ACID-CATALYSED HYDROLYSIS

OF

SUBSTITUTED STERICALLY-HINDERED

BENZOATE ESTERS

by

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M.Sc., University of Toronto, 1971

A thesis submitted in conformity with

the requirements for the degree of

DOCTOR OF PHILOSOPHY

in the

UNIVERSITY OF TORONTO

September, 1975

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To Mom + Dad
without whose support + love
I would not be writing this
now and who have sustained
me through 28 years of growing
up to reach this milestone in
my career.

To

Barbara

Yosef

and Pesach

whose devotion, love and encouragement

have sustained me through to completion

and have taught me how joyous life can be

ראשית חכמה יראת ה'

The fear of the Lord is the beginning of wisdom.
(Psalm 111:10)

To Him I offer the following prayer of thanks,

ברוך ה', שהחיינו וקיימנו והגיענו לזמן הזה.

And to B. a statement of faith,

גם זה יעבור.

up to ~60-75% H_2SO_4, depending on the particular ester. The $\Delta S^{\ddagger}$ values become positive at higher acidities indicating a change to an A-1 mechanism.

The effects of substituents on methyl benzoate hydrolysis in 40.0% and 90.5% H_2SO_4 support the view that the operating mechanisms at these two acidities are A_{Ac}-2 and A_{Al}-1 respectively. The protonation behaviour of the four esters was studied at 10°C and for methyl benzoate at 25°C as well. The slopes of the ionisation plots indicate a lower requirement for solvent stabilisation of the protonated substrates than for acetates, giving 'm' values of 0.8-0.9. The parameters from the protonation studies were used to treat the rate data by means of the 'r' hydration plots and the calculation of transition state activity coefficients, log $f_{\ddagger}^{*}$.

For the latter, the activity coefficients of the neutral esters - methyl para-toluate, methyl ortho-toluate and methyl 2,6-dimethyl benzoate - were measured in 0-70% H_2SO_4 at 25°C. Both the 'r' plots and the log $f_{\ddagger}^{*}$ calculations give further corroboration to the change in mechanism for each of the esters, and all the treatments included in this study give results which agree well with one another. Some of the difficulties of interpreting the results of the 'r' hydration plots

were partly resolved by the log $f_{\ddagger}^{*}$ treatment. The latter method and its results have been discussed in detail and it shows promise as a clear and meaningful way in which to analyse the dependence of acid-catalysed reactions in the acidity of the medium.

In the dilute to moderately concentrated acid region, the order of rates of the four esters is:

methyl benzoate > methyl p-toluate > methyl ortho-toluate >> methyl 2,6-dimethyl benzoate

In the concentrated acid region, this order is reversed, in accord with what is known concerning the steric and electronic effects on acid-catalysed ester hydrolysis.

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ACKNOWLEDGEMENTS

I would like to thank Professor K. Yates who proposed the topic for this research and supervised it through the myriad obstacles encountered in the path to its completion.

My appreciation and thanks go to the various members of our research group. In addition to providing for the endless rounds of coffee which sustained the author in his quest for the ultimate truth, they engaged me in many discussions concerning the research presented herein, some results of which bore fruit. In particular, I wish to thank Professor Bob McClelland and an especial vote of gratitude goes to George Mandrapilias. Without his constant loyalty, good camaraderie and oft-times colourful language, life would have been dull indeed.

A grumbling thanks go to the various instruments employed in this research, some of which worked some of the time, and none of which worked all the time.

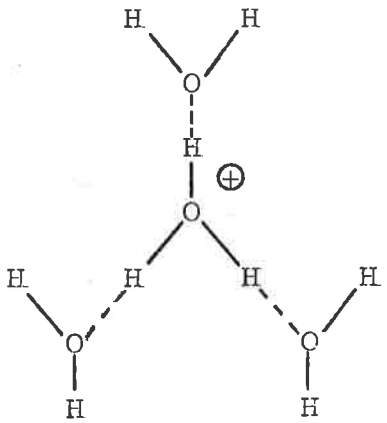
Financial aid from the Ontario Government, National Research Council and the Walter Sumner Foundation, all of whom provided Scholarships, and from Professor K. Yates is also gratefully acknowledged.

I - INTRODUCTION

I. ACID-CATALYSED REACTIONS

Many organic reactions are known to be catalysed by aqueous mineral acids and, in particular, the reactions of carboxylic acid derivatives such as esters, amides and acid halides have long been the subject of investigation. As early as 1792, the catalytic action of dilute acids and alkali on esterification and hydrolysis was reported.[1] These two reactions, which are microscopic reverses of each other, have in fact been a major subject of mechanistic studies for many years. It is only in the last thirty years or so, however, that extensive work has been carried out on reactions of carboxylic acid derivatives with the aim of determining the effect of catalysis in various acidic and alkaline media. This work was reviewed by Bender,[2] based on information available, but he concerned himself mainly with those reactions which occur upon nucleophilic attack at the carbonyl centre.

Reactions in dilute acid usually show rate increases proportional to the stoichiometric concentration of the hydronium ion, H_3O^+. This yields no mechanistic information however, except that the reaction is acid-catalysed. In more concentrated acids a variety of rate-acidity dependences are observed, enabling a more detailed investigation into the mechanisms of acid-catalysed reactions. The essential difference between reactions in these two acid regions arises from the changing activity of the hydronium ion. Bell[3] has postulated that in acid strengths up to ∿8 m., the hydrogen ion is hydrated by an average of four water molecules; this was supported by other evidence.[4,5] This seems reasonable in view of the number of strong hydrogen bonds that can be formed:



In the relatively dilute acid media for which this was found, there are sufficient water molecules available for this extent of hydration. However, the

situation alters dramatically as the concentration of acid increases beyond 8 m. (≃44% H_2SO_4), since the water activity begins to decrease considerably. Also, the activity of the hydrogen ion starts diverging significantly from its stoichiometric concentration. It is this chemical phenomenon that is the basis of the varied behaviour observed for reactions catalysed by strong mineral acids. The rates of such reactions range from those which are so rapid that they can no longer be followed by conventional techniques, to reactions that go through rate maxima at a certain acid concentration and then slow down until they are too slow to be conveniently measured. Most reactions of carboxylic acid derivatives fall somewhere between these two extremes. The main problems that have engaged the attention of chemists in attempting to draw mechanistic conclusions from these different kinetic behaviours have involved determining the "effective" acidity of an acid medium and relating the reaction rates to some function of the acidity and/or the activity of water in the medium.

II. ACIDITY FUNCTIONS

(i) CONCEPT

The first major breakthrough in analysing these reactions was the definition and formulation of the protonating ability of an acid solution by Hammett in 1932.[6] Since most organic molecules act as weak Brønsted bases in strong enough acid, the equilibrium reaction for protonation of a base, B, may be written as,

$$B + H^+ \rightleftharpoons BH^+$$

The equilibrium constant for dissociation of the protonated base is then expressed as,

$$K_{BH^+} = \frac{a_{H^+}a_B}{a_{BH^+}} = \frac{a_{H^+}f_B}{f_{BH^+}} \cdot \frac{[B]}{[BH^+]}$$

The first term was then defined as an acidity function, the ability of the acid medium to protonate the base, B,

$$h_o = \frac{a_{H^+}f_B}{f_{BH^+}} \qquad \ldots(1)$$

or, in its more common logarithmic form,

$$H_o = -\log h_o = -\log \frac{a_{H^+} f_B}{f_{BH^+}} = pK_{BH^+} - \log \frac{[BH^+]}{[B]} \quad \ldots(2)$$

In dilute aqueous acid solutions, all activity coefficients approach unity and hence $H_o = -\log a_{H^+} = pH$. The value of the function H_o in more concentrated acids appears to depend on the base B. Hammett assumed that for similar bases, B and C, of the same charge type,

$$\frac{f_B}{f_{BH^+}} \simeq \frac{f_C}{f_{CH^+}}$$

or,

$$\log \frac{f_B f_{CH^+}}{f_{BH^+} f_C} \simeq 0 \quad \ldots(3)$$

Ionisation ratios, $[BH^+]/[B]$, are usually only measurable over 2-3 units of H_o. Therefore in order to establish the H_o behaviour over a wide range of acidity it is necessary to determine the protonation of a series of similar indicators which have successively overlapping ionisation ratios over a range of acid concentrations. If a base, C, is chosen which ionises in a similar manner to B - that is, it obeys equations (1) - (3) above, then its protonation behaviour may be written as

$$H_o = pK_{CH^+} - \log \frac{[CH^+]}{[C]} = - \log \frac{a_{H^+} f_C}{f_{CH^+}} \quad \ldots(4)$$

Combining equations (2) and (4) and rearranging,*

$$\log \frac{[BH^+]}{[B]} - \log \frac{[CH^+]}{[C]} = pK_{BH^+} - pK_{CH^+} + \log \frac{f_B f_{CH^+}}{f_{BH^+} f_C} \quad \ldots(5)$$

Hence,

$$\log \frac{[CH^+]}{[C]} = \log \frac{[BH^+]}{[B]} - pK_{BH^+} + pK_{CH^+} - \log \frac{f_B f_{CH^+}}{f_{BH^+} f_C}$$

Therefore, $$\log \frac{[CH^+]}{[C]} = -H_o + pK_{CH^+} - \log \frac{f_B f_{CH^+}}{f_{BH^+} f_C} \quad \ldots(6)$$

Assuming that the activity coefficient postulate (equation (3)) holds, equation (6) reduces to equation (4).

$$\log \frac{[CH^+]}{[C]} = -H_o + pK_{CH^+}$$

This method of using indicators whose ionisation ratios overlap in successively increasing regions of acidity, together with the necessary implication that

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*It must be assumed that the presence of B or C in spectroscopic quantities does not appreciably affect the hydronium ion activity of the medium.

in very dilute acid solution H_o = pH, requires that all values of pK_{BH^+} of the various indicators be anchored to that of a base, X, which is sufficiently basic that its protonation behaviour can be measured in the pH region. The base that was used as this reference point was p-nitroaniline, whose $pK^{25^o}_{BH^+} = 1.00$. From this value, the ionisation behaviour of successively weaker bases can then be measured and extended into the very concentrated acid region.

The logarithm of the ionisation ratios should follow the H_o acidity function with unit slope and give the thermodynamic dissociation constant as the intercept. The assumptions in this treatment appear to hold reasonably well for a number of different indicators, especially the primary anilines used by Hammett for his original acidity function, H_o. Unit slopes in the plot of log $[BH^+]/[B]$ versus H_o were observed in many cases. A great deal of work has been devoted to these studies, and have been comprehensively reviewed in two recent monographs.[7,8]

(ii) BREAKDOWN

About 1960, it became apparent that the assumptions involved in the formulation of H_o were not universally valid. The main indication was that many types of base did not give unit slope against H_o in

their ionisation behaviour.[9,10] The reason appeared to be that it was not just charge type but also structural type and the site of protonation that were necessary conditions for obtaining similar slopes of the ionisation plots. For a series of indicators for which these conditions held, an acidity function appropriate to that series could be constructed:

$$H_X = -\log \frac{a_{H^+} f_X}{f_{XH^+}} = pK_{XH^+} - \log \frac{[XH^+]}{[X]}$$

A variety of acidity functions are now known, including those for aromatic amides (H_A),[9] tertiary anilines (H_o)[11,10] and aliphatic esters (H_E).[11] These scales differ from one another and from H_o considerably, but seem to be valid when used to describe the ionisation of bases of the same structural type. Hammett's formulation worked as well as it did since he used mostly primary anilines to establish the original H_o scale. In acids above 60% H_2SO_4 however, where he used indicator bases that were not primary anilines, the scale was re-evaluated using more weakly basic primary anilines and found to be significantly different.[12]

(iii) LINEAR INTERDEPENDENCE OF ACIDITY FUNCTIONS

Although most neutral bases do not give a unit slope when a logarithm of their ionisation ratio is

plotted against H_o (equation (2)), linear relationships are usually obtained.

$$\log \frac{[SH^+]}{[S]} = m(-H_o + pK'_{SH^+}) \qquad ...(7)$$

Since the ionisation ratio of the base, S, may also be written:

$$\log \frac{[SH^+]}{[S]} = -H_o + pK_{SH^+} + \log \frac{f_S f_{BH^+}}{f_{SH^+} f_B} \qquad ...(6)$$

Equation (7) implies that the activity coefficient ratio is not vanishing, but is also linear in H_o.

$$\log \frac{f_S f_{BH^+}}{f_{SH^+} f_B} = (1 - m)H_o + (mpK'_{SH^+} - pK_{SH^+}) \qquad ...(8)$$

If the appropriate acidity function describing the protonation of S is used,

$$\log \frac{[SH^+]}{[S]} = -H_S + pK_{SH^+} \qquad ...(9)$$

Then: $-H_S + pK_{SH^+} = -mH_o + mpK'_{SH^+}$

or: $H_S = mH_o + (pK_{SH^+} - mpK'_{SH^+}) \qquad ...(10)$

and a linear relationship among acidity functions is predicted. In equation (7) or (10), 'm' is the slope of the log $[SH^+]/[S]$ versus H_o plot, and pK'_{SH^+}

corresponds to the H_o value of the medium at which the base, S, is half-ionised.

Plots of various acidity functions against H_o have been shown[13] to exhibit good linearity over a wide range of acidity outside the dilute acid region. The linear relation, equation (10), must break down in this region since all acidity functions must approach pH. What this empirically determined linearity implies is that the values of the activity coefficient ratios, f_{BH^+}/f_B and f_{SH^+}/f_S are not strongly sensitive to incremental drifts because of the nature of the substituents in the indicators employed, such as nitro groups. If equations (6) and (9) are combined, the result should simply be equal to a logarithmic ratio of activity coefficients:

$$(H_S - H_o) = \log \frac{f_B f_{SH^+}}{f_{BH^+} f_S} \qquad \ldots(11)$$

When $(H_S - H_o)$ is plotted against acid molarity, Arnett[14] has shown that good linear plots are obtained over a wide range of acid behaviour. That this is not fortuitous has been demonstrated[15a] by plotting the activity coefficient ratio in equation (11) against $M_{H_2SO_4}$ for which good linearity was obtained for a number of acidity functions. And when the two sides of equation (11) are plotted against one another,[15b] the points fall very close to the theoretical line of slope =

1.00. What these linear behaviours demonstrate is that, to a fairly good approximation, the various acidity functions, when corrected for individual indicator behaviour, are capable of measuring some common property of the medium, namely, the proton activity variation.

(iv) ACTIVITY COEFFICIENTS

It is clear from the derivation of acidity functions that a knowledge of activities and/or activity coefficients of the various species in acid solution is necessary to obtain a greater understanding of how the reactivity of a substrate in a reaction in aqueous acid is related to the acidity of the medium. The chemical potential, or partial molar free energy, of a solute species, i, in a medium of solvent, s, is given by:

$$ {}_s\mu_i(C_i,C_s) = {}_s\mu_i^{\circ} + RT \ln {}_sf_i.C_i $$

where C_i is the molar concentration of i and ${}_sf_i$, its activity coefficient; C_s is the molar concentration of the given solvent system. The reference chemical potential ${}_s\mu_i^{\circ}$ refers to a hypothetical standard state for which $C_i^{\circ} = 1$ M, and $C_s = C_s^{\circ}$, the concentration of the pure solvent. As the concentration of the solute approaches zero, the solute-solute interactions become negligible and ${}_sf_i \rightarrow 1$.

Since the choice of standard state is arbitrary, it is usually more convenient to choose the same one for all acid media, S, namely, an ideal dilute solution in pure water, C_w^o. On this basis,

$$ {}_s\mu_i(C_i,C_s) = {}_w\mu_i^o + RT \ln {}_wf_i.C_i $$

$$ {}_s\mu_i^o - {}_w\mu_i^o = RT \ln \frac{{}_wf_i}{{}_sf_i} = RT \ln f_i $$

where f_i is the ratio of the two activity coefficients referred to the two different standard states. In other words, f_i is proportional to the free energy change in transferring one mole of the solute i from the standard state in water to the standard state in acid solution. Because these activity coefficients reflect the solute's departure from ideality due to differing solute-solvent interactions, they have been termed "medium effect activity coefficients".[16]

The above treatment holds for determining the activity coefficients of neutral solute species. Problems arise however for the measurement of ionic activity coefficients, since single-ion activity coefficients are experimentally inaccessible.[17] Nevertheless, Boyd[18] has shown that the use of a standard reference ion, involving the following approximation, allows these to be calculated.

If the reference cation, X^+, and a common anion, Y^-, are chosen, then $a_{\pm}^2(X^+,Y^-)$ can be measured exactly.

$$a_{\pm}^2(X^+,Y^-) = a_{X^+}a_{Y^-} = f_{X^+}[X^+]\, f_{Y^-}[Y^-]$$

Choosing any other cation, Z^+, of interest and the same anion,

$$a_{\pm}^2(Z^+,Y^-) = f_{Z^+}[Z^+]\, f_{Y^-}[Y^-]$$

The assumption is then made that the activity coefficient of the common anion, Y^-, is not dependent on the cation with which it is associated, but only on the particular medium (acid solution) being used. Then,

$$\frac{a_{\pm}^2(Z^+,Y^-)}{a_{\pm}^2(X^+,Y^-)} = \frac{f_{Z^+}f_{Y^-}}{f_{X^+}f_{Y^-}} \cdot \frac{[Z^+]\,[Y^-]}{[X^+]\,[Y^-]}$$

Hence:
$$\frac{f_{Z^+}f_{Y^-}}{f_{X^+}f_{Y^-}} \simeq \frac{f_{Z^+}}{f_{X^+}} \equiv f_{Z^+}{}^*$$

where the asterisk (*) indicates that the estimated cation activity coefficient is referred to the standard reference cation, X^+. If the cations being compared are not too dissimilar, and if the reference cation chosen has minimal interaction with the solvent, the assumptions implicit in this approach should be reasonably valid. This proposition can be tested with the salt activity coefficient data available, since if the single-ion

activity coefficients are truly independent of the counter-ion, the following relationship should hold.

$$\log \frac{f_{\pm}(A^+,X^-)}{f_{\pm}(A^+,Y^-)} + \log \frac{f_{\pm}(B^+,Y^-)}{f_{\pm}(B^+,X^-)} = 0. \quad ...(12)$$

Using ten different sets of salt data, Yates and McClelland[15c] tested this equation and found very good agreement for it, particularly considering that four independent activity coefficient measurements were required for each set. For the 10-70% H_2SO_4 range, most values of the left-hand side of equation (12) were less than ± 0.1.

Of the possible reference cations available, tetraethylammonium ion, TEA^+, has usually been chosen[18] in these studies. This rests on the belief that since it contains a strongly shielded cationic centre and has no functional groups capable of strong specific interactions with the solvent, its behaviour should be reasonably medium independent.

III. HYDRATION TREATMENTS

(i) ACIDITY FUNCTIONS

Assume that each species in an ionisation equilibrium is hydrated by a different number of water molecules,

$$B(H_2O)_b + H^+(H_2O)_n \rightleftharpoons BH^+(H_2O)_a + (b+n-a)H_2O$$

where the subscripts are the average number of water molecules of hydration and are not necessarily integral. Then, if B is a primary aniline following H_o,

$$H_o = pK_{BH^+} - \log \frac{[BH^+_h]}{[B_h]}$$

$$= - \log \frac{a_{H^+_h} \; f_{B_h}}{f_{BH^+_h} \; a_{H_2O}^{b+n-a}} \qquad \ldots (13)$$

This is identical to the previous definition of H_o (equation (2)) since the formal activity coefficients of the species in solution are related to the activity coefficients of the hydrated species by the equation:[19,20]

$$f_x(\text{formal}) = f_x(\text{hydrated}) \cdot a_{H_2O}^{-h}$$

Only f_x(formal) can be experimentally measured, but the assumptions involved in the various hydration treatments relate f_x(hydrated) terms only. However, by removing the effect of hydration on activity coefficient variation by placing it in the water activity term, the hope is that the hydrated activity coefficients for molecules of similar size and charge should be similar. In effect, this hydration treatment attributes all medium-dependent differences in chemical behaviour mainly to hydration - i.e., changes in hydrogen bonding of the solute species with the water molecules in solution. Such a treatment has been used to calculate the dependence of H_o on water activity in different mineral acids[21] as well as to explain the differences between the various acidity functions.[22] The success of this treatment in explaining, at least qualitatively, some of the properties of solute molecules in aqueous acid solutions lends some credence to its validity, despite the fact that the hydration numbers (a, b, etc.) and the activity coefficients of the hydrated species cannot be measured directly.

