g.-mol.^{-1} litre x 10^{-2}</th>
<th>Amount of reacted ester (x) g.-mol.^{-1} litre x 10^{-2}</th>
<th>x</th>
<th>a(a - x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.02</td>
<td>0.6055</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1200</td>
<td>2.32</td>
<td>0.5405</td>
<td>0.0650</td>
<td>19.8</td>
<td></td>
</tr>
<tr>
<td>2400</td>
<td>3.38</td>
<td>0.4865</td>
<td>0.1190</td>
<td>40.4</td>
<td></td>
</tr>
<tr>
<td>3600</td>
<td>4.24</td>
<td>0.4425</td>
<td>0.1630</td>
<td>60.8</td>
<td></td>
</tr>
<tr>
<td>4500</td>
<td>4.86</td>
<td>0.4120</td>
<td>0.1935</td>
<td>77.6</td>
<td></td>
</tr>
<tr>
<td>5400</td>
<td>5.36</td>
<td>0.3870</td>
<td>0.2185</td>
<td>93.2</td>
<td></td>
</tr>
</tbody>
</table>

From graph 1 \( k = 17.5 \times 10^{-3} \) litre g.-mol.^{-1} sec.^{-1}

### Ethyl 1-naphthoate in 85% ethanol at 50°C

<table>
<thead>
<tr>
<th>Time (secs.)</th>
<th>Volume of alkali required to neutralise excess acid (ml.)</th>
<th>Amount of unreacted ester (a) g.-mol.^{-1} litre x 10^{-2}</th>
<th>Amount of reacted ester (x) g.-mol.^{-1} litre x 10^{-2}</th>
<th>x</th>
<th>a(a - x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.49</td>
<td>0.5785</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>900</td>
<td>1.66</td>
<td>0.5695</td>
<td>0.0090</td>
<td>2.74</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>1.81</td>
<td>0.5625</td>
<td>0.0160</td>
<td>4.90</td>
<td></td>
</tr>
<tr>
<td>2700</td>
<td>1.96</td>
<td>0.5550</td>
<td>0.0235</td>
<td>7.32</td>
<td></td>
</tr>
<tr>
<td>3600</td>
<td>2.12</td>
<td>0.5470</td>
<td>0.0315</td>
<td>9.96</td>
<td></td>
</tr>
<tr>
<td>4500</td>
<td>2.28</td>
<td>0.5390</td>
<td>0.0395</td>
<td>12.66</td>
<td></td>
</tr>
<tr>
<td>5400</td>
<td>2.36</td>
<td>0.5350</td>
<td>0.0435</td>
<td>14.06</td>
<td></td>
</tr>
<tr>
<td>6300</td>
<td>2.50</td>
<td>0.5280</td>
<td>0.0505</td>
<td>16.52</td>
<td></td>
</tr>
</tbody>
</table>

From graph 2 \( k = 2.63 \times 10^{-3} \) litre g.-mol.^{-1} sec.^{-1}
Graph 1
Ethyl 2-naphthoate 60°C

\[ k = 17.5 \times 10^{-3} \text{ litre.g.mol}^{-1}\text{sec}^{-1} \]

Graph 2
Ethyl 1-naphthoate 50°C

\[ k = 2.63 \times 10^{-3} \text{ litre.g.mol}^{-1}\text{sec}^{-1} \]
### Methyl 2-naphthoate in 85% methanol at 40°C

<table>
<thead>
<tr>
<th>Time (secs.)</th>
<th>Volume of alkali required to neutralise excess acid (ml.)</th>
<th>Amount of unreacted ester (a) (g.-mol. litre(^{-1}) x (10^2))</th>
<th>Amount of reacted ester (x) (g.-mol. litre(^{-1}) x (10^2))</th>
<th>(x) (\frac{1}{a(a-x)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.38</td>
<td>1.284</td>
<td>0</td>
<td>0.85</td>
</tr>
<tr>
<td>1200</td>
<td>0.80</td>
<td>1.263</td>
<td>0.0210</td>
<td>1.30</td>
</tr>
<tr>
<td>2400</td>
<td>1.14</td>
<td>1.246</td>
<td>0.0376</td>
<td>2.34</td>
</tr>
<tr>
<td>3600</td>
<td>1.47</td>
<td>1.230</td>
<td>0.0538</td>
<td>3.40</td>
</tr>
<tr>
<td>4800</td>
<td>1.83</td>
<td>1.212</td>
<td>0.0715</td>
<td>4.59</td>
</tr>
<tr>
<td>6000</td>
<td>2.22</td>
<td>1.192</td>
<td>0.0914</td>
<td>5.97</td>
</tr>
<tr>
<td>7200</td>
<td>2.50</td>
<td>1.178</td>
<td>0.1054</td>
<td>6.96</td>
</tr>
<tr>
<td>8400</td>
<td>2.76</td>
<td>1.166</td>
<td>0.1183</td>
<td>7.89</td>
</tr>
</tbody>
</table>