For example, the breakdown of the Hammett acidity function concept can be explained in the following manner. If the protonation of another base, S, which obeys an acidity function H_s, not equal to H_o, is written in terms of hydrated species,

$$S(H_2O)_s + H^+(H_2O)_n \rightleftharpoons SH^+(H_2O)_p + (s+n-p)H_2O$$

Then,

$$H_s = -\log \frac{a_{H^+}\, f_{s_h}}{f_{SH^+}\, a^{s+n-p}_{H_2O}} \qquad \ldots(14)$$

Subtracting equation (14) from equation (13), the equivalent expression for protonation of an H_o-type base, gives:

$$(H_o - H_s) = \log \frac{f_{s_h}\, f_{BH^+}}{f_{SH^+}\, f_{B_h}} + [(b-a) - (s-p)] \log a_{H_2O}$$

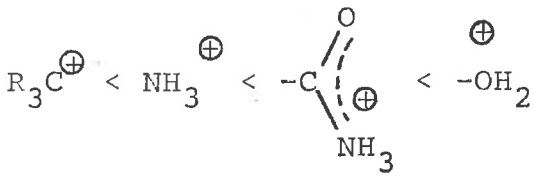
The hydration treatment assumes that the activity coefficient ratio vanishes, and that neutral molecules hydrate only to a small and similar extent, i.e. $b \simeq s$. Therefore

$$H_o - H_s \simeq (p-a) \log a_{H_2O}$$

In other words, the difference between two acidity functions can be explained in terms of the relative hydration of the protonated substrate molecules characteristic of the two different functions. Since $\log a_{H_2O}$ is negative, if $p < a$ (SH^+ less hydrated than BH^+), then $H_o > H_s$, or $(-H_o) < (-H_s)$. This agrees qualitatively with the known order of acidity functions,[23]

$$-H_R > -H_o > -H_A > -H_{ROH}$$

since the expected order of hydration of the various ionic species is:



In general, the less rapidly a base protonates with increasing acidity (that is, the lower the value for the slope, m, in a plot of log $[SH^+]/[S]$ vs. H_o), the more hydrated is the protonated substrate. Moreover, it becomes more destabilised relative to a less hydrated species, as more water molecules of hydration are being removed.

(ii) RATE-ACIDITY CORRELATIONS

As indicated earlier (p. 3), the main problem for chemists in attempting to explain the variety of behaviour of hydrolysis of carboxylic acid derivatives in mineral acids have been in relating the rate of the reaction to the effective acidity and/or the water activity of the medium. Reactions in the dilute acid region are of little interest, since these rates are generally proportional to the concentration of the acid catalyst and otherwise yielding very few details

concerning reaction mechanism. For those reactions, however, which proceed via an initial protonation of the substrate, followed by a rate-determining formation or breakup of an intermediate,

$$S + H^+ \rightleftharpoons SH^+ \rightarrow \ddagger \rightarrow \text{products}$$

a quantitative treatment should at least attempt to make use of the acidity-function concept.

A. ZUCKER-HAMMETT HYPOTHESIS

Zucker and Hammett[24] were the first to use this idea in their analysis of a number of acid-catalysed reactions for which data were available at the time (1939). They found that the reactions considered could be grouped into two categories. Those for which a molecule of water was present in the transition state of the rate-determining step (A-2 reactions) showed a linear relation between the logarithm of the pseudo-first order rate constant (log k_ψ) and the logarithm of the molar concentration of the acid catalyst (log $C_{H_3O^+}$). Those reactions for which the protonated substrate decomposed unimolecularly in the rate-determining step (A-1 reactions) exhibited linearity between log k_ψ and the acidity function H_o of the acid medium. Both relations were predicted and found to have unit slopes.

A-2: $\log k_\psi = -\log C_{H_3O^+}$ (+ constant)

A-1: $\log k_\psi = -H_o$ (+ constant).

The rate equation for an A-2 reaction may be schematically written as,

$$S + H^+ \rightleftharpoons SH^+$$

$$SH^+ + H_2O \xrightarrow{k_2} \ddagger \rightarrow \text{products}$$

Application of the Brønsted rate law gives

$$\text{rate} = k_\psi \left([S] + [SH^+] \right) = \frac{k_o f_{SH^+}}{f_\ddagger} \cdot [SH^+] \cdot a_{H_2O}$$

Hence,

$$k_\psi = \frac{k_o}{K_{SH^+}} \cdot \frac{f_s}{f_\ddagger} \cdot f_{H^+} \cdot a_{H_2O} \cdot \frac{[S]}{[S] + [SH^+]} \cdot [H^+]$$

For the case in which the substrate is largely in the unprotonated form ($[SH^+] \ll [S]$), taking logarithms and rearranging gives,

$$\log k_\psi = \log [H^+] + \log \frac{k_o}{K_{SH^+}} + \log \frac{f_S f_{H^+} a_{H_2O}}{f_\ddagger}$$

and the expected relationship results if the activity coefficient term vanishes. The only justification for

this seems to be that the transition state consists of a substrate molecule, a proton and a molecule of water; and since the A-2 reactions examined did appear to follow log $[H^+]$, there might indeed be some basis for making this assumption.

Similar treatment for an A-1 reaction

$$S + H^+ \rightleftharpoons SH^+ \xrightarrow{k_2} \ddagger \rightarrow \text{products}$$

gives

$$k_\psi = \frac{k_o}{K_{SH^+}} \cdot \frac{f_s}{f_\ddagger} \cdot a_{H^+}$$

again considering the case of $[S] >> [SH^+]$. Substituting for a_{H^+} in terms of the acidity function h_o (equation (1)) gives

$$k_\psi = \frac{k_o}{K_{SH^+}} \cdot \frac{f_s}{f_\ddagger} \cdot \frac{f_{BH^+}}{f_B} \cdot h_o$$

Taking logarithms and rearranging yields the equation

$$\log k_\psi = -H_o + \log \frac{k_o}{K_{SH^+}} + \log \frac{f_s f_{BH^+}}{f_\ddagger f_B}$$

If the transition state structure is assumed to be similar to that of a protonated Hammett-type base, the activity coefficient ratio again cancels, and the expected relation results.

This treatment would then appear to provide a distinction between A-2 and A-1 reactions, and it was applied over the following years to a number of different reactions with varying degrees of success. An extensive review in 1957[25] surveying the available literature indicated the merits and weaknesses of the relations. One of the discrepancies pointed out was that another A-2 reaction, the A-S_E2 mechanism, showed linearity with H_o instead of with log $C_{H_3O^+}$ as predicted. While this could be explained mechanistically, it indicated the degree of dissatisfaction afforded by this treatment. The Zucker-Hammett hypothesis continued to be subjected to criticism[26,27] at that time, in general for failures arising from the A-2 derivation. Such plots were usually curved, the slope increasing considerably in the more concentrated acids. Moreover, although the A-1 reactions were often linear in H_o, they rarely showed unit slope indicating that the activity coefficient ratio was also dependent on H_o, and not effectively zero. Salomaa[28] suggested that only when a correlation between k_ψ and $C_{H_3O^+}$ was observed could a mechanism definitely be concluded to be A-2; otherwise the conclusion had to be considered ambiguous at best.

B. BUNNETT 'ω' AND 'φ' HYDRATION TREATMENTS

These problems led to attempts to improve the basis for the correlations or to redefine the problem in terms of different concepts. Bunnett in 1961[29] used the latter approach in an effort to account for the specific role that water molecules had in the differing mechanisms. He treated acid-catalysed reactions explicitly in terms of fully hydrated species and their activity coefficients based on the following scheme for a reaction involving a rapid pre-equilibrium protonation step:

$$S(H_2O)_s + H^+(H_2O)_n \overset{\text{fast}}{\rightleftharpoons} SH^+(H_2O)_p + (s+n-p)H_2O$$

$$SH^+(H_2O)_p + rH_2O \xrightarrow[k_2]{\text{slow}} \neq (H_2O)_{p+r} \rightarrow \text{products}$$

Using the hydration definition for H_o:

$$B(H_2O)_b + H^+(H_2O)_n \rightleftharpoons BH^+(H_2O)_a + (b+n-a)H_2O$$

$$\rightarrow h_o = \frac{a_{H^+}\, h\, f_{B_h}}{f_{BH^+}\, h\, a_{H_2O}^{(b+n-a)}} \rightarrow aH^+_h = h_o \frac{f_{BH^+}\, h}{f_{B_h}} \cdot a_{H_2O}^{(b+n-a)}$$

$$\text{Then } k_\psi([S] + [SH^+]) = k_2 [SH^+]_h\, {H_2O}^r$$

Application of the Brønsted rate law, relating k_2 to k_o, gives:

$$k_\psi([S] + [SH^+]) = \frac{k_o \, a_{SH^+} \, h \, a_{H_2O}^r}{f_{\ddagger_h}}$$

$$= \frac{k_o}{K_{SH^+}} [S] \cdot \frac{f_{s_h}}{f_{\ddagger_h}} \cdot a_{H^+} \, h \cdot a_{H_2O}^{r+p-n-s}$$

$$= \frac{k_o}{K_{SH^+}} \cdot [S] \cdot \frac{f_{s_h}}{f_{\ddagger_h}} \cdot h_o \cdot \frac{f_{BH^+} \, h}{f_{BH}} \cdot a_{H_2O}^{r+(p-s)-(a-b)}$$

If one assumes that, for the dilute acid region $[S] >> [SH^+]$, then taking logarithms and re-arranging:

$$\log k_\psi = \{r+(p-s)-(a-b)\} \log a_{H_2O}$$

$$+ \log \frac{f_{s_H} \cdot f_{BH^+} \, h}{f_{\ddagger_h} f_{B_H}} + \log \frac{k_o}{K_{SH^+}} - H_o$$

or

$$(\log k_\psi + H_o)^* = [r+(p-s)-(a-b)] \cdot \log a_{H_2O} + \text{constant}$$

where constant = $\log k_o/K_{SH^+}$, on the assumption that the activity coefficient ratio vanishes since the

---

*For acids where $[S] \not> [SH^+]$, L.H.S. becomes:
$\log k_\psi(1+I) + H_o$, where $I = [SH^+]/[S]$.

activity coefficients of species of like charge ($\ddagger$ is positively charged) are presumed to be similar.

This then results in a linear relationship between ($\log k_{\psi} + H_o$) and $\log a_{H_2O}$, for which the slope was defined by Bunnett as the parameter, ω:

$$\omega = r + (p-s) - (a-b)$$

This represents the change in hydration on going from the protonated substrate to the transition state, relative to the difference in hydration on protonation of substrate and that of an H_o indicator. That is, the components of ω are defined thus:

r = change ($\pm$) in number of water molecules for $SH^+_h \rightarrow \ddagger_h$

p = molecules of hydration for SH^+_h

s = molecules of hydration for S_h

a = molecules of hydration for BH^+_h

b = molecules of hydration for B_h

In effect, this and other hydration treatments isolate one of the major effects on chemical reactivity in changing acidic media - viz. activity of water - as well as separating this effect for the rate-determining second step from the effect on the initial pre-equilibrium protonation step. As a result, this

approach resolved many of the difficulties in the Zucker-Hammett treatment, but its main drawbacks lay in occasionally curved plots, ω-values which were not consistent with other pieces of mechanistic evidence, and interpretation of the physical meaning of ω-values which were sometimes highly negative or positive.

In an attempt to improve upon this, and as a result of further correlations empirically observed, Bunnett[30] formulated a new approach to the hydration problem - the so-called 'ϕ' treatment. He found that a linear free-energy relationship existed between the second-order rate constants for acid-catalysed reactions (k_ψ/C_{H^+}) and the concentration equilibrium quotients (C_{BH^+})/($C_B C_{H^+}$) of primary anilines.

$$\log \frac{k_\psi}{C_{H^+}} = a \log \frac{C_{BH^+}}{C_B C_{H^+}} + b \qquad \ldots(15)$$

Furthermore, the protonation equilibrium ratios are similarly related,

$$\log \frac{C_{SH^+}}{C_S C_{H^+}} = a' \log \frac{C_{BH^+}}{C_B C_{H^+}} + b' \qquad \ldots(16)$$

Using as a standard base a hypothetical primary aniline with $pK_{BH^+} = 0$, $\log C_{BH^+}/C_B = -H_o$, equations (15) and (16) can then be rearranged to give

$$(\log k_\psi + H_o)^* = \phi_r\ (H_o + \log C_{H^+}) + \text{constant} \quad \ldots(17)$$

$$(\log \frac{C_{SH^+}}{C_S} + H_o) = \phi_e\ (H_o + \log C_{H^+}) + \text{constant} \quad \ldots(18)$$

where $\phi_r = (1-a)$ and $\phi_e = (1-a')$. The constant in equation (18) can be deduced from the intercept at $(H_o + \log C_{H^+}) = 0$, i.e. $H_o = -\log C_{H^+}$. The left-hand side of the equation then becomes the equilibrium concentration ratio for the protonation of the substrate, $S \rightarrow C_{SH^+}/C_S C_{H^+} = pK_{SH^+}$, the constant on the right-hand side of equation (18). The slopes, ϕ_r and ϕ_e, represent the response of the reaction rate and the response of substrate ionisation to the change in acidity, respectively. In determining ϕ values for reactions with known mechanisms, they were able to group these reactions into three categories, each of which represented a different role for water. The plots which resulted were considerably more linear than those from the 'ω' relation, but the main drawback remains the difficulty in determining the physical significance of ϕ and mechanistic conclusions from the proportionalities obtained.

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*Again, if the substrate is at least partially protonated, L.H.S. = $\log k_\psi (1 + I) + H_o$.

However, if one assumes that the involvement of water molecules in the rate-determining heterolysis step is accounted for by transition-state activity coefficient variation,

$$S + H^+ \rightleftharpoons SH^+$$

$$SH^+(+H_2O) \rightarrow \ddagger \rightarrow \text{products}$$

for which:

$$\log k_\psi = \log \frac{a_{H^+} f_S}{f_\ddagger} + \log \frac{k_o}{K_{SH^+}} \quad \ldots(19)$$

Then equation (17) may be rewritten as

$$\log \frac{f_S f_{BH^+}}{f_\ddagger f_B} = \phi_r \log \frac{f_{BH^+}}{f_B f_{H^+}}$$

assuming that the constant in equation (17) equals $\log k_o/K_{SH^+}$. Thus the observed linearity of the ϕ-plots implies a direct linear relationship between various activity coefficient terms.

It has also been shown,[30a] assuming all variations in activity coefficients are due to hydration, that ϕ is equivalent to a ratio of hydration numbers,

$$\phi = \frac{r + (p-s) - (a-b)}{(b+n-a)}$$

where the hydration numbers are as previously defined (p. 23). However, the mechanistic utility of ϕ plots, regardless of their formulation, is complicated by the large number of terms in their expression and hence limits their predictive ability.

C. YATES-McCLELLAND 'r' HYDRATION TREATMENT

A further refinement of the hydration approach to analysing the acidity dependence of rates in acid-catalysed reactions involves the attempt to determine directly the value of 'r', the number of water molecules in the rate-determining step.*

$$SH^+(H_2O)_p + rH_2O \rightarrow \ddagger(H_2O)_{p+r} \rightarrow \text{products.}$$

Yates and McClelland[13] showed that the Brønsted rate expression for this step may be written,

$$\log k_\psi + H_S = r \log a_{H_2O} + \log \frac{f_{SH^+}}{f_\ddagger} h + \text{constant} \quad \ldots(20)$$

where H_S is defined as the acidity function appropriate to the ionization behaviour of the particular substrate being studied,

---

*'r' is actually the change in hydration on going from the protonated substrate to the rate-determining transition state. This point will be discussed later.

$$H_S = pK_{SH^+} - \log \frac{[SH^+]}{[S]}$$

The assumption is then made that the hydrated transition state, $S^{\neq}_h$, and the hydrated protonated substrate, SH^+_h, are quite similar molecules in charge, size and structure, differing only by 'r' water molecules and bond re-organisation. Therefore the activity coefficient ratio, $f_{SH^+_h}/f_{\neq_h}$, is expected to vanish. This was, at the time, considered a necessary assumption since transition state activity coefficients could not be experimentally obtained. It is now possible however, to obtain a reasonable estimate of this quantity by analysing other parameters in the rate equation which can be measured (cf. next section).

The 'r' treatment, equation (20), requires a knowledge of the acidity function and/or the ionisation behaviour for protonation of the substrate whose reaction is being analysed. It is not necessary to have the substrate follow a defined acidity function so long as its ionisation behaviour is known. However Yates and co-workers[31,32] were able to use the amide acidity function, H_A, in their study of benzamide hydrolysis and obtained mechanistically satisfying results. Until recently however,[11] an acidity function based on ester protonation was not available, and thus Yates and McClelland[13] assumed a linear relationship

between the protonation of their acetate substrates and the H_o acidity function,*

$$\log \frac{[SH^+]}{[S]} = m(-H_o + pK'_{SH^+})$$

where m = slope of the ionisation plot of log $[SH^+]/[S]$ versus $-H_o$, and pK'_{SH^+} corresponds to the H_o value of the medium at which the base, S, is half-ionised (log $[SH^+]/[S] = 0$). For the esters for which they were able to measure the ionisation parameters, they obtained an average value of m = 0.62 and pK'_{SH^+} = -7.2. This enables equation (20) to be re-written in three ways depending on the extent of substrate protonation:

(i) $[S] >> [SH^+]$: $\log k_\psi + mH_o = r \log a_{H_2O}$

$$+ \log \frac{k_o}{K'^{m}_{SH^+}} \qquad \ldots(21)$$

(ii) $[SH^+] >> [S]$: $\log k_\psi = r \log a_{H_2O}$

$$+ \log k_o \qquad \ldots(22)$$

(iii) S partially protonated:

$$\log k_\psi (1+I) + mH_o = r \log a_{H_2O} + \log \frac{k_o}{K'^{m}_{SH^+}} \qquad \ldots(23)$$

---

*The validity of this assumption was discussed earlier, Section II, Part (iii), pp. 8-11.

For equation (23), $I = [SH^+]/[S] = h_o^m/K'_{SH^+}{}^m$. This correction for protonation is not necessary for the two extreme cases of essentially unprotonated (equation (21)) and completely protonated (equation (22)) substrates. However, for the larger part of the acidity range of interest - those acid solutions in which the proportion of protonated substrate is becoming increasingly large - the full expression (23), invoking the rate constant corrected for the extent of protonation of the first step, is required. It should be noted that, regardless of the form of the ordinate in equations (21)-(23), they represent the rate constant for the second step of the reaction,

$$SH^+ + rH_2O \xrightarrow{k_2} \ddagger \longrightarrow \text{products}$$

i.e. $\log k_2 = r \log a_{H_2O} + \text{constant}.$

Further, if equation (23) is rewritten so that the $K'_{SH^+}{}^m$ term is transposed to the left-hand side, then

$$\log k_\psi + mHo + \log (h_o^m + K'_{SH^+}{}^m) = r \log a_{H_2O} + \log k_o$$

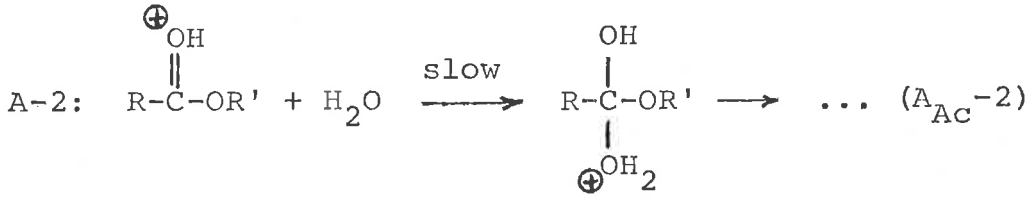
or:

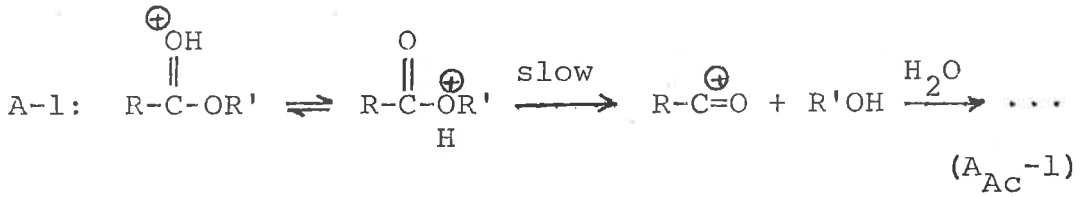
$$\log k_\psi \cdot \left(\frac{I+1}{I}\right) = r \log a_{H_2O} + \log k_o \quad \ldots(24)$$

Consequently, a plot of the left-hand side of equation (24) against $\log a_{H_2O}$ yields 'r' as the slope and

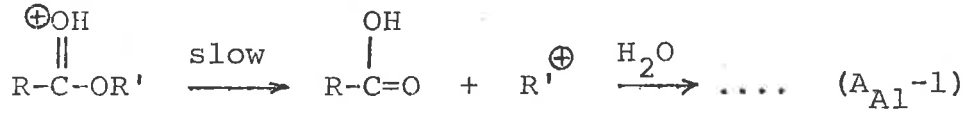
log k_o - the logarithm of the rate constant for the reaction at infinite dilution in water - directly, for this, the most general case. This was the expression used for the determination of the 'r' values of the hydrolysis of the esters contained in the present study and the ordinate is henceforth referred to as log k_2, although this is a simplification.

In effect, this hydration treatment separates the hydration change for the step in which water is playing an active role (the heterolysis step) from the hydration change for the overall reaction. This increases the predictive usefulness of the relationship, since the role of water molecules in the rate-determining step can then be determined directly. Several workers have successfully used this type of treatment to analyse rate-acidity dependence for hydrolysis[33,34] and O^{18}-exchange reactions[34] of carboxylic acid derivatives. One would naively predict an r value of 1 for an A-2 reaction and r = 0 for an A-1 reaction in agreement with their presumed mechanisms.





$$\text{A-1:}\quad R\text{-}C(=\overset{\oplus}{O}H)\text{-}OR' \rightleftharpoons R\text{-}C(=O)\text{-}\overset{\oplus}{O}(H)R' \xrightarrow{\text{slow}} R\text{-}\overset{\oplus}{C}=O + R'OH \xrightarrow{H_2O} \cdots \qquad (A_{Ac}\text{-}1)$$



$$R\text{-}C(=\overset{\oplus}{O}H)\text{-}OR' \xrightarrow{\text{slow}} R\text{-}C(OH)=O + \overset{\oplus}{R'} \xrightarrow{H_2O} \cdots\cdot \qquad (A_{Al}\text{-}1)$$

However, for those reactions satisfactorily treated with this approach,[13,33,35] 'r' values for an A-2 reaction are usually of the order of ∿2, while those for an A-1 reaction range from -0.2 to -0.8. There are reasonable explanations for these results*, but it does illustrate the approximations of the assumptions made in deriving these equations. There is, in addition, at least one case known‡ where the 'r' values lead to an erroneous conclusion regarding the mechanism, and others in which only curved 'r' plots are obtained over the whole acidity range studied.[36] The other general problem inherent in all the hydration treatments is their dependence on the presumed behaviour of the activity coefficients for the hydrated species, since only those for formally defined species are experi-

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*Cf. Results and Discussion, p. 182-4.