From graph 3 \( k = 0.96 \times 10^{-3} \) litre g.-mol\(^{-1}\) sec\(^{-1}\).

### Methyl 1-naphthoate in 85% methanol at 30°C

<table>
<thead>
<tr>
<th>Time (secs. x (10^2))</th>
<th>Volume of alkali required to neutralise excess acid (ml.)</th>
<th>Amount of unreacted ester (a) (g.-mol. litre(^{-1}))</th>
<th>Amount of reacted ester (x) (g.-mol. litre(^{-1}))</th>
<th>(x) (\frac{1}{a(a-x)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.85</td>
<td>1.259</td>
<td>0</td>
<td>0.85</td>
</tr>
<tr>
<td>582</td>
<td>3.42</td>
<td>1.131</td>
<td>0.1285</td>
<td>9.02</td>
</tr>
<tr>
<td>720</td>
<td>3.88</td>
<td>1.108</td>
<td>0.1511</td>
<td>10.82</td>
</tr>
<tr>
<td>873</td>
<td>4.40</td>
<td>1.082</td>
<td>0.1774</td>
<td>13.02</td>
</tr>
<tr>
<td>978</td>
<td>4.83</td>
<td>1.060</td>
<td>0.1989</td>
<td>14.90</td>
</tr>
<tr>
<td>1080</td>
<td>5.21</td>
<td>1.041</td>
<td>0.2177</td>
<td>16.61</td>
</tr>
<tr>
<td>1488</td>
<td>6.45</td>
<td>0.978</td>
<td>0.2806</td>
<td>22.79</td>
</tr>
</tbody>
</table>

From graph 4 \( k = 0.152 \times 10^{-3} \) litre g.-mol\(^{-1}\) sec\(^{-1}\).
Graph 3
Methyl 2-napthoate 40°C

\[ \frac{x}{a(a-x)} \text{ (litre.g- mol}^{-1} \) \\

\[ k = 0.96 \times 10^{-3} \text{ litre.g- mol}^{-1} \text{sec}^{-1} \]

Graph 4
Methyl 1-napthoate 30°C

\[ \frac{x}{a(a-x)} \text{ (litre.g- mol}^{-1} \) \\

\[ k = 0.152 \times 10^{-3} \text{ litre.g- mol}^{-1} \text{sec}^{-1} \]
**COMPLETE RESULTS** (Rate constants $\times 10^3$ in litre. g.-mol.$^{-1}$ sec.$^{-1}$)

<table>
<thead>
<tr>
<th>Ethyl 2-Naphthoate</th>
<th>Ethyl 1-Naphthoate</th>
<th>Methyl 2-Naphthoate</th>
<th>Methyl 1-Naphthoate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.68</td>
<td>0.36</td>
<td>0.152</td>
</tr>
<tr>
<td>1.63</td>
<td>0.63</td>
<td>0.33</td>
<td>0.152</td>
</tr>
<tr>
<td>30°</td>
<td>1.61</td>
<td>0.59</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>3.52</td>
<td>1.67</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>3.58</td>
<td>1.60</td>
<td>0.87</td>
</tr>
<tr>
<td>40°</td>
<td>3.47</td>
<td>1.57</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>3.77</td>
<td>1.70</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>3.66</td>
<td>1.50</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.93</td>
</tr>
<tr>
<td>8.0</td>
<td>2.63</td>
<td>2.65</td>
<td>1.22</td>
</tr>
<tr>
<td>50°</td>
<td>8.3</td>
<td>2.67</td>
<td>2.66</td>
</tr>
<tr>
<td></td>
<td>8.3</td>
<td>3.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.10</td>
<td></td>
</tr>
<tr>
<td>60°</td>
<td>17.3</td>
<td>5.8</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>17.5</td>
<td>5.9</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>17.3</td>
<td>5.9</td>
<td>6.5</td>
</tr>
</tbody>
</table>

**Mean values of rate constants ($x 10^3$ litre. g.-mol.$^{-1}$ sec.$^{-1}$)**

<table>
<thead>
<tr>
<th></th>
<th>$k(30°)$</th>
<th>$k(40°)$</th>
<th>$k(50°)$</th>
<th>$k(60°)$</th>
<th>$E$</th>
<th>log $pz$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl 2-naphthoate</td>
<td>0.36</td>
<td>0.92</td>
<td>2.65</td>
<td>6.5</td>
<td>19.7</td>
<td>10.7</td>
</tr>
<tr>
<td>Methyl 1-naphthoate</td>
<td>0.150</td>
<td>0.50</td>
<td>1.23</td>
<td>2.48</td>
<td>19.1</td>
<td>9.9</td>
</tr>
<tr>
<td>Ethyl 2-naphthoate</td>
<td>1.58</td>
<td>3.55</td>
<td>8.2</td>
<td>17.6</td>
<td>16.5</td>
<td>9.0</td>
</tr>
<tr>
<td>Ethyl 1-naphthoate</td>
<td>0.63</td>
<td>1.61</td>
<td>2.9</td>
<td>5.9</td>
<td>14.6</td>
<td>7.3</td>
</tr>
</tbody>
</table>
Graph 5
Arrhenius plots for ethyl esters

Ethyl 1-naphthoate

\[-\log k\]

\[\frac{1}{T} \times 10^3\]

Graph 6
Arrhenius plots for methyl esters

Methyl 1-naphthoate

\[-\log k\]

\[\frac{1}{T} \times 10^3\]
5. DISCUSSION OF RESULTS.

Fitzgerald\textsuperscript{11} has given his second order rate constants for the alkaline hydrolysis of ethyl 1- and 2-naphthoates in 85% ethanol in units of 100 m\textsuperscript{l}..g. of ester\textsuperscript{-1} sec.\textsuperscript{-1} and, in the more conventional units of litre. g.-mol\textsuperscript{-1} sec.\textsuperscript{-1}, they are tabulated below, together with the corresponding results reported in this thesis.

\begin{center}
\begin{tabular}{lccc}
\textbf{Ethyl 1-naphthoate in 85\% ethanol} & & \\
\hline
Fitzgerald & $1.1 \times 10^{-3}$ & $4.5 \times 10^{-3}$ & 14.6 \\
This thesis & $1.61 \times 10^{-3}$ & $5.9 \times 10^{-3}$ & 14.6 \\
\hline
\textbf{Ethyl 2-naphthoate in 85\% ethanol} & & \\
\hline
Fitzgerald & $4.1 \times 10^{-3}$ & $17.0 \times 10^{-3}$ & 14.7 \\
This thesis & $3.55 \times 10^{-3}$ & $17.6 \times 10^{-3}$ & 16.5 \\
\end{tabular}
\end{center}

The agreement of Fitzgerald's results with the results of this thesis is extremely good in view of the fact that his work was of a preliminary nature involving only two runs on each compound at each of the two temperatures. Reference has already been made to the fact that these esters require drying to constant weight after distillation, and it may be that Fitzgerald's somewhat low values for ethyl 1-naphthoate are the result of aqueous impurity. He purified ethyl 2-naphthoate by recrystallisation and not by vacuum distillation and his results for this compound are much closer to the results obtained in this thesis.