‡The reaction is the hydrolysis of p-methoxybenzyl acetate, for which the 'r' plot shows no A_{Ac}-2 region. Other evidence however indicates that, although the A_{Al}-1 mechanism is operative even in very dilute acid, it does not predominate over the A_{Ac}-2 mechanism until >20% H_2SO_4. Cf. Ref. 41.

mentally accessible. For these reasons, the hydration approach has been somewhat unsatisfactory in giving a clear indication of the reaction rate dependence on the acidity of the medium as defined by the activity coefficient behaviour in changing acidic media.

IV. TRANSITION STATE ACTIVITY COEFFICIENT BEHAVIOUR

(i) BASIC CONCEPT

As a result of these problems, a new *a priori* approach was tested in which the effects of the changing medium on the various parameters comprising the rate equation could be determined experimentally. This enabled a reasonable physical interpretation to be deduced concerning these effects on the rate of the reaction in various acidic media.

For the reaction sequence which may be expressed as

$$S + H^+ \rightleftharpoons SH^+$$

$$SH^+(+H_2O) \xrightarrow{k_2} \neq \longrightarrow \text{products}$$

it is reasonable to expect that the role of water, whether as a nucleophile and/or as a hydrating agent,

will be determined by the variation of the transition state activity coefficient behaviour without the need to include it explicitly in deriving the rate equation. Accordingly, transition state theory gives

$$\text{rate} = k_\psi ([S] + [SH^+]) = k_2 [SH^+],$$

and application of the Brønsted rate law gives

$$k_\psi = \frac{k_o}{K_{SH^+}} \cdot \frac{f_s}{f_\ddagger} \cdot a_{H^+} \cdot \frac{[S]}{[S]+[SH^+]}$$

For the case in which $[S] >> [SH^+]$,[a]

$$k_\psi = \frac{k_o}{K_{SH^+}} \cdot \frac{f_s}{f_\ddagger} \cdot a_{H^+} \qquad \ldots(25)$$

Thus, the acidity dependence of the pseudo-first order rate constant, k_ψ, is determined by that of three essentially independent variables — f_s, a_{H^+} and $f_\ddagger$ — only the last of which is experimentally inaccessible. This affords the opportunity of calculating $f_\ddagger$ by means of the other parameters in equation (25). Taking logarithms and rearranging:

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[a] If this condition is not met, a protonation correction term for k_ψ must be employed - viz. $k_\psi(1+I)$. In general, $-\log k_2 + mH_o$ (= $-\log k_\psi(1+I) - \log K_{SH^+}$) has been used in this treatment.

$$\log \frac{f_{\ddagger}^{*}}{k_o} = -\log k_{\psi}{}^{a} - \log K_{SH^+} + \log f_s + \log a^*_{H^+} \qquad \ldots(26)$$

where the asterisk (*) indicates that those quantities so-marked are determined relative to the activity coefficient of TEA^+ (cf. this section, pp. 13-14). All components on the right-hand side of equation (26) can, in principle, be experimentally obtained: k_ψ is the pseudo-first order rate constant, K_{SH^+} is the protonation equilibrium constant, and f_s is the activity coefficient of the neutral substrate. The only problems in determining these parameters arise when the reaction is very rapid.

Values for $a^*_{H^+}$ have been previously determined for H_2SO_4[37,38] and more recently for a number of other mineral acids.[39] These were obtained by means of the relation

$$\log a^*_{H^+} = \log f^*_{XH^+} - \log f_x - H_x \qquad \ldots(27)$$

for which $\log f^*_{XH^+}$ was determined using a number of suitable model indicators and H_x was the acidity function appropriate for that particular class of compound. The values for $\log a^*_{H^+}$ were determined,

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[a]Cf. footnote previous page.

via this relation, using five different and independently determined acidity functions and the agreement between them was excellent. These values also agreed remarkably well with $a^*_{H^+}$ values determined by Janata and Jansen,[40] who used a combined polarographic-glass electrode technique, involving no liquid junction, and the ferrocene-ferricinium ion couple ($Fec\text{-}Fec^+$) as the reference electrode.

The values for $f_{\ddagger}^*$ are calculated initially relative to k_o as a consequence of the derivation. This constant term can however be separated out since log $f_{\ddagger}^*$ approaches zero in dilute acid solution. Consequently, the intercept of a plot of log $f_{\ddagger}^*/k_o$ versus acid concentration gives a value for ($-\log k_o$) and thus,

$$\log f_{\ddagger}^* = \log f_{\ddagger}^*/k_o - (-\log k_o).$$

Hence it should be possible to estimate the medium variation of the transition state activity coefficient, relative to that for the standard reference ion, TEA^+, for any acid-catalysed reaction.

(ii) UTILITY

This approach has been used to analyse a number of acid-catalysed hydrolyses, mainly those of acetate esters[41] as well as the previous publication of the treatment for one of the esters involved in the present

study, methyl ortho-toluate[39]. The results obtained agreed well with mechanistic conclusions for these reactions on the basis of other evidence. This treatment also gave a more reliable picture of the hydrolysis of one ester, p-methoxybenzyl acetate, than did the previous 'r' treatment[a]. Moreover, the behaviour of the transition state activity coefficient in changing acidic media could be compared to f_S^+, the activity coefficient behaviour of model, stable cationic species. This showed how the structural characteristics and solvation requirements of the transition state are reflected in its activity coefficient behaviour.

Examples of varying behaviour of transition state activity coefficients for the hydrolysis of a series of benzyl acetates in sulphuric acid is shown in Fig. (1). The initially striking observation is that, unlike the rate-acidity profiles for these esters, which show a diversity in behaviour, a common pattern can be detected for log $f_{\ddagger}$* variation. Each ester shows an initial and continuing salting-out** with increasing acidity and in fact exhibit very similar curves in the dilute acid region. It is not until

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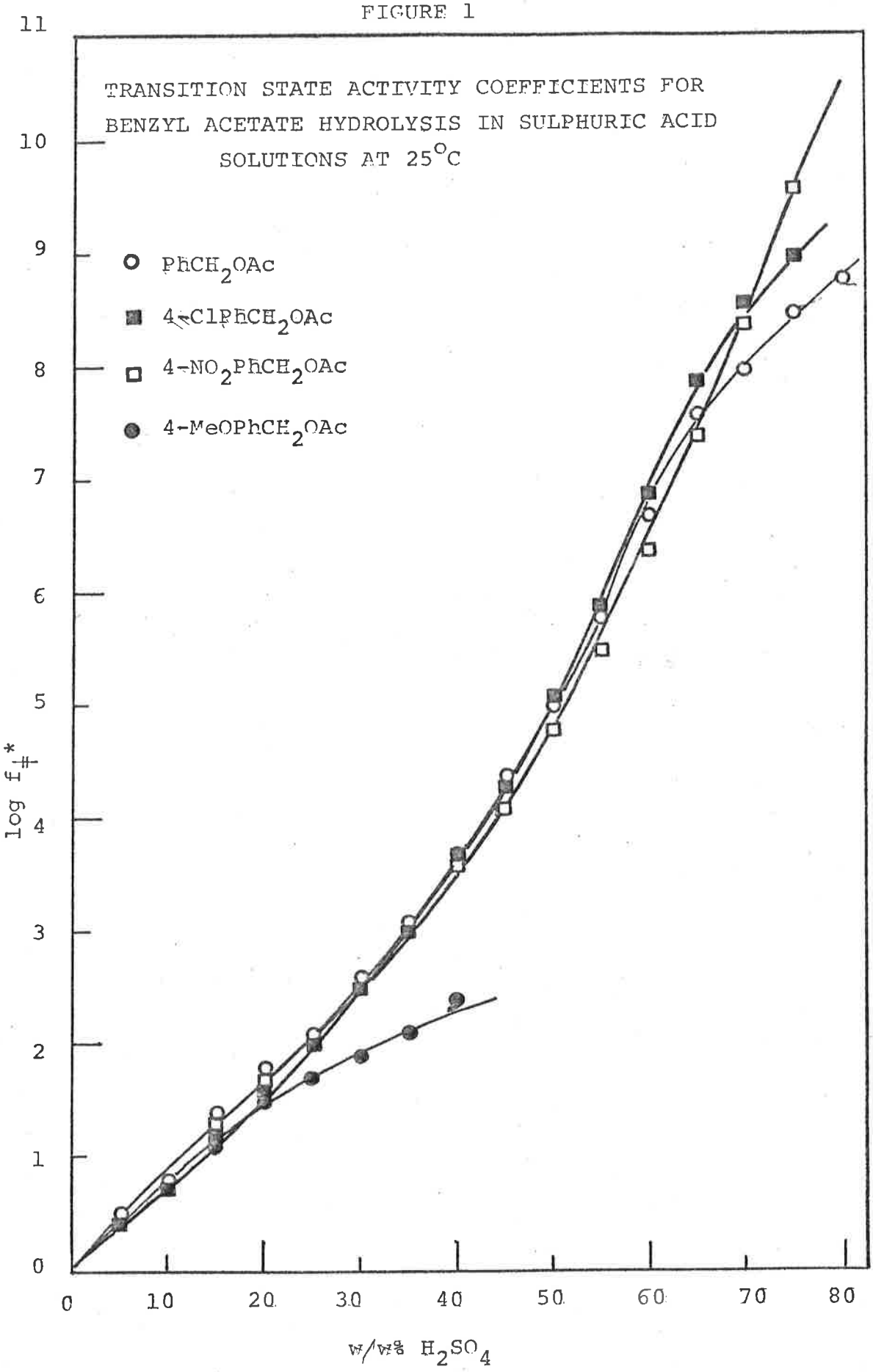
[a] Cf. Footnote, p. 34.

**In this discussion, the terms "salting-out" and "salting-in" refer to positive and negative values of log f, respectively.

FIGURE 1


TRANSITION STATE ACTIVITY COEFFICIENTS FOR
BENZYL ACETATE HYDROLYSIS IN SULPHURIC ACID
SOLUTIONS AT 25°C
PhCH2OAc
4-ClPhCH2OAc
4-NO2PhCH2OAc
4-MeOPhCH2OAc
log f‡*
w/w% H2SO4
0
1
2
3
4
5
6
7
8
9
10
11
0
10
20
30
40
50
60
70
80

some acidity is reached, the value of which is strongly dependent on ester structure, that a break from this behaviour is observed, to a curve showing a considerably smaller, albeit still positive, salting-out effect.

The two different degrees of salting-out with increasing acidity imply two different reaction mechanisms are operating, each dependent on the stability of its transition state relative to that of the other. The fact that the breaks do not occur at the same acidity but depend very much on the acetate structure supports the view that mechanistic changes are occurring*. The initial strong salting-out apparently reflects the behaviour of the transition state of an A_{Ac}-2 hydrolysis, the mechanism by which these esters react in dilute acid. The acidity range over which the mechanism changes and the type of subsequent A-1 reactions depend on the structural characteristics of the ester. In other words, the acidity where the mechanism changes is determined directly by the stability of the intermediate cation produced in the new mechanism. Fig. (2) shows how the mechanism of cyclopropylcarbinyl acetate hydrolysis changes over in the acidity range where the value of $f_{\ddagger}^{*}$ for the A-2 reaction becomes more salted-out than that for the A-1 reaction.

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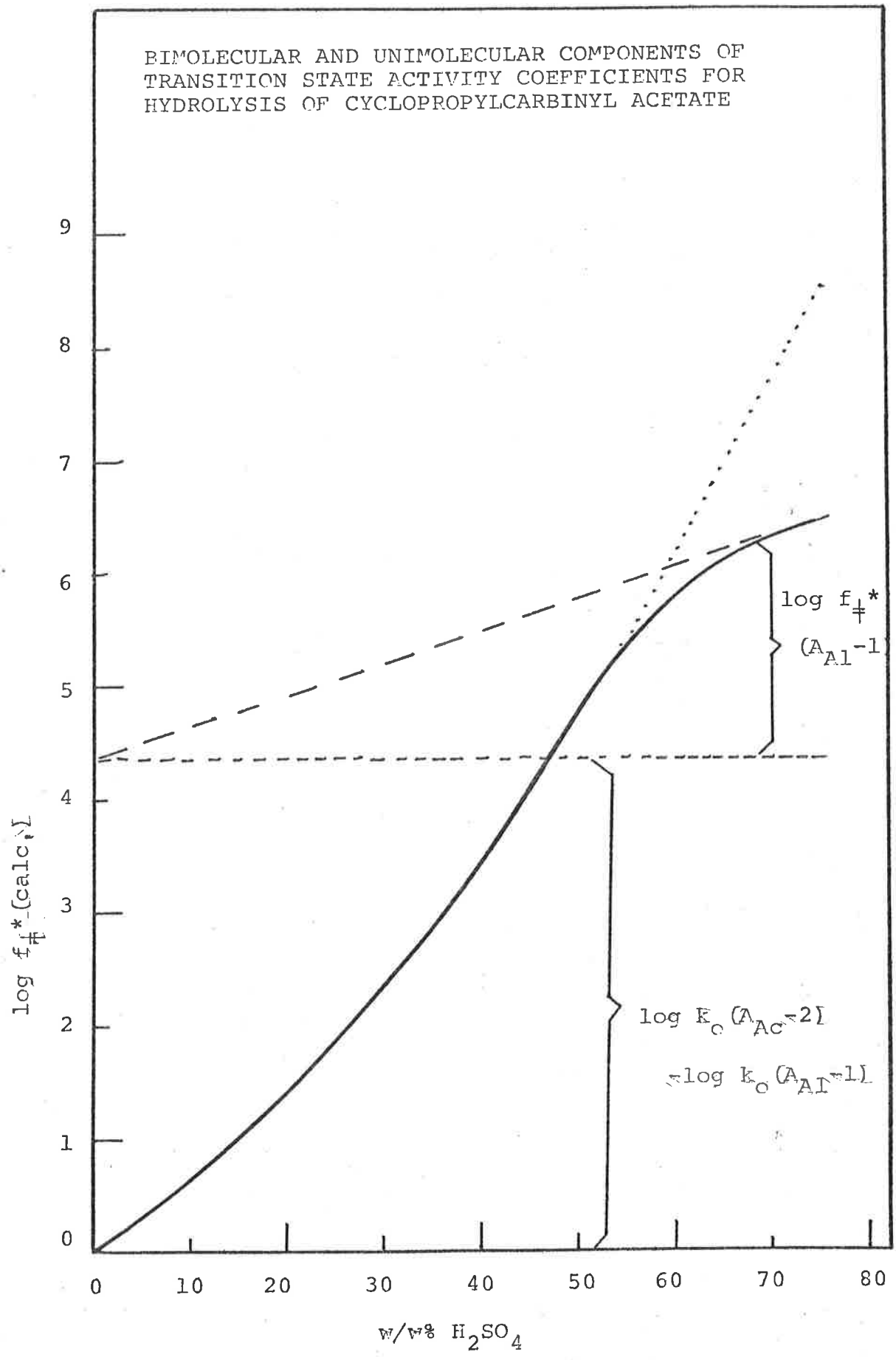
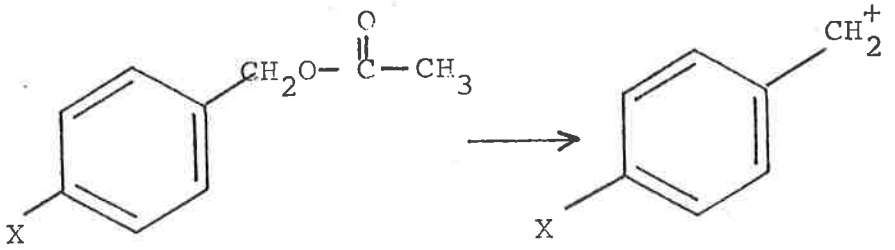
*This was also found to be the case for the 'r' plots.

FIGURE 2


BIMOLECULAR AND UNIMOLECULAR COMPONENTS OF TRANSITION STATE ACTIVITY COEFFICIENTS FOR HYDROLYSIS OF CYCLOPROPYLCARBINYL ACETATE
log $f_{\ddagger}$*(calc.)
9
8
7
6
5
4
3
2
1
0
0
10
20
30
40
50
60
70
80
w/w% H_2SO_4
log $f_{\ddagger}$* (A_{Al}-1)
log k_o (A_{Ac}-2)
-log k_o (A_{Al}-1)

Finally, it was observed that the variation in the acidities where the change in activity coefficient behaviour for the transition state occurs - i.e. where the unimolecular reaction becomes important - is consistent with what would be expected for the relative order of stability of the carbonium ions produced by these esters[42]



$X = OCH_3 > H > Cl > NO_2$

(iii) COMPARISON WITH MODEL COMPOUNDS FOR TRANSITION STATE STRUCTURE

The values for log $f_{\ddagger}^*$ for the A-2 and A-1 hydrolyses of the acetate esters were compared with the activity coefficients, f_+^*, of selected cationic species as shown in Fig. (3).[a] A considerable difference

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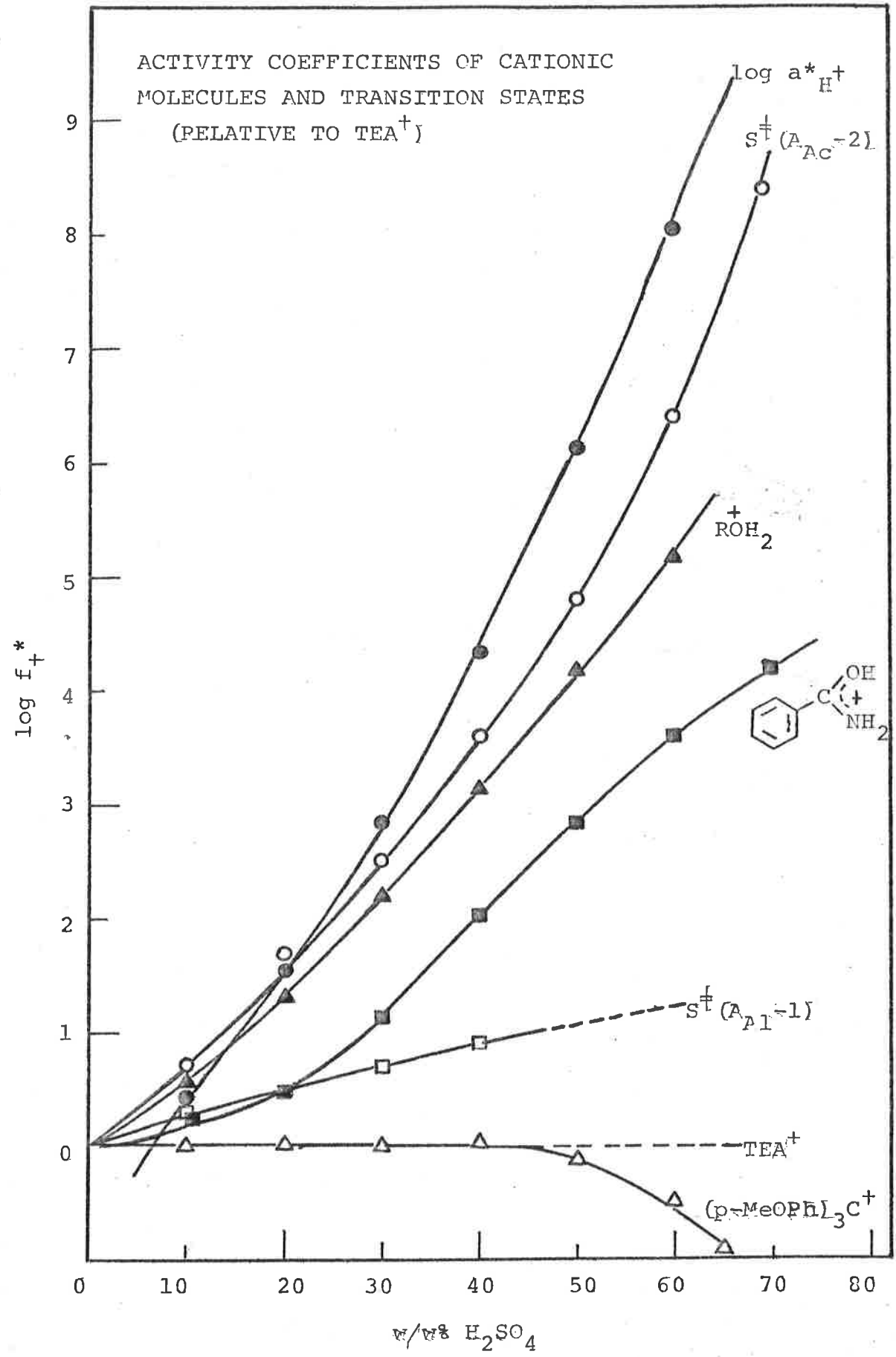
[a] It should be noted that the log $f_{\ddagger}^*$ values in plots such as Fig. (1) are calculated relative to the log k_o value for the A-2 reaction. The value of log k_o for the A-1 reaction, determined by extrapolation, is several orders of magnitude smaller than that for the A-2 mechanism. It is the log $f_{\ddagger}^*$ relative to the log k_o value for the A-1 reaction that is plotted in Fig. (3) for the $S^{\ddagger}(A_{Al}-1)$ graph.