Comparison of the results for the methyl esters with those of Bergmann and Hirschberg\textsuperscript{8} (both series of experiments being carried out under identical conditions) shows a large difference in the absolute values. A further significant point arising from the comparison is that the order of reactivity now found for the two esters is the reverse of that indicated by the results of Bergmann and Hirschberg. Certain features of the reported work by these two authors is worthy of further comment.
The hydrolysis was carried out by firstly weighing out the ester in a 100 ml. measuring flask, adding the equivalent amount of alkali from a butette, and then most of the methyl alcohol. After keeping the mixture in a thermostatted bath for five minutes and then diluting to the mark, 10 ml. aliquots were run into ice-cold water at definite time intervals and titrated with 0.1 N hydrochloric acid.

Their results are tabulated below, with (t) the time in minutes; (a) the initial concentration of alkali, and hence of ester in cc's of 0.1 N acid per 100 ml., and (a - x) their concentration (in the same units) at a time (t). The velocity constants are then according to Bergmann and Hirshberg, given by the equation

\[ k = \frac{100x}{at(a - x)} \]

<table>
<thead>
<tr>
<th>Methyl 1-naphthoate in 85% methanol at 60°</th>
<th>Methyl 2-naphthoate in 85% methanol at 60°</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4966 g. of ester; a = 26.81</td>
<td>0.5158 g. of ester; a = 27.79</td>
</tr>
<tr>
<td>t  a - x  k</td>
<td>t  a - x  k</td>
</tr>
<tr>
<td>11.5 26.6 0.0256 46</td>
<td>23 26.4 0.0252 76</td>
</tr>
<tr>
<td>23 26.4 0.0252 76</td>
<td>33 26.3 0.0219 108</td>
</tr>
<tr>
<td>33 26.3 0.0219 108</td>
<td>48.5 26.2 0.0179 137</td>
</tr>
<tr>
<td>48.5 26.2 0.0179 137</td>
<td>58.5 26.1 0.0173 178</td>
</tr>
<tr>
<td>58.5 26.1 0.0173 178</td>
<td>74.5 26.0 0.0156 239</td>
</tr>
<tr>
<td>Mean value of k = 0.0206</td>
<td>Mean value of k = 0.0153</td>
</tr>
</tbody>
</table>

Bergmann and Hirshberg have omitted to state the units in which their rate constants are expressed. Recalculation of their rate constants indicates that a factor of 1000, not the factor of 100 occurring in their equation, gives the values listed and this factor of 1000 would give rate constants expressed in units of litre. g.-mol. \(^{-1}\) min. \(^{-1}\). A comparison of the rate constants obtained by Bergmann and Hirshberg expressed in litre. g.-mol. \(^{-1}\) sec. \(^{-1}\) and the results reported in this thesis, in the same units, is given in the table below.
Their quotation of results to three figures, despite an average deviation of three on the second figure, has proved misleading to later workers and it would appear that the work of Bergmann and Hirshberg was done to obtain an estimate of the order of the rate of reaction only, and not to determine accurately the rate constants. In their analytical method, and in the method of this thesis, it is essential that the differences in acid titres (Bergmann's procedure), or alkali titres when excess acid is titrated (method of this thesis), be considerable for accurate determinations of rate constants. Bergmann and Hirshberg used 0.1 N hydrochloric acid and it is clear from the above results that the differences of volumes of acid titrated are of the same order as the errors involved in the titrations. Had they used for example, a 0.01 N solution of acid which can be standardised to the same accuracy and also titrated to almost the same accuracy, the differences in volumes of acid titrated would have been far greater, enabling better results to be obtained. Furthermore the reactions have apparently been taken to only ca. 3% hydrolysis for the 1-compound and 8% hydrolysis for the 2-compound. This is hardly conducive to accuracy since such reactions take some time to settle down and, in addition, the greater the percentage hydrolysis the greater are the volume differences in titrations and consequently the better is the accuracy of the determined value for the rate constant.

The large number of runs carried out at four temperatures in the present investigation show that at all temperatures methyl 2-naphthoate reacts more rapidly than the corresponding 1-ester and, since the precautions adopted in the method have combined to give accurate reproducible rate constants,

<table>
<thead>
<tr>
<th>Rate constant of methyl 1-naphthoate in 85% methanol at 60°</th>
<th>Rate constant of methyl 2-naphthoate in 85% methanol at 60°</th>
</tr>
</thead>
<tbody>
<tr>
<td>(litre g.·mol⁻¹ sec.⁻¹)</td>
<td>(litre g.·mol⁻¹ sec.⁻¹)</td>
</tr>
<tr>
<td>Bergmann and Hirshberg</td>
<td>0.343 x 10⁻³</td>
</tr>
<tr>
<td>This Thesis</td>
<td>2.48 x 10⁻³</td>
</tr>
<tr>
<td></td>
<td>0.255 x 10⁻³</td>
</tr>
<tr>
<td></td>
<td>6.5 x 10⁻³</td>
</tr>
</tbody>
</table>
it is justifiably felt that Bergmann's work is of insufficient accuracy to challenge the validity of the results now reported.

The results of this thesis then, are in line with the experimental work of Fitzgerald and the theoretical predictions discussed in the introduction, ethyl 2-naphthoate reacting more rapidly than ethyl 1-naphthoate and correspondingly methyl 2-naphthoate reacting more rapidly than methyl 1-naphthoate.

A further point of interest is in connection with the relative rates of reaction of the methyl and ethyl esters of a given naphthaic acid. At any particular temperature the rate constant for the hydrolysis of ethyl 2-naphthoate in 85% ethanol is higher than that for the hydrolysis of methyl 2-naphthoate in 85% methanol. Correspondingly ethyl 1-naphthoate in 85% ethanol reacts more rapidly than methyl 1-naphthoate in 85% methanol. Bearing in mind the mechanism for ester hydrolysis it would be expected that if the reactions had been carried out in the same solvent the more highly inductive ethyl group should bring about a decrease in the rate of reaction of the ethyl esters. Ingold23, for example, found that the rate constants for the hydrolysis of methyl acetate and ethyl acetate in 85% ethanol were in the ratio of 1:0.601.

This illustrates the activating effect of the methyl group which has a lower I effect than the ethyl group. The comparison of rate constants of reactions in different solvents is liable to many complicating factors although some effects, which would tend to increase the rate of reaction of the ethyl esters in ethanol relative to the rates of reaction of the methyl esters in methanol, can be sorted out.

Evidence has been produced by Caldin and Long24 that in solutions made by dissolving sodium hydroxide in ethanol much of the hydroxyl ion is replaced by ethoxide ion, the equilibrium \( \text{OH}^- + \text{EtOH} \rightleftharpoons \text{OEt}^- + \text{H}_2\text{O} \) lying well to the right. They measured the equilibrium constant

\[
K = \frac{[\text{OEt}^-][\text{H}_2\text{O}]}{[\text{OH}^-][\text{EtOH}]} \quad \text{at 25}^\circ \text{C using solutions made by dissolving}
\]


sodium or sodium hydroxide in ethanol-water mixtures. By using trinitrotoluene, which ionizes to give an intensely coloured ion in the presence of ethoxide ions, the concentration of ethoxide ions in the solution was determined and that of the hydroxide ions found by determining the total base concentration by titration. They found that in a solution made by dissolving sodium hydroxide in ethanol containing x% water by weight, the percentage p of the base which is present as ethoxide ion is (if the concentration of base is not so large as to alter appreciably the percentage of water in the solvent) as follows.

\[
x = 0.2 \quad 0.5 \quad 1 \quad 2 \quad \% \text{ water}
\]

\[
p = 99 \quad 98 \quad 96 \quad 94 \quad \% \text{ ethoxide ion}
\]

Only a limited range of ethanol-water mixtures has been studied and it is not possible to gauge, by extrapolation, the percentage of ethoxide ion concentration for an 85% ethanol-water solvent. It is clear, however, that this percentage will be high.

A somewhat similar relationship is likely to hold for hydroxide ions in methanol, and a different value for the equilibrium constant, \( k = \frac{[\text{MeO}^-][\text{H}_2\text{O}]}{[\text{OH}^-][\text{EtO}]} \), will mean that the hydroxyl ion concentration of the solution is different from that of an ethanolic solution. The higher reaction rate of the ethyl esters may be caused by the value of \( K \) being higher for methanol, the concentration of hydroxide ions in methanol being less than in a solution of ethanol of identical total base strength.