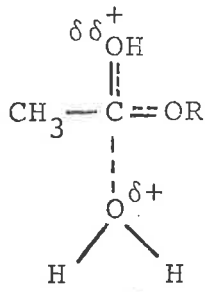
FIGURE 3


ACTIVITY COEFFICIENTS OF CATIONIC MOLECULES AND TRANSITION STATES (RELATIVE TO TEA+)
log a*H+
S‡ (AAc-2)
ROH2+
S‡ (AAl-1)
TEA+
(p-MeOPh)3C+
log f+*
9
8
7
6
5
4
3
2
1
0
0
10
20
30
40
50
60
70
80
w/w% H2SO4

in behaviour is observed, ranging over about 11 logarithm units by 70% H_2SO_4. Apart from the proton activity, log $a^*_{H^+}$, the A_{Ac}-2 transition state exhibits the greatest salting-out effect yet observed for a cationic species, even greater than that for a protonated alcohol, ROH_2^+. The A_{Al}-1 transition state is salted-in relative to all the oxonium-ion species, but is still considerably salted-out with respect to long-lived carbonium ions, such as the <u>tris</u>-p-methoxyphenyl carbonium ion, $(H_3CO-C_6H_4-)_3C^+$. Similar behaviour would be expected for the A_{Ac}-1 transition state and is in fact observed (vide infra).

The main factors that appear important in accounting for this diverse behaviour are the degree of charge delocalisation and the presence of hydrogen-bonding interactions of the type O-H...OH_2, in which water acts as a proton acceptor. Increased delocalisation leads to lower solvation requirements and hence less salting-out. On the other hand, decreasing water activity as the acidity is increased leads to a greater salting-out and this becomes more pronounced as the number of hydrogen-bonding sites on the cationic species is increased.

If the A_{Ac}-2 transition state can be postulated as a structure closely resembling a tetrahedral intermediate,



it can be shown that both these factors favour an increasingly destabilised transition state species. Depending on the degree to which C-O bond making is advanced, the positive charge is fairly localised on the oxygen of the incoming water molecule ($\delta^+ > \delta\delta^+$). Moreover, there is an increased need for hydrogen-bonding interactions, particularly since there are three electronegative oxygen atoms attached to the same carbon. The hydrogen bonds are needed to help counter the destabilisation of the positive charge. As a result, the transition state becomes increasingly salted-out as the ability of the solvent to provide this stabilisation decreases.

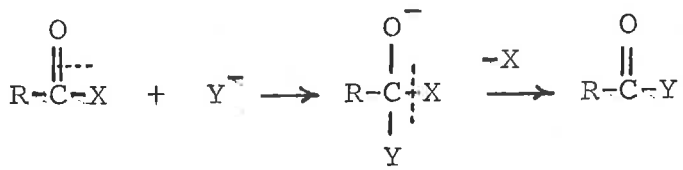
Similar arguments have been proposed to explain the much lower salting-out effect on the A_{Al}-1 transition state activity coefficient. The important conclusion is that the behaviour of transition state activity coefficients in changing acid media not only gives results that support other mechanistic evidence for these reactions, but also give a picture that is physically meaningful, particularly in terms of explaining

their behaviour as compared to analogous but stable species whose activity coefficient variation is also known.

It thus appeared desirable to apply this method of analysing the rate-acidity dependence of the reactions studied herein, both to compare with the previously obtained results, as well as to give a meaningful physical interpretation as to how the changing nature of transition state activity coefficients results in changes of mechanism.

V. MECHANISMS OF ESTER HYDROLYSIS

The unique feature of reactions involving carboxylic acid derivatives, as opposed to simple S_N1 or S_N2 reactions, is their ability to add a nucleophile to the carbonyl centre, followed by the breaking of a bond which may or may not be the same cleavage as that leading to the products from the reaction. This is most clearly seen in the following example:



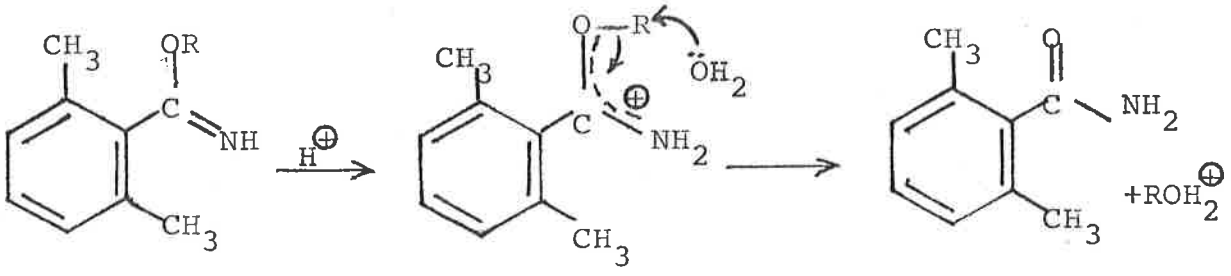
The π-bond of the carbonyl is the initial bond to be broken, but it is the C-X bond cleavage that yields the products of the reaction. As a result, this general class of compounds may react by a number of different mechanisms depending on three factors:

(i) whether acid or base catalysed

(ii) position of bond cleavage

(iii) molecularity of the reaction.

In general, carboxylic acid derivatives have only one position of cleavage that leads to products, viz. the bond between the acyl group ($R-\overset{O}{\overset{\|}{C}}-$) and the leaving group. Until recently, it was believed that only esters had another option - the bond between the hydrocarbon moiety of the alcohol and the ether oxygen, i.e. $R-\overset{O}{\overset{\|}{C}}-O\overset{\vdots}{+}R'$. However, the hydrolysis of methyl and ethyl 2,6-dimethyl benzimidates has been shown[43] to proceed through an analogous alkyl-nitrogen bond cleavage.



These three categories of options lead to 2^3 or 8 possible mechanisms of which six have been observed.[44] A number of classifications of these mechanisms have been proposed,[2,45,46] but the one

that has received the widest usage has been that proposed by Day and Ingold[45] in their early work which provided the basis for many of the studies of ester hydrolysis which followed. The definitions used by them to define the categories of reaction are:

A = acid-catalysed

B = base-catalysed

Ac = acyl-oxygen fission ($R-\overset{\overset{O}{\|}}{C}-O-$)

Al = alkyl-oxygen fission ($-\overset{\overset{O}{\|}}{C}-O-R'$)

1 = unimolecular rate-determining step

2 = bimolecular rate-determining step.

On this basis, they proposed the following classification:

REACTION MECHANISM	ACID-CATALYSED	BASE-CATALYSED
(1) Unimolecular Acyl Fission	A_{Ac}-1	B_{Ac}-1
(2) Bimolecular Acyl Fission	A_{Ac}-2	B_{Ac}-2
(3) Unimolecular Alkyl Fission	A_{Al}-1	B_{Al}-1
(4) Bimolecular Alkyl Fission	A_{Al}-2	B_{Al}-2

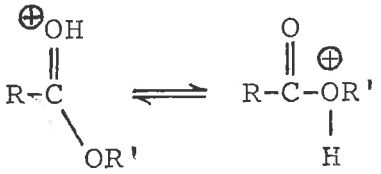
Of these eight possibilities, the A_{Al}-2 and B_{Ac}-1 have not been observed to date. All the others are known, the particular mechanism operating depending on the reaction conditions and the specific ester being hydrolysed. Since the present study is devoted to acid-catalysed hydrolyses, the following discussion

will concern itself only with the three acid-catalysed mechanisms - $A_{Ac}2$, $A_{Ac}1$ and $A_{Al}1$. Several authors have reviewed the various pieces of evidence supporting the different mechanisms.[7,46-49] Accordingly, only that material required for the purpose of the present thesis will be presented.

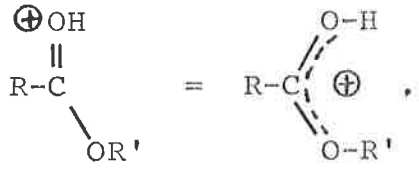
(i) PROTONATION OF CARBOXYLIC ACID ESTERS

Acid-catalysed hydrolyses show the inverse solvent isotope effect indicative of a pre-equilibrium protonation step.[50] In addition, Bell[51] has interpreted results with methyl acetate in terms of specific hydronium ion catalysis. Carboxylic acids and their esters act as quite weak bases,[52] although they appear to be fully protonated in 100% H_2SO_4.[53,54]

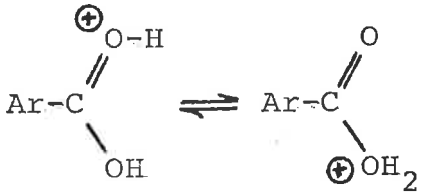
In principle an ester may protonate on either of its two oxygen atoms:



Several studies[55-57] have led to general agreement that protonation occurs predominantly on the carbonyl oxygen, a result which is expected to give a more stable product due to the possibility of delocalization:



Most of these studies have however been done in super-acid systems, using nmr techniques, and may or may not resemble the behaviour of these species under normal kinetic conditions. Nevertheless, Stewart and Yates[52] compared the protonation of benzoic acids with that of acetophenones using u.v. spectrophotometry in concentrated sulphuric acid solutions. They observed very similar behaviour between the two. On the basis that the ketones must protonate on the carbonyl oxygen, they concluded that the benzoic acids must be protonating in a similar manner. They did however suggest that the protonated acid probably exists as an equilibrium mixture of the two forms,

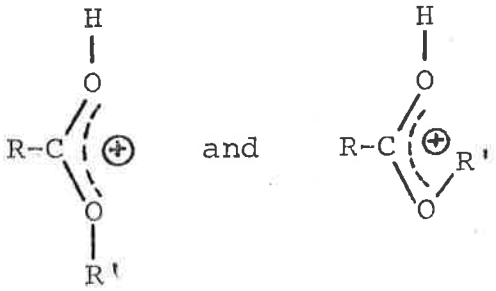


(I) (II)

although the equilibrium would be expected to favour (I) over (II). The relevant feature for kinetic studies, though, is not whether $[I] > [II]$ but whether II exists in any significant concentration at all in order to

provide a pathway for a different mechanism. In at least one ester hydrolysis mechanism, A_{Ac}-1, it is necessary to postulate the presence of a kinetically significant amount of the ether-protonated form as the most reasonable means by which bond cleavage occurs.

Finally, it is important to know the conformation of the protonated ester in order to understand the steric requirements of the hydrolysis mechanism. Of the two most likely possibilities,



(III) (IV)

the transoid* structure (IV) appears to be the preferred conformation according to several authors.[58-60] This seems reasonable, since in this case the non-bonded repulsions between R and R' will be at a minimum.

(ii) A_{Ac}-2 ESTER HYDROLYSIS MECHANISM

This is the mechanism by which the majority of esters hydrolyse under normal reaction conditions. In

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*'Transoid' refers to the conformational relation between R and R'.

order to establish the details of this, or any, mechanism it is necessary to know which bonds are broken as well as the molecularity of the reaction. Several methods have been used to establish that acyl-oxygen cleavage is occurring in this mechanism. Among these are product studies, O^{18}-isotope exchange,[61] and reactions involving the hydrolysis of esters of optically active alcohols.[62,63] All the available evidence corroborates the view that in dilute to moderately concentrated acid media, most esters hydrolyse via acyl-oxygen cleavage.

The order of the reaction with respect to water has not been as clearly understood and has been the main area of interest in studying ester hydrolysis in recent years.[49] The uncertainty arises from the fact that in dilute aqueous acid solutions the water concentration is in such large excess to that of the substrate that it does not enter into the rate expression of the reaction. The hydrolysis of methyl acetate in acetone containing just enough water to react with the ester does show second-order kinetics,[64] first order each in ester and water. These conditions do not resemble those of a normal acid-catalysed ester hydrolysis, however, and what was observed may simply have been a rate increase due to an increase in polarity as water was added. There are a number of different methods which can be used to deduce the role of water

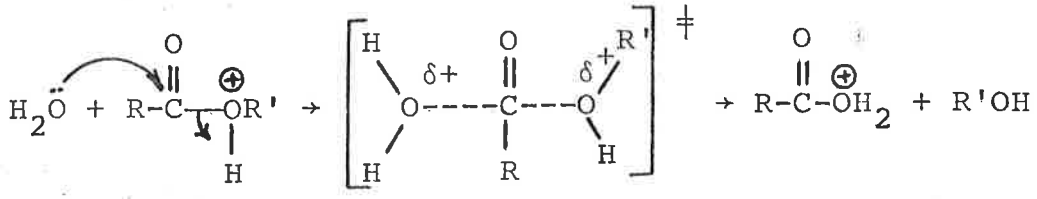
in these reactions, including substituent effects, activation parameter calculations and various hydration parameter treatments. These will be discussed in more detail in the section on Results and Discussion.

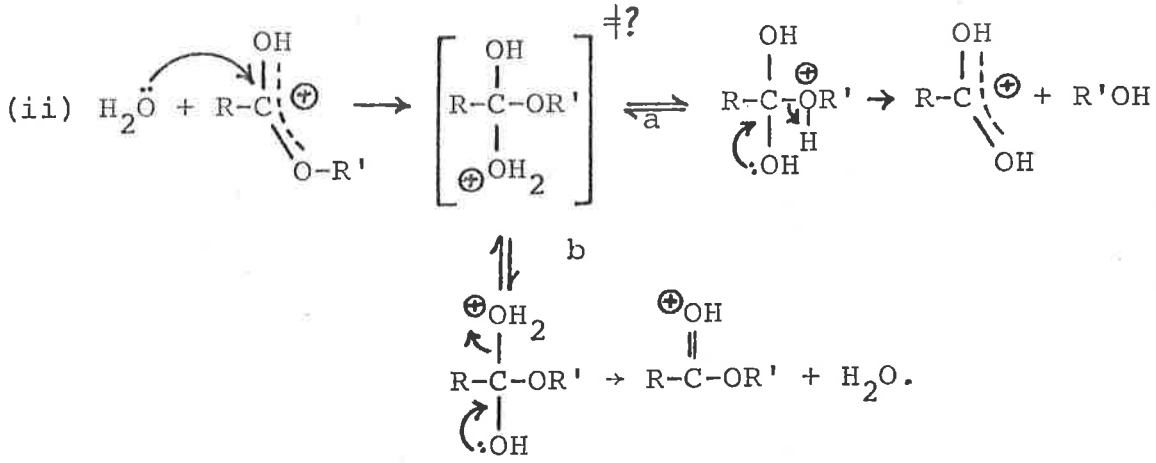
The conclusion that has been reached from these different studies is that there are generally two molecules of water involved in the rate-determining heterolysis step of the reaction:

$$SH^+ + 2\ H_2O \rightarrow \ddagger \rightarrow \text{products}$$

This has been explained by various authors[13,35,65] as implying the involvement of a water molecule acting as a proton transfer agent in addition to the nucleophilic water molecule.

The question then arises as to what does the transition-state of the $A_{Ac}2$ hydrolysis reaction look like, in order to obtain a detailed picture of the reaction mechanism. There are two possibilities which may be considered: (i) a direct S_N2-type displacement on the sp^2 carbonyl centre, and (ii) an addition-elimination mechanism. The possible pathways for each are:

(i) 



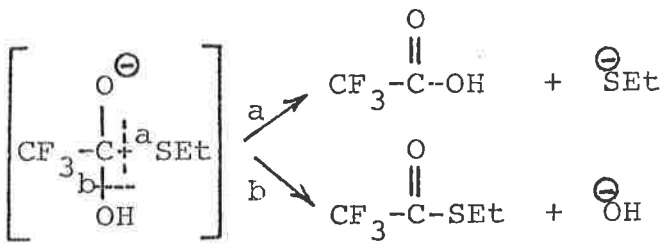
There are two points to consider about mechanism (ii). The first is that the proton transfers involved are relatively rapid, the energy barrier having been calculated to be ∿3,6 kcal/mole.[66] The second feature, a consequence of the first, is that if the carbonyl oxygen is isotopically labelled, the oxygens become essentially equivalent as a result of this mechanism, and isotopic exchange would be expected to occur. This would result in ester starting material to be recovered with at least a partial loss of label. Such a result would not be expected from mechanism (i) in which the carbonyl oxygen atom is not directly involved in the reaction. Another argument against (i) is that a direct displacement at an sp^2 centre has never been established. But the critical experiment is one involving isotope exchange, and Bender[67] was the first to demonstrate this. The acid-catalysed hydrolysis of carbonyl oxygen-labelled ethyl benzoate hydrolysis exhibited O^{18}-exchange between

the unreacted ester and the solvent, giving

$$\frac{k_{hydrolysis}}{k_{exchange}} = 5.2$$

The fact that the extent of exchange reaction is as high as ∿20% strongly suggests that a tetrahedral adduct is formed and that it must be an intermediate, since the lifetime of a transition state is only momentary and would not have sufficient time in which proton transfer could occur leading to an exchanged ester. But this experiment proves only that a tetrahedral intermediate is formed and not necessarily that it lies on the reaction co-ordinate. However, the behaviour of the exchange and hydrolysis reactions are so similar that there can be little doubt that the tetrahedral intermediate must indeed be on the reaction pathway. Moreover, O^{18}-labelled methyl mesitoate, which is known to hydrolyse by an A_{Ac}-1 mechanism, shows no oxygen exchange.[68] In addition, Lane and co-workers,[35] in their hydration treatment for the hydrolysis and exchange reactions of ethyl acetate in aqueous H_2SO_4 solutions found similar 'r' values for the two reactions, 2.00 and 1.87 respectively. This is one more piece of evidence for the similarity of the two reactions, strongly implying a common rate-determining step. Bender and Heck[69] analysed a slightly different reaction, the hydrolysis of ethyl trifluorothiolacetate,

which results in an unsymmetrical tetrahedral intermediate having two different leaving groups:

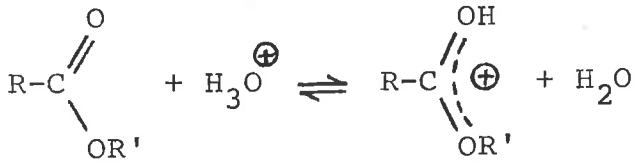


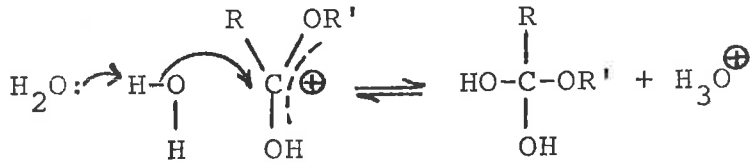
In this reaction they were able to show conclusively that the tetrahedral intermediate formed must lie on the reaction pathway.

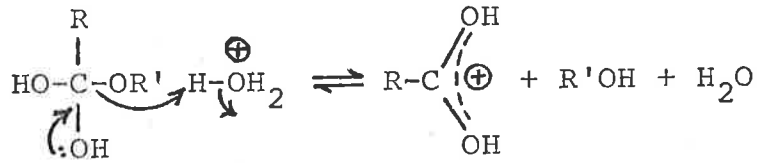
Because of the short lifetime of symmetrical tetrahedral intermediates relative to the rate of proton transfers, such species have never been observed directly in aqueous solution. However, considerable evidence[70] is available which tends to firmly establish their existence. Thus, although some uncertainty still exists as to whether or not the tetrahedral adduct formed in normal A_{Ac}-2 ester hydrolyses is a true intermediate, it seems reasonable to conclude on the basis of the above results that they do form as intermediates in the reaction rather than as transition states.

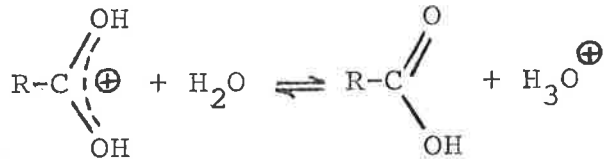
Kirby has concluded,[48] on the basis of all the accumulated evidence, that the most complete scheme for A_{Ac}-2 ester hydrolysis can be shown as follows. A steady-state treatment for the formation of the tetrahedral intermediate results in the rate expression: $\nu = k[E][H_3O^+][H_2O]$, where k is a composite of several

rate constants, and the mechanism explains most of the available observations*.

(a) 

(b) 

(c) 

(d) 

(iii) A_{Ac}-1 ESTER HYDROLYSIS MECHANISM

The evidence is considerably clearer concerning the mechanistic details of this and the other unimolec-

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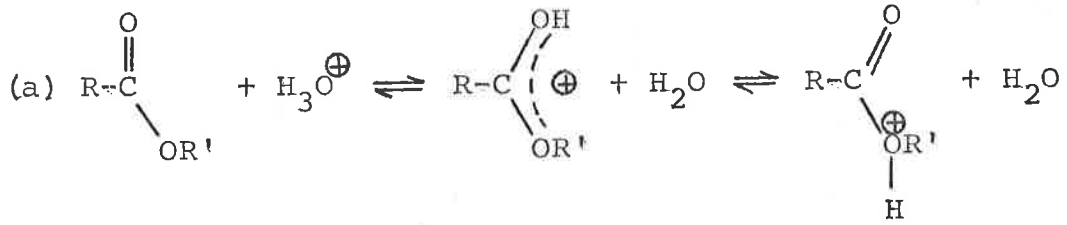
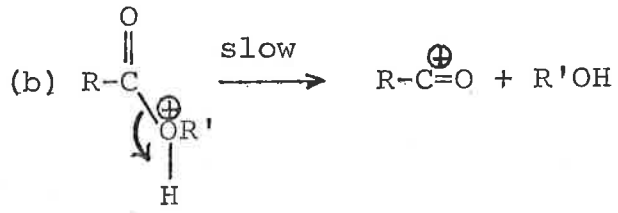
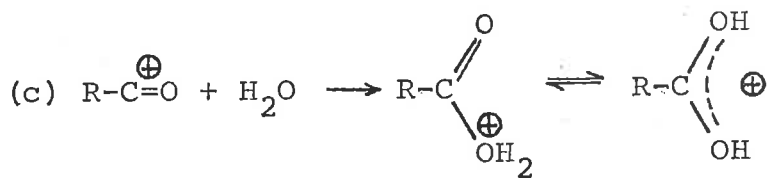
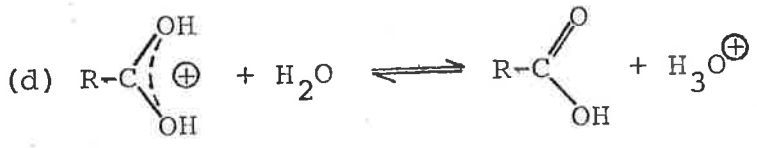
*The single piece of evidence he cites that is difficult to reconcile with the mechanism is the $\Delta S^{\ddagger}$ values of A_{Ac}-2 hydrolysis. These are more positive than one would have thought for what is effectively a termolecular reaction, but the entropy terms are difficult to predict, a priori, with any confidence.

ular reaction, A_{Al}-1. Both mechanisms necessarily produce a positively-charged species in the heterolytic step, since they react via the protonated ester. In the A_{Ac}-1 mechanism, unimolecular acyl-oxygen fission, the protonated oxonium ion first undergoes a rate-determining bond cleavage to yield an acylium ion, $R\text{-}C\overset{\oplus}{O}$. This is then attacked rapidly by a water molecule, in the case of hydrolysis, or by an alcohol molecule, as in the case of esterification of sterically-hindered carboxylic acids.[71] This results in a protonated carboxylic acid or ester respectively, which, upon proton loss, gives the final products of the reaction.



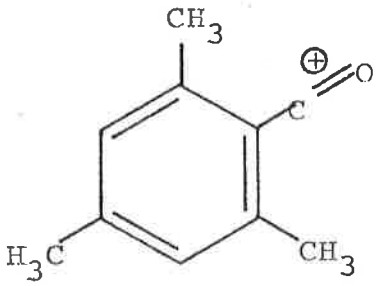






It should be noted, in this case, that acyl-oxygen cleavage cannot be proved by isotopic exchange studies, since there is no intermediate species produced in which the oxygen of the ester becomes equivalent to the oxygen derived from the incoming solvent molecule. Hence confirmation for this mechanism must derive from more indirect sources. The most telling evidence is provided by substituent studies which predict a negative ρ value, based on polar effects in the acyl moiety for an acyl-oxygen cleavage, and a positive ρ for substitution in the alcohol moiety. The opposite conclusions are expected for alkyl-oxygen cleavage. These studies have confirmed many cases where A_{Ac}-1 hydrolysis is believed to occur, the details of which will be discussed later in the Results and Discussion section. The unimolecularity of the reaction has also been shown from other evidence, such as activation parameter studies and various hydration treatments. These points will be discussed later as well.

There are many esters known which form the acylium ion in the more concentrated acid region (>70% H_2SO_4) but only one which has been confirmed as being formed in the dilute acid region - i.e. the mesitoylium ion:[68]

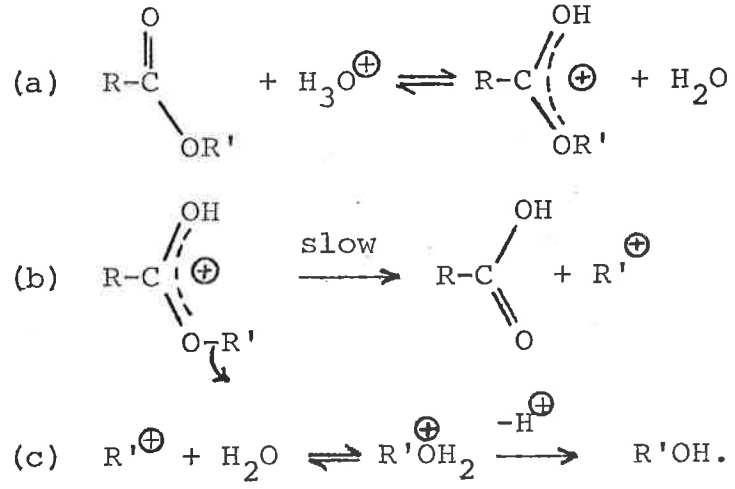


In general, the formation of these acylium ions requires a certain degree of internal stabilisation. The reason for this is that as the medium acidity is increased, the availability of water molecules from the solvent to provide solvent stabilisation decreases. Consequently, it is not until some acidity is reached, for which the oxonium ion produced by the A_{Ac}-2 mechanism becomes more salted-out than the acylium ion produced from the A_{Ac}-1 mechanism, that the acylium ion, A_{Ac}-1, mechanism takes over as the predominant pathway for reaction.

Finally, when methyl esters do react by means of an A-1 mechanism, they always do so by acyl-oxygen rather than alkyl-oxygen cleavage. The reason for this is that the latter mechanism would produce the very unstable methyl carbonium ion, CH_3^+. This is true no matter how electron-withdrawing the substituents in the acyl moiety may be,[72,73] which would also greatly destabilise even the acylium ion formed. However, for ethyl esters, as the degree of electron-withdrawing ability of substituents in the acyl moiety increases, the mechanism of hydrolysis switches over from A_{Ac}-1 to A_{Al}-1.[73]

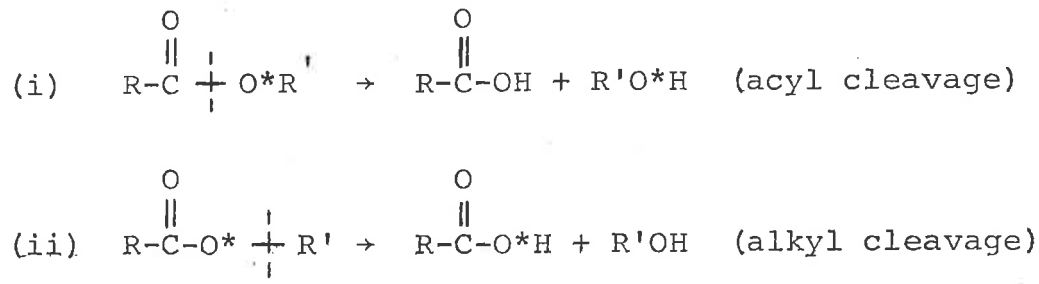
(iv) A_{Al}-1 ESTER HYDROLYSIS MECHANISM

This mechanism produces a carbonium ion as a result of the heterolysis step, which in turn reacts with a molecule of water to produce a protonated alcohol. The carboxylic acid is produced directly from the bond fission.



The probability that a hydrolysis proceeds via this mechanism becomes greater with increasing stability of the carbonium ion produced. Thus even in dilute acids, esters of tertiary alcohols are hydrolysed in this fashion, resulting in relatively stable tertiary carbonium ions.[13,49]

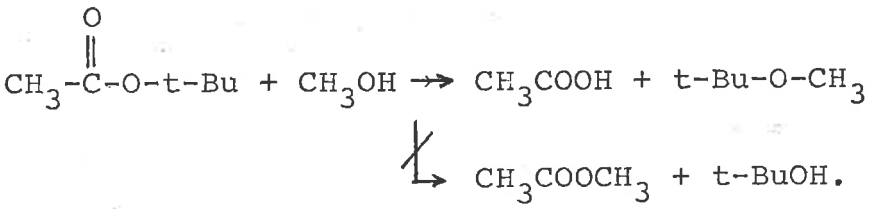
The position of cleavage can be determined directly from isotope labelling studies. For an ester labelled on the ether oxygen, acyl-oxygen fission will produce a labelled alcohol product, with the opposite result expected for alkyl-oxygen cleavage.



(i) $R\text{-}C(=O)\text{-}O^{*}R' \rightarrow R\text{-}C(=O)\text{-}OH + R'O^{*}H$ (acyl cleavage)

(ii) $R\text{-}C(=O)\text{-}O^{*}\text{-}R' \rightarrow R\text{-}C(=O)\text{-}O^{*}H + R'OH$ (alkyl cleavage)

t-Butyl acetate, hydrolysed in 0.2 N $HClO_4$, produced[74] the unlabelled alcohol, confirming cleavage (ii). Moreover, solvolysis of this ester in methanol gave the ether and acetic acid,[75] rather than the usual ester interchange products. This provides further support for alkyl-oxygen fission.



$CH_3\text{-}C(=O)\text{-}O\text{-}t\text{-}Bu + CH_3OH \rightarrow CH_3COOH + t\text{-}Bu\text{-}O\text{-}CH_3$

$\not\rightarrow CH_3COOCH_3 + t\text{-}BuOH.$

Similar results have been obtained in the acid hydrolysis of triphenylmethyl benzoate in aqueous dioxan.[76]

The unimolecularity of this reaction can be deduced both directly and indirectly. The latter means involves the calculation of activation parameters. The entropy of activation for t-butyl acetate hydrolysis in 60% aqueous HCl is +13.1 e.u.,[77] clearly indicative of a unimolecular reaction. More direct evidence is obtained from the hydrolysis of esters of optically active alcohols. A bimolecular attack on the alkyl carbon will produce an alcohol with inverted configuration,

whereas unimolecular heterolysis will result in a planar carbonium ion which gives a racemic alcohol product. Racemisation was observed in the hydrolysis of methyl-ethylisohexylcarbinyl acetate in 70% aqueous dioxan.[78]

VI. PURPOSE AND PLAN OF THE THESIS

The present work has its origins in the studies by McClelland[13] on acetate hydrolysis mechanisms in sulphuric acid. Two of the esters investigated were ortho-substituted phenyl acetates which gave results different from those of the para-isomers. Ortho-nitro phenyl acetate hydrolysed more slowly than the para-nitro phenyl acetate throughout the entire acidity range. But the ortho-carboxy ester, although initially reacting more slowly than the para-carboxy phenyl acetate in dilute acid, started to increase in rate at ∿62% H_2SO_4 and by 72% H_2SO_4 was reacting about five times faster than the para-carboxyphenyl acetate.

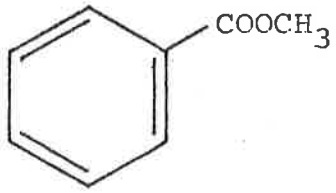
One possible explanation for the rate retardation in dilute acid is steric hindrance to solvation of the protonated ester, thereby lowering the concentration of the protonated ortho-substituted ester relative to that of the para-isomer. Although this effect would be expected to operate for both the nitro- and carboxy-

phenyl acetates, the latter would be expected to favour protonation by formation of a strong intramolecular hydrogen bond with the bound proton. Such stabilisation can occur only intermolecularly with the para-carboxy ester. Moreover the nitro group is far less basic than the carboxy group, and the possibility of intramolecular stabilisation of the protonated ortho-nitro phenyl acetate is consequently much less.

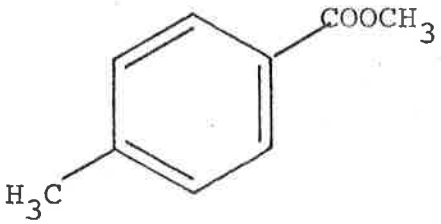
Most studies of ester hydrolysis, especially of aromatic esters, have been concerned mainly with electronic effects on the rates of reaction. It has long been known[79] however that the relative rates of hydrolysis of sterically hindered esters can not be explained on the basis of electronic effects alone. The most obvious indication of this is the fact that the rate constants of esterification of a series of carboxylic acids fail to correlate with the ionisation constants of the same carboxylic acids,[80] whereas good linearity is observed for meta- and para-substituted benzene derivatives. This led Taft[81] to devise a relation by means of which the polar and steric effects on the rates of esterification and hydrolysis could be separated and used to account for the observed rates of reaction. For the most part, however, these relations have involved mainly the reactions of aliphatic carboxylic acids,[81-83] and very little information is available in the litera-

ture on comparable studies of steric effects in aromatic ester hydrolysis.

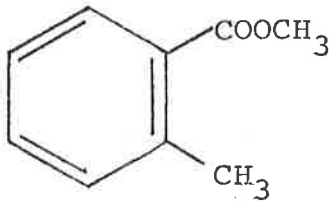
For this reason, together with the anomalous behaviour of the ortho-substituents in acetate hydrolysis reported above, the present study attempts to analyse quantitatively the behaviour of a series of methyl-substituted benzoate esters hydrolysing in sulphuric acid media. The esters included in the present work are:



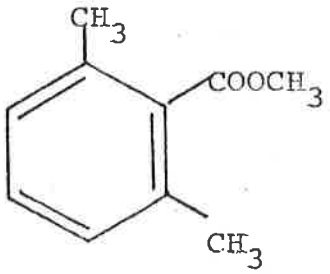
Methyl Benzoate (MB)



Methyl para-Toluate (MPT)



Methyl ortho-Toluate (MOT)



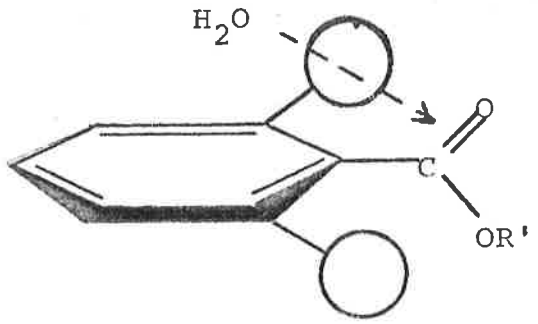
Methyl 2,6-dimethyl Benzoate (2,6-MDMB)

The choice of methyl groups substituted on the benzene ring was preferred in order to provide a constant bulk proximity effect and to rule out the specific interactions that may be attributed to ortho-nitro and ortho-carboxy substituents. Benzoate esters were chosen instead of acetates as this would place the steric effects of ortho substituents closer to the reaction centre. Moreover, only the methyl esters were studied in order to keep one structural parameter constant.

Aqueous sulphuric acid was the medium of choice for several reasons. This acid exhibits a wide range of protonating ability and water activity over the 0 → 100 w/w% acidity region, making this an exceptionally suitable medium for following many acid-catalysed reactions. The high dielectric constant of sulphuric acid solutions favours heterolytic splitting of the bonds with the formation of ionic products. Finally, the physical and chemical properties of this acid are well-characterised in the literature, making available the necessary data for analysing the reactions studied herein and allowing comparisons with other acid-catalysed reactions to be made.

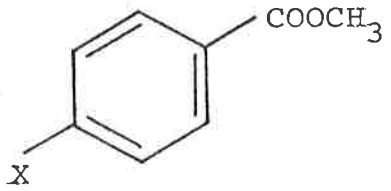
Bender[2] has concluded from a number of studies that the water molecule in an A_{Ac}-2 hydrolysis mechanism attacks the carbonyl centre in a direction perpendicular to the plane of the carboxylic ester group. If this

group is twisted out of the plane of the benzene ring in aromatic esters, as will be shown for the 2,6-dimethyl benzoate, then the incoming nucleophile will attack in a direction in line with the sterically bulky group,



This is expected to drastically lower the rate of the A_{Ac}-2 reaction, and consequently the effect of sterically hindering methyl groups on the rate of hydrolysis was studied in dilute as well as concentrated acid media.

The hydrolysis reactions for each ester substrate were studied over as wide a range of acidity and temperatures as possible in order to elucidate the detailed mechanisms of these reactions under a variety of reaction conditions. Polar substituent effects on the hydrolysis of methyl benzoate at different acid concentrations were also studied using three additional esters:



; $X = OCH_3$, Cl, NO_2

Since there is no acidity function known for the ionisation of aromatic esters in sulphuric acid, the protonation behaviour of each of the esters included in this study was determined. This enabled the application of the 'r' hydration treatment in analysing the rate-acidity dependence of these hydrolyses. Transition state activity coefficients were calculated using the relation,

$$\log f_{\ddagger}^{*} = -\log k_2 + mH_o + \log f_s + \log a^{*}_{H^+} + \log k_o$$

for which the values of f_s, the neutral substrate activity coefficients, were also experimentally obtained. Finally, the determinations of activation parameters for the different hydrolyses in various acid solutions gave additional information concerning the reaction mechanisms.

EXPERIMENTAL

I. REAGENTS

(i) PREPARATION AND STANDARDISATION OF SULPHURIC ACIDS

Sulphuric acid solutions of less than 95% (w/w) were prepared by diluting CIL reagent grade acid (95% minimum) with distilled water to the appropriate concentration. Acids more concentrated than 95% were prepared by mixing the reagent grade concentrated acid with Fisher reagent fuming sulphuric acid (30%).

Originally, the acids were standardised either by titration against NaOH[84] or by the use of a density balance. The densities were matched by a computer program with densities from the literature[85] for the temperature at which the densities were measured. With the later acquisition of an Anton Paar Precision Density Meter Model No. DMA 02C, however, the accurate determination of the concentrations of the sulphuric acid solutions, from their measured densities, became much simpler.*

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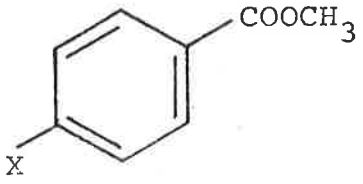
*Cf. Appendix A for formulae for calculating w/w% H_2SO_4 from the densities.

The only restriction on the use of these last two methods is that the density of sulphuric acid goes through a maximum at about 98% at 25°C, resulting in some ambiguity as to which side of the maximum, in terms of w/w% of the acid solution, did the measured density lie. Standardising solutions of concentration greater than ∿96%, therefore, required titration against NaOH. In any case, titrations were carried out on a number of acids to check against results from the density meter measurements.

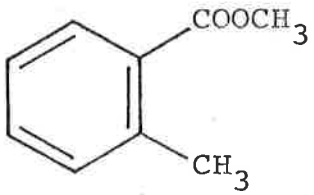
(ii) PREPARATION OF SUBSTRATES FOR KINETIC MEASUREMENTS

All the benzoic acids used were commercially available and were recrystallised from methanol-water to constant melting point. The methyl esters of these acids were synthesised in all cases but one by the Fisher esterification method.[86,87] These esters were:



; X = OCH_3, CH_3, H, Cl, NO_2

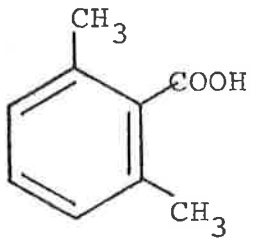
and



Although the ortho-toluic acid is hindered to some extent, the ester was still prepared in yields of 60-70% by this method.

A typical synthesis of the methyl ester of a benzoic acid involved adding a solution of 95% H_2SO_4 in anhydrous CH_3OH to a weighed out portion of the benzoic acid. The solution was then refluxed, with stirring, for 1-2 hr. It was then cooled to room temperature, neutralised with $NaHCO_3$ and extracted with CH_2Cl_2. The extracted solution was washed with saturated NaCl solution, dried and the ester recovered after the solvent was removed under vacuum. The product was purified by further distillation.

The one exception to this method is 2,6-dimethyl benzoic acid:



which is severely hindered at the carboxylic acid centre. A number of methods have been proposed over the years for the esterification of this type of carboxylic acid,[88-92] but the method of choice was Newman's.[71] A solution of 95% H_2SO_4 and 30% oleum, in 10-fold excess of the molar equivalent of the carboxylic acid, was added to the substrate acid, with stirring, at $\sim 5^{o}C$ in an ice-water bath. When dissolution was complete, the

solution was stirred for a few more minutes and then poured carefully into a flask containing previously-cooled anhydrous methanol.

After about 20 min. of stirring in the ice-bath, the solution was extracted with $CHCl_3$, neutralised with $NaHCO_3$, and then washed with water and a saturated NaCl solution. The organic solution was dried and the ester recovered after removing the solvent under vacuum. The ester was purified by further distillation to give ∿70-75% yield of pure product.

Physical properties and u.v. spectra of the esters are given in Appendix C. Methanolic solutions of the substrates, in the appropriate concentrations, were prepared prior to kinetic measurements.

II. KINETIC METHODS

(i) CHOICE OF WAVELENGTH:

The method for choosing the wavelength at which to follow the reaction was based on the desire to find that wavelength for which the maximum absorbance change could be observed during the course of the hydrolysis. This could be one of two wavelengths, and depending on the reaction conditions, either method was used. The main difficulty in many of these hydrolyses is that there was usually very little difference (0.1-0.2

absorbance units) between the spectra of the starting ester and the product acid, especially in dilute sulphuric acid. Therefore, when the spectral change was sufficiently large, method (A) was used, and when small, method (B).