Woodland, Carlin and Warner\textsuperscript{25} have confirmed an investigation by Hine and Hine\textsuperscript{26}, which showed that methanol is a stronger acid than water. Hine and Hine have evaluated the relative acidity of ethanol, methanol and water and their results show the following values for the equilibrium constants of the acid forming reactions:-
\[ \begin{align*}
H_2O + H_2O & \overset{K_e}{\longrightarrow} H_3O^+ + OH^- \quad K_e = 1.2 \quad (1) \\
MeOH + H_2O & \overset{K_e}{\longrightarrow} H_3O^+ + MeO^- \quad K_e = 4.0 \quad (2) \\
EtOH + H_2O & \overset{K_e}{\longrightarrow} H_3O^+ + EtO^- \quad K_e = 0.95 \quad (3)
\end{align*} \]

Considering these reactions, it follows that in reaction (2) more cations would be produced relative to reaction (3). Bearing in mind the equilibrium reaction (1) it is apparent that for solutions of methanol and ethanol into which have been introduced equivalent amounts of alkali, less hydroxide ions would be present in the methanol solution than in the ethanol solution. Because attack by methoxide ions on the methyl ester merely re-produces the ester, the lower concentration of hydroxide ions in the methanolic solution results in a lower rate of hydrolysis of the methyl ester than would be expected from the amount of sodium hydroxide introduced into the solvent. Clearly then, the addition of the same amount of sodium hydroxide to solutions of ethanol and methanol actually leads to a higher concentration of hydroxide ions in ethanol than in methanol. The apparent discrepancy between the rates of the ethyl and methyl esters might therefore be satisfactorily explained on this basis.

Furthermore, as a general rule the rate of a reaction between an ion and a molecule should decrease with increasing dielectric constant of the medium. The dielectric constant of 85% methanol is slightly higher than that of 85% ethanol in the range 20° - 60° which further suggests the rate constants of the ethyl esters should be greater in value than those of the corresponding methyl esters. This factor, however, is probably of minor importance compared with the question of actual hydroxide ion concentration discussed above.

From the results obtained it is possible to calculate the value of the Hammett substituent or σ constant of the fused benzene ring in the 2-naphthyl derivative. This is of interest as the two recorded values by Hammett and by Price...
and Michel differ appreciably. The constant which enables a correlation between the structure of compounds and their chemical reactivity to be made, is defined by the Hammett equation

$$\log \left( \frac{k}{k^0} \right) = \sigma \rho$$

Here $k$ and $k^0$ are the rate or equilibrium constants for reactions of the substituted and the unsubstituted compounds respectively, $\sigma$ is the substitution constant which depends solely on the nature and position of the substituent group and $\rho$ is the reaction constant, which depends on the reaction, the conditions under which it takes place and the nature of the side chain.

Jaffe lists the reaction constants at 25°, 35° and 50° of the reaction

$$\text{ArCOOC}_2\text{H}_5 + \text{OH}^- \rightarrow \text{ArCOO}^- + \text{C}_2\text{H}_5\text{OH}$$

in 85% ethanol. By evaluating the rate constants reported in this thesis for ethyl 2-naphthoate at 25°, 35° and 50° from the Arrhenius plot shown in graph 5, the $\sigma$ constant for the group at these temperatures may be obtained from the simple relationship

$$\log k_{\text{Et. 2-Nap.}} - \log k_{\text{Et. Benzoate}} = \sigma \rho$$

The following table can therefore be compiled,

<table>
<thead>
<tr>
<th>Temp.</th>
<th>$k \times 10^3$ litre.g.-mol.$^{-1}$sec.$^{-1}$</th>
<th>$\rho$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°</td>
<td>0.96</td>
<td>2.537</td>
<td>0.074</td>
</tr>
<tr>
<td>35°</td>
<td>2.36</td>
<td>2.464</td>
<td>0.060</td>
</tr>
<tr>
<td>50°</td>
<td>8.2</td>
<td>2.322</td>
<td>0.050</td>
</tr>
</tbody>
</table>