(A) A solution of the ester in the desired acid was prepared in a concentration sufficient to give a spectrum with a maximum absorbance of ∿1.2 units. The initial spectrum of this solution was then measured, at room temperature, on either a Unicam SP800 UV Spectrophotometer or a Cary-16 UV Spectrophotometer. The solution was then transferred to an ampoule, sealed, and placed in a bath at ∿50°C overnight.* The solution was then transferred back to the same cell, cleaned and dried, and the "product" spectrum recorded. The best wavelength was then determined by tabulating the absorbances of the initial and final spectra at a number of wavelengths, and choosing that value for which ΔA was the largest.

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*The ampoule was originally put in an oven at ∿120°C to ensure complete reaction overnight. It was soon discovered that several of the ester solutions, particularly the ortho-substituted ones, decomposed subsequent to hydrolysis, as evidenced by the colour change of the solution and its uv spectrum. It was thus decided to use milder conditions, analogous to those of the actual hydrolysis reaction, although this would mean only 2-3 half-lives of reaction in some cases. However, since only the wavelength of greatest change in the spectra was sought, it was of no consequence if the reactions were not, in fact, 100% complete.

Since, for most of these reactions, the absorbance of the product was greater than that of the ester, the starting concentration had to be chosen so that the final spectrum would not have an absorbance maximum of greater than about 1.8 units. For the actual study of the kinetics, this concentration could then be adjusted somewhat to give the maximum absorbance change at the chosen wavelength.

In general, it was found that the most suitable wavelength was at a value slightly lower than the λ_{max} (i.e. ~2-3 nm.) in the spectrum of a particular ester in a given acid. Finally, this method was useful for reactions in >70 w/w% H_2SO_4, for which the differing medium effects on ester and product acid were much more pronounced than in dilute acid, and resulted in greater changes in absorbance over the course of the reaction.

(B) The technique used here was essentially the same as for the first method, except that a region was chosen in which the absorbance of the starting ester was small, relative to that at the λ_{max} position. If, however, the concentration of ester were increased to give $A_{product} \simeq 1.8$ units, the value for $\Delta A (= A_{product} - A_{ester})$ was significantly large. This, on the other hand, created solubility problems due to the high concentration of ester in the sulphuric acid solution.

To obviate this difficulty, the solution of ester in acid was first prepared in a vial, stoppered and shaken mechanically for about 5 minutes. This was usually long enough to ensure complete dissolution. Furthermore, since this method was used for those reactions in which the absorbance change was small, viz. in <70 w/w% H_2SO_4, the rate of hydrolysis was quite slow at room temperature. Therefore, hydrolysis during the preparation and shaking period was negligible. In all other respects, the procedure used in this technique was identical to that in method (A).

Typical spectra of methyl benzoate and its product acid are shown at various acid concentrations in Fig. (4).

(ii) MEASUREMENT OF REACTION RATES

In general, for reasons which will be discussed later,* the hydrolysis rates of benzoate esters are much slower than those of the aliphatic analogs. Consequently, many of the reactions could not be studied at 25°C in the dilute to moderately concentrated acid region (<60 w/w% H_2SO_4). This necessitated two different methods, therefore, for following the kinetics of hydrolysis.

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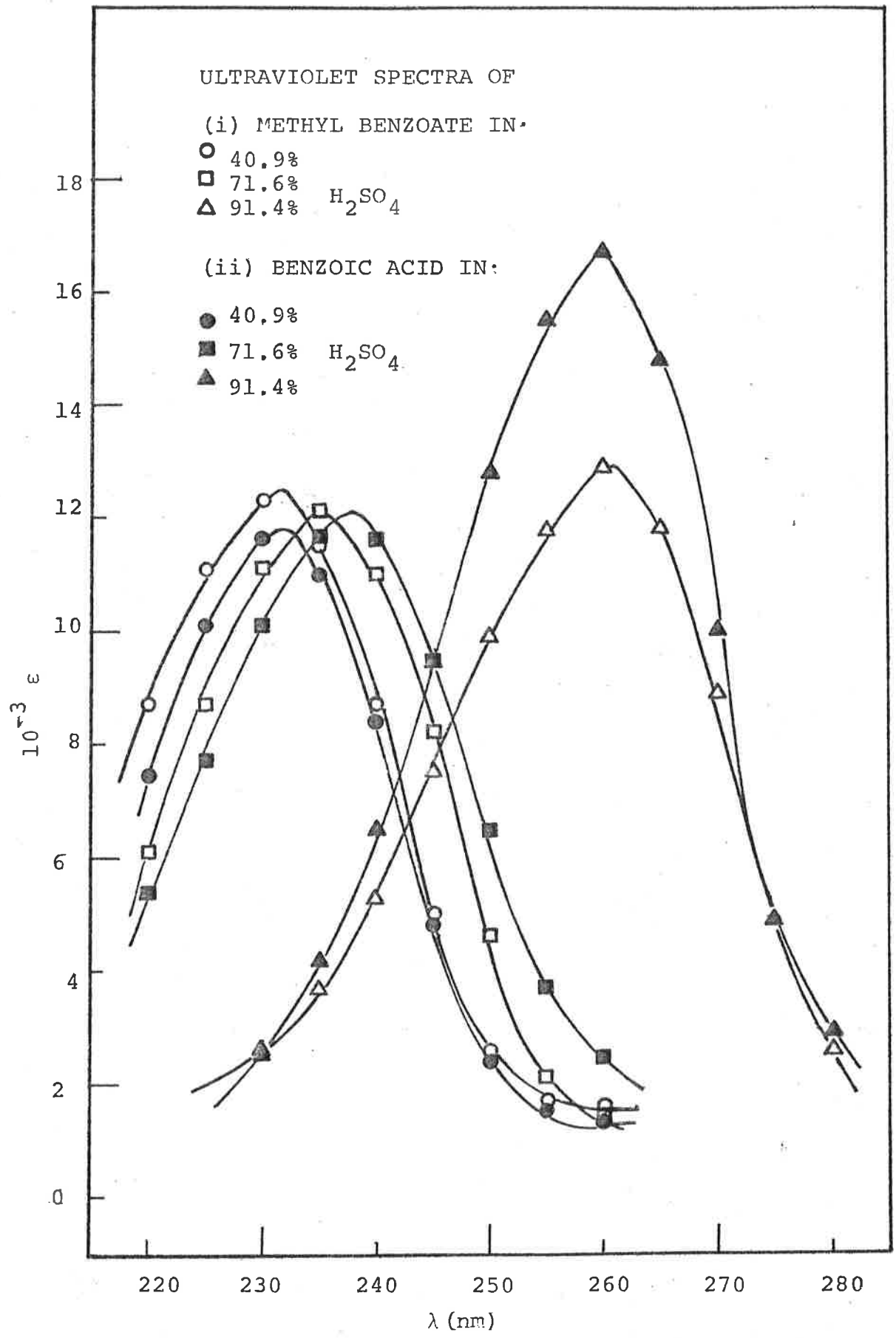
*Cf. Results and Discussion, p. 168.

FIGURE 4


ULTRAVIOLET SPECTRA OF
(i) METHYL BENZOATE IN:
40.9%
71.6%
91.4% H2SO4
(ii) BENZOIC ACID IN:
40.9%
71.6% H2SO4
91.4%
10^-3 ε
0
2
4
6
8
10
12
14
16
18
220
230
240
250
260
270
280
λ (nm)

(A) SAMPLING TECHNIQUE

Fifty mls. of the appropriate aqueous sulphuric acid solution were put into a flask to which a suitable amount of substrate ester stock solution in methanol was added. This was stoppered, shaken for ∿5 min. to ensure complete solubility of the ester, and then divided into fourteen ampoules containing about 3 mls. of solution each. These were sealed and placed in a bath of the desired temperature to equilibrate. The bath temperature was measured with a thermometer, calibrated against an NBS thermometer, which was readable to $\pm$ 0.05°C. The temperature control was $\pm$ 0.1°C.

Kinetic points were obtained by removing ampoules from the bath and quickly quenching them in ice water. They were then allowed to equilibrate to room temperature before reading. Absorbances were measured at the chosen wavelength(s) on a Cary-16 UV Spectrophotometer, which was thermostatted at 25°C with a Neslab TE-9 Thermostatic Bath and Circulator, using a 1.00-cm. cell. Because of possible variations in the cell, the absorbance of a blank cell, containing only sulphuric acid of the appropriate concentration, was measured several times, and an average value for the reference absorbance was then determined.

Runs were usually followed to at least two half-lives, which could be from several days to 2-3 weeks. Four of the original fourteen ampoules were set aside for infinity readings, which were measured after an estimate of at least 10 half-lives, and good agreement was usually found in three of these. For reactions with half-lives less than about 4-5 hours, the in-situ technique was used.

(B) IN-SITU TECHNIQUE

The kinetics of reactions with reasonably short half-lives were followed on either the Cary-16 UV Spectrophotometer (single cell only), or the Unicam SP. 800 or SP. 1800 UV Spectrophotometers (on which up to four runs could be measured simultaneously). All these instruments had auxiliary recorders and were thermostatted with circulating water baths whose temperature could be varied up to $\sim 75^{\circ}C$. The bath temperature was usually not in close agreement with the cell temperature, however, and the latter had to be measured separately each time a run, or series of runs, was performed. The thermometer used was the same as for the sampling technique to minimise errors in the temperature reported.

A reaction was initiated by first thermostatting one or more clean, dry 1.00-cm. quartz cells in the cell block of the particular instrument being used. It was

found that blank cells containing only the sulphuric acid solution being used did not undergo any spectral change during the course of the reaction. Consequently, for most of the kinetic runs using this technique, the cell positions in the reference side of the cell block were left empty.

A concentrated stock solution of the ester substrate in methanol was injected via a Hamilton syringe into a vial containing several mls. of the sulphuric acid solution. Depending on the ester and the acid concentration, from 5-10 µl of ester solution was added to 3-7 mls. of the sulphuric acid. The vial was then stoppered, shaken, and the contents transferred to the cell in the spectrophotometer. The recorder was then activated and the kinetic plots followed.

For the very fast runs of half-lives of only a few minutes, the sulphuric acid solution was first brought to temperature equilibrium in the cell, and the stock ester solution injected directly into it. Since these were usually the very concentrated acids, complete dissolution was attained in a few seconds by quickly removing the cell, inverting it a few times, and replacing it in the cell block. Since these were pseudo-first order reactions in all cases, there was no problem if 1-2 min. elapsed between starting the reaction and starting the recorder, except for the very fast reactions, for which the modified procedure was used.

These *in situ* reactions were generally able to be followed to completion, or, at least, to several half-lives.

III. CALCULATION OF HYDROLYSIS RATE CONSTANTS

Where an infinity value was obtained, the rate constants were obtained by plotting $\ln |A_t - A_\infty|$ versus *time*, using a least-squares program to determine the best fit for the data. The slope of this line was equal in magnitude, though opposite in sign, to the rate constant for the reaction.

For slower reactions, which were not followed to an infinity absorbance value, the Guggenheim technique[93] was employed. This involved plotting $\ln |A_{t+\Delta t} - A_t|$ versus *time*, where $\Delta t > 2$ half-lives. Again, the absolute value of the slope of this plot was equivalent to the pseudo-first order rate constant.

Several runs were calculated by both methods. That is, an infinity value was estimated from the absorbance value at one half-life, which was obtained via the Guggenheim method. Recalculating the rate constant, using an "infinity" plot, gave agreement to $\pm$ 2%.

Typical data for these reactions are shown in Table (1) and Fig. (5).

TABLE 1a: ABSORBANCE DATA FOR HYDROLYSIS OF METHYL PARA-TOLUATE IN 30.97% H_2SO_4 AT 54.6°C

t (min)	A_1	A_2[a]	$\ln\Delta A$[b]
0	0.139	0.1878	-3.020
10	0.1415	0.1875	-3.079
20	0.143	0.1865	-3.135
30	0.1447	0.1875	-3.151
40	0.146	0.1878	-3.175
50	0.1485	0.1883	-3.224
60	0.1498	0.189	-3.239
70	0.152	0.1895	-3.283
80	0.154	0.189	-3.352
90	0.1556	0.1896	-3.381
100	0.157	0.1896	-3.423
110	0.159	0.1896	-3.487
120	0.160	0.1898	-3.513
130	0.1615	0.1898	-3.565
150	0.1644	0.190	-3.665
170	0.167	0.190	-3.772
190	0.169	0.191	-3.817
210	0.1715	0.1908	-3.948
230	0.173	0.1908	-4.029
250	0.1746	0.191	-4.111

$|m| = k = 4.521 \times 10^{-3}$ min.$^{-1}$

$b = -2.986$

$r = -0.9989$

$\sigma_y = 0.015$

$\sigma_m = 0.056 \times 10^{-3}$

$\sigma_b = 0.0075$

[a] $A_2 = A_{t+\Delta t}$, where $\Delta t = 500$ min.

[b] $\ln\Delta A = \ln(A_2 - A_1)$

TABLE 1b: ABSORBANCE DATA FOR HYDROLYSIS OF METHYL PARA-TOLUATE IN 88.59% H_2SO_4 AT 25.0°C

t (min)	A	$\ln\Delta A$[a]
0	0.1878	-2.042
10	0.1752	-2.144
20	0.165	-2.235
30	0.1566	-2.317
40	0.149	-2.397
50	0.142	-2.477
60	0.1356	-2.556
70	0.130	-2.631
80	0.1245	-2.711
90	0.1197	-2.786
100	0.1142	-2.879
110	0.111	-2.938
120	0.1068	-3.020
130	0.1019	-3.126
140	0.099	-3.194
150	0.0941	-3.322
160	0.0928	-3.358
170	0.0876	-3.455
180	0.087	-3.541
200	0.0803	-3.803
220	0.078	-3.912
240	0.0753	-4.057
260	0.0723	-4.248
280	0.0699	-4.431
300	0.0683	-4.576

$|m| = k = 8.410 \times 10^{-3}$ min.$^{-1}$

$b = -2.043$

$r = -0.9997$

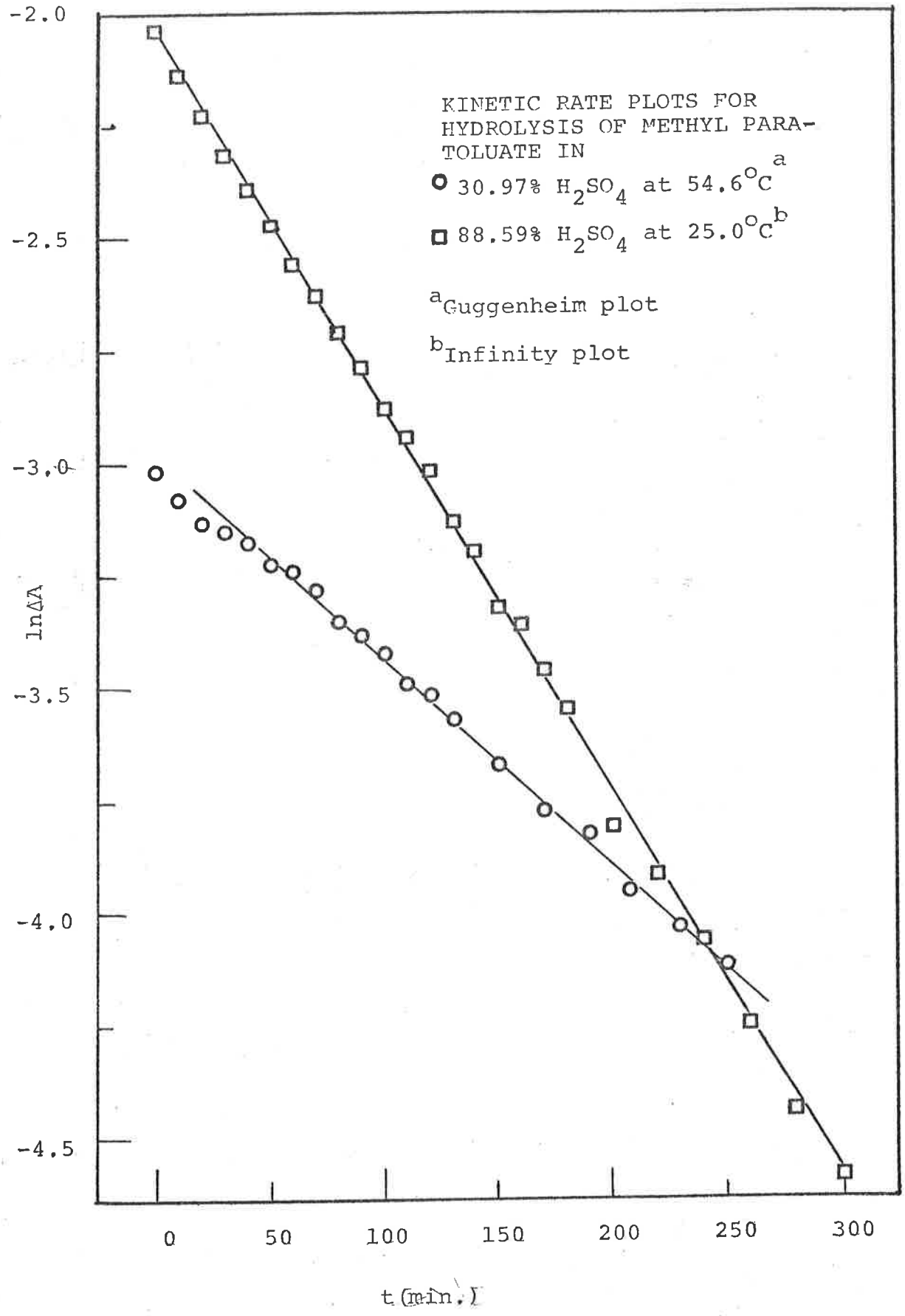
$\sigma_y = 0.020$

$\sigma_m = 0.047 \times 10^{-3}$

$\sigma_b = 0.0072$

[a] $\ln\Delta A = \ln(A_t - A_\infty)$, where $A_\infty = 0.058$

FIGURE 5


KINETIC RATE PLOTS FOR HYDROLYSIS OF METHYL PARA-TOLUATE IN
30.97% H_2SO_4 at 54.6°C[a]
88.59% H_2SO_4 at 25.0°C[b]
[a]Guggenheim plot
[b]Infinity plot
-2.0
-2.5
-3.0
-3.5
-4.0
-4.5
lnΔA
0
50
100
150
200
250
300
t (min.)

It must be conceded that a good deal of scatter was found among some multiple runs for a particular set of reaction conditions. This was especially true for the very slow runs (e.g. in dilute acid at 25°C) and the very rapid runs (i.e. in concentrated acid at higher temperatures), thus making it difficult to obtain an accurate estimate of the "true" rate constant.

It was therefore necessary to determine rate data at several different temperatures for a given substrate in a specific sulphuric acid solution. This was done for two reasons. First of all, activation parameters were desired for the different esters in both the dilute acid and concentrated acid region, to observe how the change in mechanism between the two "halves" of the acidity range is reflected in the thermodynamic activation quantities, especially $\Delta S^{\ddagger}$. Secondly, reasonably accurate activation parameters allowed rate constants at lower temperatures in the dilute acid region to be calculated where they were not easily obtained experimentally. This, in turn, enabled smooth curves to be drawn through the different points on the rate-acidity profiles, and to average the rate data in such a way as to permit continuous curves to connect all the rate constants, obtained both experimentally and by means of the activation plots. This eliminated most of the scatter in the rate profiles.

This technique basically involves calculating a non-linear regression curve subject to two constraints:

(a) it should give the minimum deviation of the experimental points from the calculated curve over the whole acidity range; and

(b) it should give reasonably linear activation plots for a given ester in a specific acid at a series of temperatures, in agreement with the assumption of linearity implicit in the Arrhenius-type equation based on transition state theory:

$$k_\psi = \frac{k_B T}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT}$$

where:

k_ψ = pseudo-first order rate constant (sec^{-1})

T = absolute temperature (^oK)

k_B = Boltzmann's constant (erg $^oK^{-1}$)

h = Planck's constant (erg-sec)

R = gas constant (cal $^oK^{-1}$ $mole^{-1}$)

$\Delta S^{\ddagger}$ = entropy of activation (cal $^oK^{-1}$ $mole^{-1}$ = e.u.)

$\Delta H^{\ddagger}$ = enthalpy of activation (cal $mole^{-1}$)

Taking natural logarithms and rearranging:

$$\ln \frac{k_\psi}{T} = \frac{\Delta S^{\ddagger}}{R} + \ln \frac{k_B}{h} - \frac{\Delta H^{\ddagger}}{RT} \quad \left(\ln \frac{k_B}{h} = 23.76\right)$$

Thus, a plot of $\ln k_\psi/T$ versus $1/T$ gives:

$$\Delta H^{\ddagger} = -R \times \text{slope}$$

$$\Delta S^{\ddagger} = R(\text{intercept} - 23.76)$$

This process was performed by trial-and-error until reasonably valid rate profiles were obtained for the rate data at different temperatures. Two sample sets of data for determining the activation parameters for methyl benzoate are given in Table (2) and Fig. (6). The values at 42.0% H_2SO_4 represent those for an A-2 mechanism, and those at 84.0% H_2SO_4, for an A-1 mechanism.

IV. PROTONATION BEHAVIOUR OF THE ESTER SUBSTRATES

The extent of protonation of the benzoate esters was determined from their spectral changes in the ultra-violet region. An appropriate amount of sulphuric acid solution was weighed into each of three 10-ml. volumetric flasks for each acid concentration that was used. These were then stoppered and cooled in an ice bath. Due to the rapid hydrolysis of methyl ortho-toluate and methyl 2,6-dimethyl benzoate in the more concentrated acids, the protonation behaviour of these esters was studied at 10°C.

In fact only methyl benzoate was studied at both 10°C and 25°C, while the other three - methyl para- and ortho-toluate, and methyl 2,6-dimethyl benzoate -

TABLE 2

DATA FOR ACTIVATION PLOTS OF METHYL BENZOATE HYDROLYSIS IN:

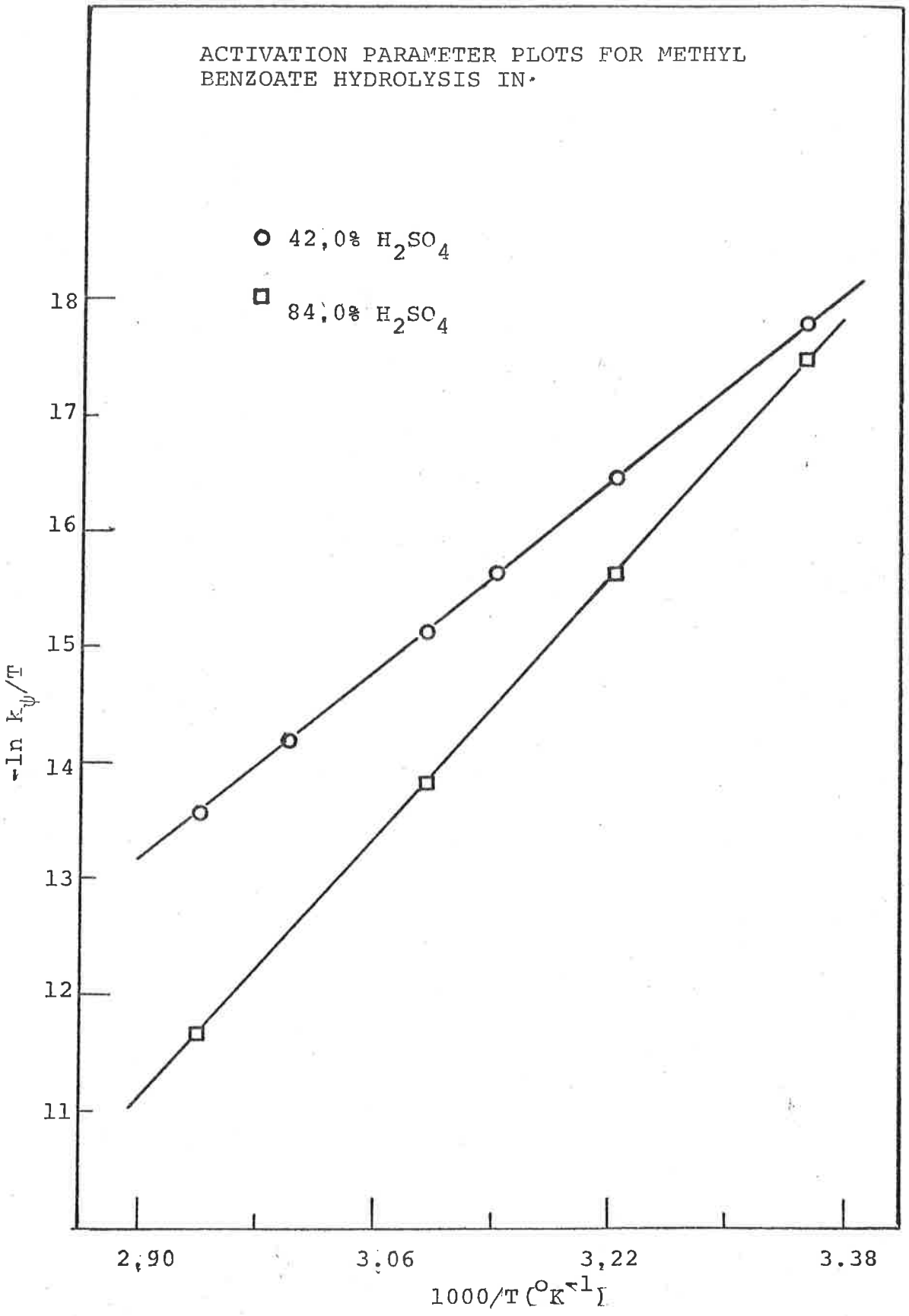
(1) A-2 REGION: 42.0 w/w% H_2SO_4

T (^oC)	$10^3/T$ ($^oK^{-1}$)	ln k_ψ/T (sec.$^{-1}$ $^oK^{-1}$)	$\Delta H^\ddagger$ (kcal./mole)	$\Delta S^\ddagger$ (e.u.)
25	3.354	-17.780		
37	3.224	-16.463		
45	3.143	-15.634	20.22	-14.7
50	3.095	-15.129		
60.1	3.001	-14.186		
67	2.940	-13.571		

(2) A-1 REGION: 84.0 w/w% H_2SO_4

25	3.354	-17.455		
37	3.224	-15.641	27.73	+11.1
50	3.095	-13.831		
67	2.940	-11.676		

FIGURE 6


ACTIVATION PARAMETER PLOTS FOR METHYL BENZOATE HYDROLYSIS IN·
42.0% H_2SO_4
84.0% H_2SO_4
18
17
16
15
14
13
12
11
$-\ln k_\psi/T$
2.90
3.06
3.22
3.38
$1000/T\ (^oK^{-1})$

were studied only at 10°C. Although the preferred temperature is 25°C, the fact that the basicity of methyl benzoate was determined at both temperatures allowed certain conclusions to be drawn for the other esters at 25°C.

The absorbance readings were measured on the Cary-16 UV Spectrophotometer, whose cell block was thermostatted at 10 ± 0.2°C by means of a Neslab PBC-4 Bath Cooler. A clean, dry cell was placed in the holder to equilibrate at the chosen temperature, and a value for the reference absorbance was obtained by measuring the absorbance of the cell containing only the sulphuric acid solution being used three times and taking an average value.

Then, with the cleaned, empty cell equilibrating once more in the cell holder, 8 µl. of a previously prepared and cooled stock methanolic solution of ester substrate was injected into one of the three volumetric flasks for that particular acid concentration sitting in the ice bath. The flask was stoppered, shaken quickly and the solution transferred to the cell. Absorbance readings were made at two different wavelengths for both the sample and the reference solutions. These wavelengths were the values of λ_{max} in the spectra of the particular ester being studied in the most dilute and and most concentrated acid solutions employed. The

reason for choosing λ_{max}, as will be discussed later,* was to obtain "flat" regions of absorbance in order to minimise medium effects. The values for pK'_{SH^+} determined at the two wavelengths agreed to within $\pm$ 5%.

There were two major difficulties with these esters. The first was the rate of hydrolysis of the methyl ortho-substituted benzoates in the concentrated acid region. Although these reactions were slowed down considerably by studying their behaviour at 10°C, there was still some hydrolysis observed over a period of a few minutes.

Since solubility was not a problem in this acid region, it was possible to prepare the solution of ester in acid and transfer it to the cell within less than a minute. As a result, although a change in absorbance was observed when the solutions were left to sit in the cell for 5-10 min., no extrapolation to zero-time was considered necessary, since the absorbances could be obtained with reasonable stability and accuracy when the solution was initially transferred to the cell.

The other problem, and a more serious one, was that it was not possible to obtain a value for the extinction coefficient of the fully protonated ester,

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*Cf. Results and Discussion, p. 115-118.

ε_{SH^+}, with absolute certainty. The reason for this was that, although it was only necessary to use data in the range for which: $-1 < \log [SH^+]/[S] < +1$ for the pK_{SH^+} determination for each of these esters, which usually required a sulphuric acid concentration only up to ∿90 w/w%, it was, nevertheless, necessary to go to even higher concentrations of acid to obtain a flattening-out of the ε vs. H_o profile, in order to determine a reliable value of ε_{SH^+}. The problem was that the esters usually sulphonated at acid strength >97% w/w, and this increased the absorbance dramatically. Accordingly, it was necessary to extrapolate the curve of the ionisation profile in the concentrated acid region to be able to estimate a reasonable value for ε_{SH^+}. This procedure is possibly subject to some error, but this was minimised by choosing a value which would give the best fit of the data to the curve, as judged by the sum of the squares of the deviations of the points from the line, and which gave the best fit to the linear regression line for log I (= $[SH^+]/[S]$) vs. $-H_o$, as judged by the correlation coefficient.

When the pK_{SH^+} values were calculated, it was found that the basicity constants for methyl benzoate at both 10° and 25°C agreed to within less than 1%. These values necessitated determining the H_o acidity function at 10°C according to the method of Johnson et al.[94] Further details concerning the calculations and

interpretations of these results are given in Part I of the Results and Discussion section.

V. ACTIVITY COEFFICIENTS FOR THE NEUTRAL SUBSTRATES IN ACID SOLUTION

As discussed in the Introduction, the variation in behaviour of the activity coefficient of the transition state, $f_{\ddagger}^*$, with the change in acid concentration, can be determined by analysing the rate equation for a pseudo-first order reaction in terms of its activity coefficient components:

$$\text{i.e. } \log (f_{\ddagger}^*/k_o) = -\log k_\psi (1+I) - \log K_{SH^+} + \log f_s + \log a^*_{H^+}$$

All the terms on the right-hand side of the equation are experimentally measurable. The determination of the rate constants and substrate basicity have already been discussed. Values for $a^*_{H^+}$, the activity of the proton relative to the reference ion, tetraethylammonium (TEA^+), in sulphuric and several other aqueous acids have recently been published.[39] This leaves only f_s, the activity coefficient of the neutral ester in various aqueous sulphuric acid solutions, to be determined. The data for methyl

benzoate and methyl mesitoate in 0 → 40% H_2SO_4 have been previously obtained.[95]

To obtain f_s values for the other three esters - methyl para- and ortho-toluate and methyl 2,6-dimethyl benzoate - the distribution method was employed.[15] Two problems arise for this determination of neutral activity coefficients, both of which limit the maximum acid concentration that can be used to obtain the activity coefficients. One is the increasing rate of hydrolysis of these esters in the more concentrated acids; the other is the extent of protonation of the ester substrates, making the determination of the activity coefficient of the neutral species difficult, if not impossible, to obtain experimentally. A number of attempts have been made to overcome this problem,[96] but these have met with only partial success and, in any case, have limited utility.* It is, however, possible to tolerate 5-10% protonation without seriously impeding the determination of f_s for the neutral species.

Thus, for both these reasons, it was necessary to set an upper limit of about 70% H_2SO_4 (60% for the 2,6-dimethyl benzoate) for obtaining the activity coefficient of a neutral ester. The experimental technique involved preparing and partitioning the solutions in a glove box thermostatted at 25°C.[97] A

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*For further discussion, cf. Ref. 15, pp. 335-336.

typical example of how these activity coefficients were obtained is as follows.

A stock solution of the ester was prepared in Spectroanalysed ACS cyclohexane in a concentration sufficient to give a maximum absorbance, after partitioning with an aqueous acid layer, of 1.8 units in the aqueous layer without further dilution. An average value ≃50 was found for the partitioning coefficient of the solute ester between the organic and aqueous acid layers. For a cell of pathlength 1.00 cm., this means:

$$C_{aqueous} = \frac{1.8}{\varepsilon_{max}}, \quad C_{organic} = \frac{90}{\varepsilon_{max}}$$

Consequently, a solution of ester of concentration $(90/\varepsilon_{max})$, where ε_{max} is the extinction coefficient at λ_{max} for the ester in the dilute acid region, was prepared in the cyclohexane solvent.

Since the partition coefficient was so high, the solution of ester in the organic layer, after partitioning, had to be diluted and read in a 1-mm. cell in order to obtain an absorbance reading on the spectrophotometer. The dilution factor cancels out of the final expression for calculating f_s, and, furthermore, the ester concentration in the organic layer after partitioning is relatively constant, except for the partitioning with the more concentrated acids.

Each acid was studied in duplicate and in pure water itself, in triplicate, since this latter value entered into the calculation for the activity coefficients in all the other acid solutions. For each aqueous acid studied, a test tube was filled with 5 ml. of that acid solution and placed in the glove box. To this was added 5 ml. of the ester stock solution; the test tube was then stoppered and shaken mechanically for 3 min. A dropper was then used to transfer an aliquot from the lower, aqueous layer to the 1.00-cm. uv cell.

Similarly, a 1.0-ml. aliquot of the organic layer was transferred to a 10-ml. volumetric flask, containing about 8 ml. of the cyclohexane solvent. This was then filled with cyclohexane to the mark, stoppered and inverted a few times to ensure homogeneity. The 1-mm. cell was filled with an aliquot from this organic solution.

The absorbances of these solutions were measured on the Cary-14 Recording UV-Spectrophotometer at the λ_{max} value for that specific ester in dilute acid. The absorbances of pure organic solvent and the pure aqueous acid solutions being used were measured several times and averaged to give $A^{org}_{reference}$ and $A^{aq}_{reference}$ respectively. It was found that the two layers separated very shortly after shaking was ceased, except for the solution that was partitioned with pure water. In this case, the solutions required standing for a longer period

of time and were usually left overnight before the cells were filled and the absorbances read. Since the rate of hydrolysis of ester in pure water was virtually negligible, this posed no problem.

Two more pieces of data were required before calculation of f_s was possible, that is the absorbance of known concentrations of the ester solute in pure water and in the various aqueous acid solutions studied. From this, the extinction coefficients of the ester in the respective solutions at the wavelength being used could be obtained.*

VI. SPECTRAL CHANGES AND ANALYSIS OF PRODUCTS

The spectra of the starting esters and the expected product benzoic acids were taken in the ultraviolet region from 220-300 nm. in three different sulphuric acid concentrations: 40.88, 71.60 and 91.55%. This covered the range from essentially unprotonated benzoate ester (or acid) to the predominantly protonated form. It provided a check on the determination of the best wavelength at which to follow the kinetics of hydrolysis, as well as an accurate spectrum of a reaction mixture after hydrolysis is complete. This latter spectrum was necessary for two reasons. The first is

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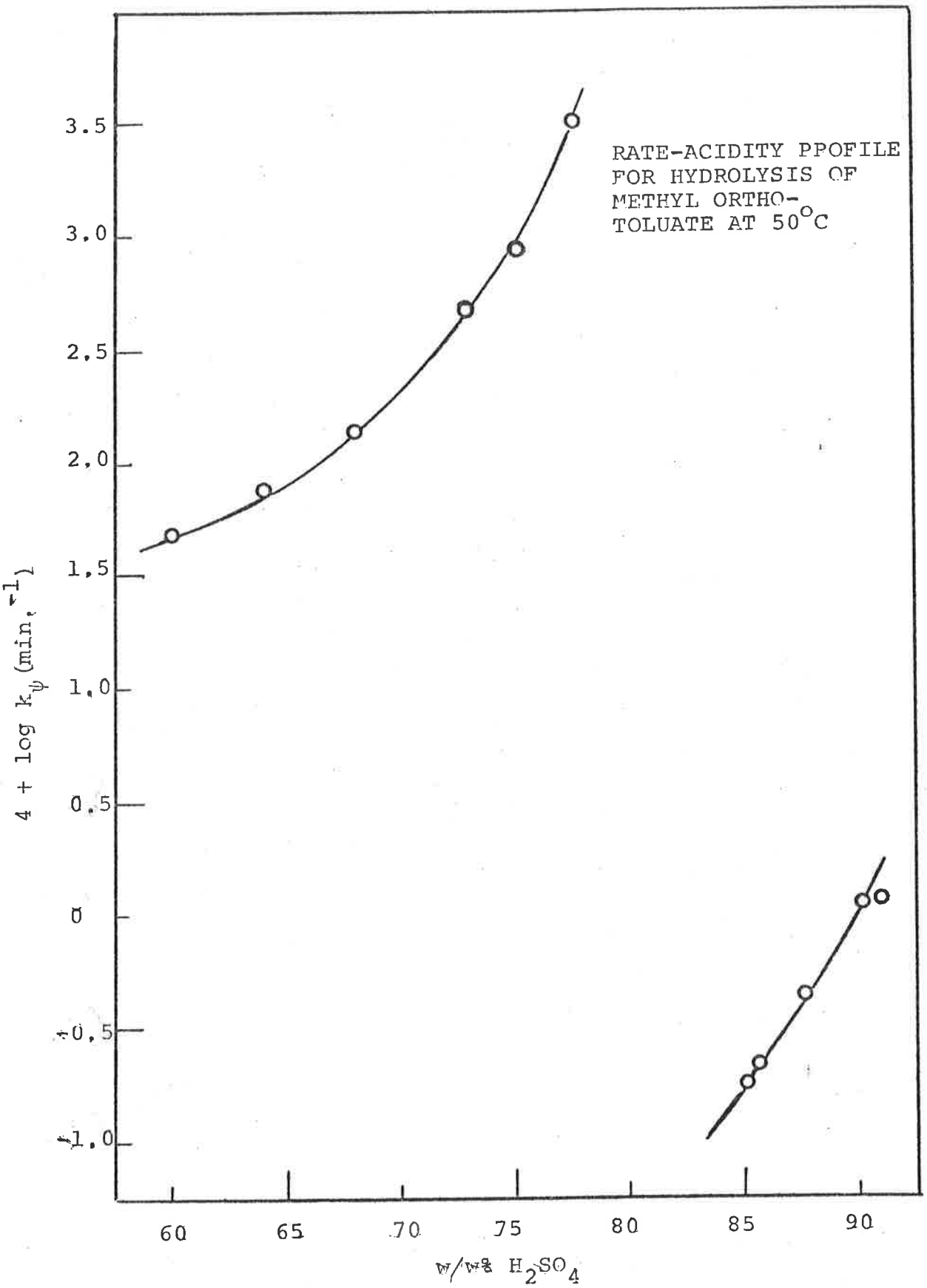
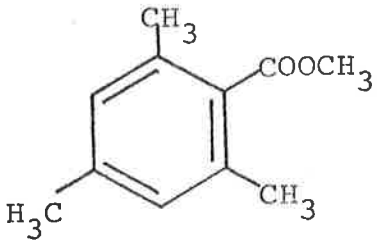
*Cf. Appendix B for formulae for calculating f_s.

that it was observed, in several reactions involving the ortho-substituted esters, that in the highly concentrated acid region at temperatures >25°C, a much slower rate of hydrolysis or other reaction appeared to be occurring. In Fig. (7), the rate profile for hydrolysis of methyl ortho-toluate at 50°C, shows this as a discontinuity in the curve. Under these conditions, the expected extremely rapid rates were no longer observed. The second reason is that in the protonation behaviour studies for all four ester substrates, there was a marked increase in the absorbance at the λ_{max} of the unprotonated ester at >98% sulphuric acid, prior to which it had been decreasing and levelling off as the extent of ester protonation was becoming more significant.

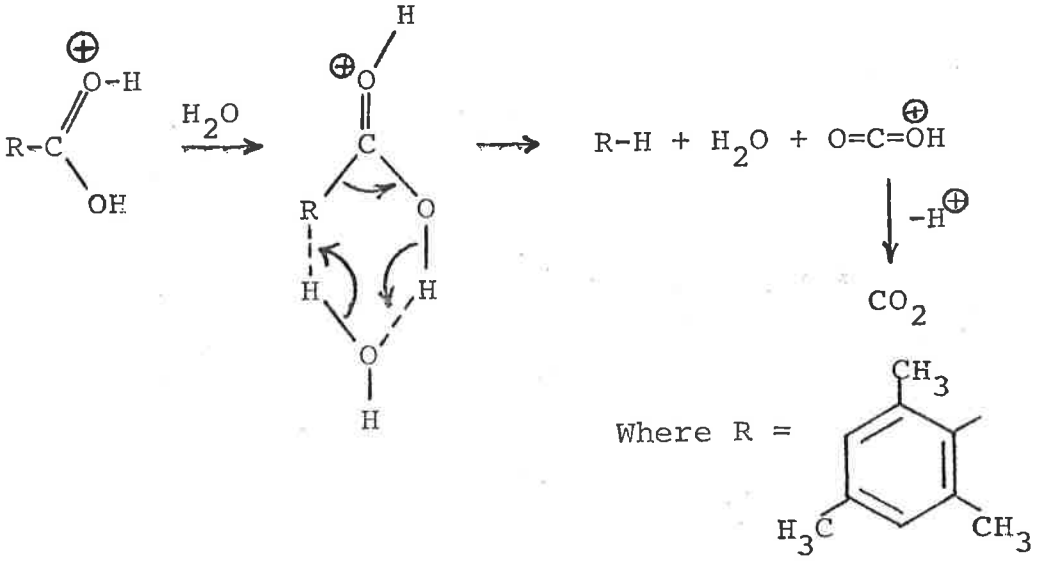
This anomalous behaviour has two possible explanations, both of which involve reactions other than, and probably subsequent to, ester hydrolysis. One is sulphonation of the aromatic moiety in concentrated acid - a problem that is probably not too serious until very high acid concentrations are reached, especially at lower temperatures.[98] The other is decarboxylation of the resulting sterically-hindered benzoic acid after hydrolysis is complete. This has, in fact, been shown to happen with methyl mesitoate;

FIGURE 7


RATE-ACIDITY PPOFILE FOR HYDROLYSIS OF METHYL ORTHO-TOLUATE AT 50°C
4 + log k_ψ (min.$^{-1}$)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
-1.0
60
65
70
75
80
85
90
w/w% H_2SO_4



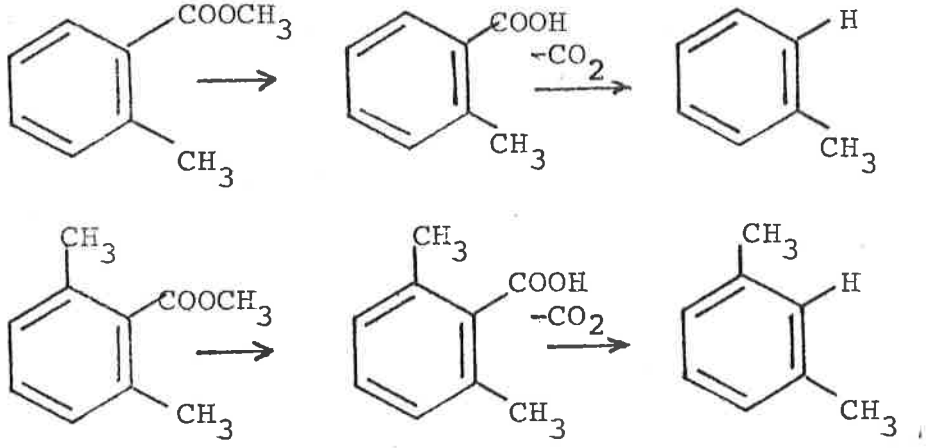
a compound which differs from methyl 2,6-dimethyl benzoate only by the presence of an extra methyl group para to the ester site. The mechanism proposed for this reaction was:[99,100]



This mechanism was supported, among other pieces of evidence, by the proportionality between log k_{ψ} and log $C_{H_3O^+}$, indicating a bimolecular attack by water on the protonated ester prior to the transition state.