Price and Michel carried out the saponification of many substituted ethyl 2-naphthoates in 70% dioxane and as no reaction constant was available for the reaction, they subjected three corresponding ethyl benzoates to hydrolysis in 70% dioxane at 25°. The value of $\rho$ was found to be 2.313 by plotting the logarithms of the rate constants for the three ethyl benzoates against their respective $\sigma$ values. As there appears to be an error in the calculation of these results
they are listed below.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$k_{150} \times 10^3$</th>
<th>$k_{250} \times 10^3$</th>
<th>$k_{400} \times 10^3$</th>
<th>E.K.cal.</th>
<th>log $pz$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl benzoates.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>3.43</td>
<td>10.7</td>
<td>14.0</td>
<td>7.82</td>
<td>0</td>
</tr>
<tr>
<td>p-Cl</td>
<td>12.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-CH$_3$</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl 2-naphthoates</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>3.46</td>
<td>11.3</td>
<td>14.7</td>
<td>8.38</td>
<td>0.019</td>
</tr>
<tr>
<td>6-OCH$_3$</td>
<td>1.5</td>
<td>4.79</td>
<td>14.3</td>
<td>7.69</td>
<td>-0.155</td>
</tr>
<tr>
<td>7-OCH$_3$</td>
<td>2.85</td>
<td>9.33</td>
<td>14.7</td>
<td>8.2</td>
<td>-0.035</td>
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<tr>
<td>8 NH$_2$</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
<td>-0.196</td>
</tr>
<tr>
<td>5 NH$_2$</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
<td>-0.059</td>
</tr>
<tr>
<td>8 N(CH$_3$)$_2$</td>
<td>2.46</td>
<td>9.14</td>
<td>14.8</td>
<td>8.23</td>
<td>-0.062</td>
</tr>
<tr>
<td>8 NO$_2$</td>
<td>9.12</td>
<td>20.0</td>
<td>13.5</td>
<td>8.19</td>
<td>+0.322</td>
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<tr>
<td>5 NO$_2$</td>
<td>14.1</td>
<td>31.4</td>
<td>13.7</td>
<td>8.53</td>
<td>0.416</td>
</tr>
</tbody>
</table>

Thus the $\sigma$ value for the substituent group should be

$$= \log 3.46 - \log 3.43$$

$$= 0.0016$$

This is a value differing by a factor of ten from their quoted result of 0.019. As the $\sigma$ constants for the other substituents are apparently correct it appears possible at first sight that the value of 3.46 has been printed in error. However, in order that the value of 0.019 be obtained, the value of $k_{25}$, ethyl 2-naphthoate should be $3.78 \times 10^{-3}$, but this value does not give the correct values for $E$ and log $pz$, whilst the value of $3.46 \times 10^{-3}$ does. It appears that Price and Michel's calculation of the $\sigma$ constant for the fused benzene ring in the 2-naphthyl derivative is incorrect.

Price and Michel also state that Hammett lists a value of 0.117 for the $\sigma$ constant of the fused benzene ring in the 2-naphthyl derivative, with a probable error indicated as $\pm 0.10$, and suggest their value of 0.019 lies within the error limit. They have however, misquoted Hammett's value which
is 0.170 with a probable error of ±0.10 and even their quoted value of 0.019 lies outside this range, whilst the difference between the correct Hammett value and the corrected value of 0.0016 is even greater. The three results of this thesis, viz. 0.074, 0.060 and 0.050, lie inside the error by Hammett for his value, but differ by a considerable amount from the value of Price and Michel.

By virtue of the general applicability of the Hammett equation, σ constants must be essentially independent of the nature of the reacting side chain. Some important exceptions to this statement have been observed; for example, two different substituent constants have been assigned by Hammett to the nitro group in the para position. This duality of substituent constants for electron-attracting substituents is connected with the resonance of structures I and II;

\[ R - \text{aryl} - \gamma \quad \text{versus} \quad R' = \text{aryl} - \gamma \]

different σ constants describing the effect of R, depending on whether or not structure II is important. The situation is similar, but even more complicated in ethyl 2-naphthoate, the benzenene ring A

\[ A \rightarrow \text{Et} \]

being capable of exhibiting both +M and -M effects (cf. nitro group with -M effect) and in dealing with reactions of different electron demand a range of σ values could be expected. This view seems to be supported by the variation of the values of Price and Michel, Hammett and the writer, but the problem is worth pursuing by choosing reactions of vastly different characteristics in respect of electron demand at the reaction site.
BIBLIOGRAPHY

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