It was therefore desirable to determine accurately the spectra of the esters and their carboxylic acid products in several different acids. Spectra of toluene and m-xylene were measured in the same acids to

determine the spectra of the expected decarboxylation products of the ortho-substituted benzoate esters.



Stock solutions of the ester substrates and acid products of known concentration, determined by weight, were prepared in ACS methanol and their spectra scanned in methanol over the uv range of interest. Triplicate scans of the spectrum of each substrate in this solvent were obtained and the extinction coefficients averaged to determine accurately the value for ε at the λ_{max} of each substrate. This was necessary in order to determine the concentration of substrate in the aqueous acid solutions into which the stock substrate solution was subsequently injected. Blank cells, containing only the methanol solvent, were also scanned, since this alcohol absorbs quite strongly at λ <250 nm. The absorbance of the solution containing ester was then corrected for

the reference absorbance at various wavelengths and, particularly, at λ_{max}.

With the concentrations of the different stock substrate solutions accurately known, this procedure was repeated for each of the esters and carboxylic acids in 40.88%, 71.60% and 91.55% H_2SO_4. These were also carried out in triplicate, the spectra being scanned from 220-300 nm. The volumes of stock solution used were varied depending on the maximum absorbance in the various acids, but were generally in the range 3-10 µl. This was injected, with a syringe, into a 1.00-cm. uv cell containing 3.0 mls. of sulphuric acid solution. The cell was then stoppered, inverted several times to ensure homogeneity and inserted into the cell holder of the Cary-14 Recording UV Spectrophotometer. The spectrum was taken immediately, at room temperature. Reference spectra of the aqueous acid solutions were also determined to give corrected values for the substrate absorbance in each acid.

Solubility was not a problem except for 2,6-dimethyl benzoic acid and its methyl ester in 40.88% H_2SO_4. This was overcome by shaking a solution of the substrate in the acid in a vial for 5 min. before putting it into the cell and recording. The spectra of this ester and that of methyl ortho-toluate in 91.55% H_2SO_4 posed a different problem - that of their rapid hydrolysis rates. Spectra extrapolated to zero-time were not

obtained, however, as this would have been very tedious to do over the entire spectral region. Instead, the spectra were measured as quickly as possible from the time of ester injection (<30 sec.) and a good spectral difference between the ester and that of the product acid was obtained. This was possible because the hydrolysis reaction was not significantly far-advanced, and no complications, such as a subsequent decarboxylation, are observed for these esters at 25°C. From the point of view of product studies, whose main concern is to determine the extinction coefficients of the possible products of hydrolysis and/or subsequent reactions, it was of little consequence if the esters were, in fact, hydrolysing.

Once the spectra of starting esters and products were obtained, hydrolyses of these esters were carried out in the three sulphuric acid solutions at 50°C. A 10-ml. solution of substrate in acid was prepared and divided into three 3-ml. portions each. Two of these were transferred each to a 5-ml. ampoule which was then sealed. The ampoules were placed in an oil bath thermostatted at 50 ± 0.1°C. The remaining 3-mls. of solution was transferred to a uv cell and the initial spectra of esters and products were thus obtained to provide a basis of comparison for the spectra of the products of hydrolysis in the various acid solutions and to determine accurately the concentration of substrate used in each

case for the calculation of the extinction coefficients. Although the initial solutions of substrate in acid were mechanically shaken for a few minutes for dissolution in the 40.88% H_2SO_4, this was not done for the 91.55% H_2SO_4 in order to obtain the initial spectra of these compounds as quickly as possible.

Of each pair of ampoules in the bath, one was removed after an estimated one half-life, quenched in ice-water and warmed to room temperature before recording its spectrum. The other was subjected to the same procedure after the reactions were calculated to have gone to completion, i.e. ∿10 half-lives. The results are shown in Table 3 (a-d).

The hydrolysis of methyl benzoate (Table 3a) clearly gives the product benzoic acid in all three acids studied.* The differences between the extinction coefficients of the hydrolysis product and benzoic acid itself are well within experimental error. Methyl para-toluate spectra were not determined in this study, since it was considered to behave in a manner similar to methyl benzoate with no unusual products expected from its hydrolysis.

The results for methyl ortho-toluate hydrolysis (Table 3b) again show the expected product, ortho-toluic

*At the time these product studies were carried out, a check on the H_2SO_4 concentrations revealed a minor change from those in which the earlier spectra had been obtained.

TABLE 3a: EXTINCTION COEFFICIENTS FOR PRODUCT OF METHYL BENZOATE HYDROLYSIS IN H_2SO_4 AT 50°C

w/w% H_2SO_4	λ (nm)	ε_{MB}	ε_{prod}	ε_{BA}
40.94	220	8700	7480	7450
	225	11100	10110	10080
	230	12330	11560	11600
	235	11490	10850	11000
	240	8720	8300	8410
	245	4970	4790	4820
	250	2590	2330	2420
	255	1720	1440	1480
	260	1590	1280	1320
71.58	220	6110	5360	5360
	225	8660	7570	7710
	230	11050	10080	10120
	235	12100	11660	11670
	240	11030	11490	11570
	245	8210	9520	9520
	250	4560	6460	6450
	255	2050	3640	3670
	260	1380	2390	2450
91.44	230	2640	2810	2570
	235	3710	4100	4160
	240	5330	6130	6520
	245	7480	8770	9480
	250	9880	11820	12770
	255	11780	14450	15540
	260	12890	15410	16660
	265	11840	13710	14800
	270	8910	9180	9970
	275	4940	5000	4930
	280	2600	3240	2870

TABLE 3b: EXTINCTION COEFFICIENTS FOR PRODUCT OF METHYL o-TOLUATE HYDROLYSIS IN H_2SO_4 AT 50°C

w/w% H_2SO_4	λ (nm)	ε_{MOT}	ε_{prod}	ε_{OTA}
40.94	220	5310	5480	5750
	225	6730	6730	7220
	230	7830	7650	8340
	235	7800	7450	8270
	240	6530	6160	6970
	245	4410	4080	4810
	250	2370	2350	2730
	255	1270	1390	1550
71.58	220	3980	3780	3670
	225	5500	5030	5120
	230	7290	6730	7030
	235	8610	8090	8500
	240	8760	8590	9080
	245	7340	7910	8460
	250	4940	6170	6390
	255	2540	4090	4110
	260	1380	2640	2590

	λ (nm)	ε_{MOT}	ε^{MOT}_{prod}	ε_{OTA}	ε^{OTA}_{prod}	$\varepsilon_{Toluene}$
91.44	230	1590	2340	1590	2350	-
	235	2210	3010	2400	3290	2920
	240	3350	4170	4010	4770	966
	245	4850	5750	6160	7040	331
	250	6920	7660	9040	9600	340
	255	9090	9720	12200	12290	504
	260	10880	11260	14650	14180	671
	265	11070	11400	15040	14200	871
	270	9370	9630	12580	11580	922
	275	5950	6180	7640	7120	811
	280	2910	3100	3540	3450	595
	285	1740	1980	1880	2140	161
	290	1500	1870	1720	2100	48

TABLE 3c: COEFFICIENTS FOR PRODUCT OF HYDROLYSIS OF METHYL 2,6-DIMETHYL BENZOATE IN H_2SO_4 AT 50°C

w/w% H_2SO_4	λ (nm)	ε_{MDMB}	ε_{prod}	ε_{DMBA}
40.94	220	3900	3730	4410
	225	2580	2290	2560
	230	2310	2000	2140
	235	2200	1910	2000
	240	1820	1620	1750
	245	1350	1180	1330
	250	970	820	970
	255	730	620	770
	260	710	590	750
71.58	220	2870	3680	3720
	225	2610	2530	2470
	230	2550	2350	2330
	235	2620	2350	2430
	240	2440	2280	2380
	245	2030	2000	2160
	250	1480	1630	1740
	255	1050	1270	1350
	260	878	1090	1130

	λ (nm)	ε_{MDMB}	$\varepsilon^{MDMB}_{prod}$	ε_{DMBA}	$\varepsilon^{DMBA}_{prod}$	$\varepsilon_{m\text{-}xylene}$
91.44	230	1160	-	1070	-	-
	235	1220	6120	1140	6110	-
	240	1510	3010	1420	3130	3050
	245	1930	1760	1840	1870	764
	250	2450	1430	2350	1570	344
	255	3050	1350	2930	1480	434
	260	3630	1360	3450	1470	635
	265	4020	1370	3790	1460	842
	270	4030	1400	3800	1470	1110
	275	3690	1300	3400	1340	990
	280	2850	1230	2700	1270	969
	285	2070	839	1950	909	293
	290	1560	645	1460	730	143

TABLE 3d: EXTINCTION COEFFICIENTS FOR PRODUCT OF METHYL o-TOLUATE HYDROLYSIS IN 91.44% H_2SO_4 AT 50°C AFTER 110 hr.

λ (nm)	ε_{MOT}	$\varepsilon^{ESTER}_{prod}$	ε_{OTA}	$\varepsilon^{ACID}_{prod}$	$\varepsilon_{Toluene}$
230	1590	5950	1590	5780	-
235	2210	6430	2400	6360	2920
240	3350	7330	4010	7420	966
245	4850	8270	6160	8430	331
250	6920	8850	9040	9040	340
255	9090	9030	12200	9270	504
260	10880	8750	14650	8910	671
265	11070	7610	15040	7740	871
270	9370	5980	12580	6010	922
275	5950	4180	7640	4080	811
280	2910	2900	3540	2710	595
285	1740	2480	1880	2310	161
290	1500	2490	1720	2350	48

acid, after reaction in 40.94% and 71.58% H_2SO_4. The agreement here is not quite as good as for methyl benzoate, but it is evident that nothing unusual is happening to this ester in moderately concentrated sulphuric acid, even at 50°C. However, the results in 91.44% H_2SO_4 indicate that some other reaction besides hydrolysis is occurring. Table 3b gives the extinction coefficients after 11.7 hr. of reaction and reveals that the main reaction is still hydrolysis. But the extinction coefficients of the ester product are smaller than those of ortho-toluic acid itself. In the low wavelength end of the spectrum, on the other, the extinction coefficients of the product are greater than those expected. These results imply that some other product may be present in at least a minor amount.

Table 3d - the extinction coefficients of MOT hydrolysis after 110 hr. of reaction - show this even more clearly. The λ_{max} has shifted hypsochromically from ∿265 nm. to ∿255 nm., and the extinction coefficients of both the ester and carboxylic acid products are considerably lower than expected. In addition, the spectra of the two products are virtually identical. These results could conceivably be explained by the incursion of the decarboxylation reaction which follows hydrolysis, as the extinction coefficients of the decarboxylation product, toluene, are much smaller than those for the toluate systems. The absorbance values

observed during the actual kinetic runs did decrease continuously over a period of 3-400 hr. in accord with the production of a species with lower extinction coefficients.

It is difficult to conclude exactly what is happening except that, for practically all the kinetics measured for methyl ortho-toluate in acids <85-90%, simple hydrolysis is occurring. Moreover, for those reaction conditions in which some other reaction is taking place, it proceeds subsequent to initial hydrolysis as evidenced from the very close similarity in the spectra of the products from methyl ortho-toluate and ortho-toluic acid. The rate constant of hydrolysis of this ester at 25°C in 90% H_2SO_4, ~0.50 min^{-1}, supports the view that hydrolysis at 50°C is over almost instantaneously. Consequently, in those kinetic studies carried out at this temperature in >85% acid, another reaction, most likely decarboyxlation, was being observed.

The spectral results for methyl 2,6-dimethyl benzoate and its product carboxylic acid, shown in Table 3c, permit similar conclusions to be drawn. In 40.94% and 71.58% H_2SO_4, the ester appears to be hydrolysing in a normal fashion to 2,6-dimethyl benzoic acid. But in 91,44% H_2SO_4, two observations may be made. The first is that the ester ester had, in fact hydrolysed almost completely by the time the spectrum was obtained, despite

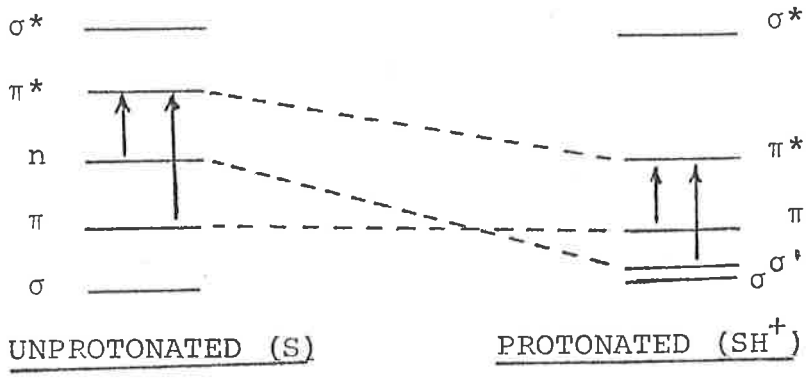
the shortness of the time interval between preparing the solution and measuring its spectrum. The second is that after only 12 hours, the spectra of the ester and carboxylic acid products agree very closely with each other, but not with the expected spectrum of the carboxylic acid. The spectra are clearly composites of the dimethyl benzoic acid and m-xylene, the product of decarboxylation. It is not certain from these results just what the relative concentrations of each are, but there appears to be a significant amount of m-xylene present.

Again the same conclusions may be drawn here as for the ortho-toluate system. There is another reaction occurring under these conditions, subsequent to hydrolysis, and it is most probably decarboxylation. However, since there were no kinetic studies measured with this ester under conditions where this reaction is likely to occur, there was no problem in interpreting the rate results in terms of the usual hydrolysis mechanisms. It therefore seems safe to conclude that the products of all the reactions included in the present study are in fact those resulting from hydrolysis of the esters.

RESULTS AND DISCUSSION

I. THE PROTONATION BEHAVIOUR OF BENZOATE ESTERS

The protonation of methyl para-toluate, methyl ortho-toluate and methyl 2,6-dimethyl benzoate in sulphuric acid was studied at 10°C from the spectral changes in the ultraviolet region. The behaviour of the parent ester, methyl benzoate, was investigated at both 10°C and 25°C in order to evaluate the temperature dependence of protonation for this class of organic base. Spectra of methyl benzoate in various acid solutions at room temperature are shown in Fig. 4. The spectra of methyl para- and ortho-toluate are similar to these in that they show an intense maximum ($\log \varepsilon \simeq 4$) in the 230-245 nm. range in dilute acid, which shifts to the 260-280 nm. range attributable to a $\pi \rightarrow \pi^*$ transition. The reasons for the spectral change with increasing acid concentration are attributable to changes in the relative spacing of the energy levels as the ester base is protonated. These levels for the un-ionised and protonated species can be depicted schematically as follows:



As the ester is protonated, the 'n' electrons of the carbonyl oxygen become "σ'" electrons, with the formation of the $\rangle\overset{+}{O}\text{-}H$ bond. The σ' → π* transition requires greater energy than did the n → π* transition. As a result, the absorbance maximum for this is shifted to somewhat shorter wavelengths. Furthermore, it appears[101] that the π*-level is lowered considerably more than the π-level as the ester becomes protonated.* This results in a red shift to longer wavelengths in going from the unprotonated to the protonated form. The overall result is that the absorbance for the π → π* transition generally obscures that for the n → π* transition in concentrated acid, or else the latter is shifted to such short wavelengths that it is not observed in the normal uv region at all.

The spectra of methyl 2,6-dimethyl benzoate are different from those of the other esters on two counts.

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*Although this appears to be the current explanation of this phenomenon, it is not clearly understood and warrants further investigation.

First of all, the extinction coefficients throughout the ultraviolet region are much smaller than those for the other esters, in the dilute acid range. This is probably due to the fact that the electronic transitions are less favoured as a result of steric crowding. Secondly, no distinct absorbance maxima are observed in the 220-290 nm. range, but rather the absorbance keeps increasing as the wavelength becomes shorter. Presumably, there is a $\pi \rightarrow \pi^*$ transition in the far uv, because there is little or no conjugation between the aromatic ring and the carbonyl double bond. There are, however, two shoulders in the spectra in dilute acid - one at 232.5 nm. and the other at 272 nm. The spectrum of this ester changes quite dramatically with increasing protonation, so that by ~92% H_2SO_4, the $\pi \rightarrow \pi^*$ transition appears as a maximum at ~268 nm. for reasons enunciated previously for the other esters.

The basicity constants, pK_{SH^+}, were determined in all cases at the two wavelengths of maximum absorbance for the essentially unprotonated ester and the protonated form. Use of absorbance data at these two wavelengths, however, gave slightly different results for the slopes of the ionisation plots. Therefore, a technique was employed whereby the calculation of pK_{SH^+} was based on the difference in extinction coefficients at the two λ values chosen. This usually resulted in an intermediate value of pK_{SH^+}, but all three were

averaged to give a value that could be used with considerable confidence.

Hammett and co-workers[102] have given an excellent analysis of the phenomenon commonly observed in concentrated acid solutions known as the "medium effect", and the importance of choosing wavelengths for studying the ionisation of an organic base at which this effect can be minimised. Ideally, what should happen as an ester, S, is protonated to give SH^+ is that the total absorbance of a solution in a given acid should be the sum of the individual absorbances of S and SH^+,

$$A_{total} = A_S + A_{SH^+}$$

This assumes that each species absorbs independently in the presence of one another and that their absorbances obey the Beer-Lambert law. These assumptions are known to be valid for a wide variety of similar cases. From this, the determination of the ionisation ratio, I, is easily calculated

$$A_{soln.} = \varepsilon_S[S] + \varepsilon_{SH^+}[SH^+] = \varepsilon_{obsd.}([S] + [SH^+]) \quad (28)$$

Hence,

$$\frac{[SH^+]}{[S]} = I = \frac{\varepsilon_S - \varepsilon}{\varepsilon - \varepsilon_{SH^+}} \quad (29)$$

What is sometimes observed, however, is a small but consistent change in the extinction coefficient of the ester absorbance in an acid range in which it is known to be completely in one of the two forms, S or SH^+. Also the spectra, over a range of acid concentration in which the ester is protonating, may fail to pass through a common isobestic point. Normally, this would indicate the presence of more than two species in solution. However, the fact that an isobestic point is not observed can also be attributed to a lateral displacement, with no change in absorbance intensity, of the ester spectrum, due to the effect of the medium on the uv behaviour of the ester. Consequently, constant values for the extinction coefficients of the completely unprotonated and completely protonated forms of the ester, ε_S and ε_{SH^+} respectively, cannot be accurately determined.

There are a number of ways of accounting for this medium effect on the determination of pK_{SH^+}, but as Hammett et al, pointed out, the most important consideration is to choose wavelengths where the absorbance is relatively flat over a certain spectral range. Since this will be true for the λ_{max} values of the unprotonated and protonated ester forms, these were the values chosen.

In order to check as to which calculation of the pK_{SH^+} gave the best fit to the observed data, two methods

were employed. Katritzky and co-workers[103] assumed that the medium effect and the protonation are both approximately linear in H_o.

$$\varepsilon_B = \varepsilon^o_B + G_B . H_o \qquad (30)$$

$$\varepsilon_{BH^+} = \varepsilon^o_{BH^+} + G_{BH^+} . H_o \qquad (31)$$

$$\log I = \log \frac{[BH^+]}{[B]} = m(-H_o + pK'_{BH^+}) \qquad (32)$$

where G_B, G_{BH^+} represent the medium-dependent coefficients of the extinction coefficients of the unprotonated and protonated species respectively. Similarly, ε^o_B and $\varepsilon^o_{BH^+}$ are the true extinction coefficients of these two species respectively. The data for methyl orthotoluate were treated by this method, in which G_B, ε^o_B were calculated by drawing a linear-regression line through the points in the dilute acid, and G_{BH^+} was assumed to be zero, since the titration curve was fairly flat in this region. The calculated curve was obtained by substituting equations (30) and (31) into (28),

$$\varepsilon = (\varepsilon^o_S + G_S . H_o) \cdot \left(\frac{1}{1+I}\right) + \varepsilon^o_{SH^+} \left(\frac{I}{1+I}\right)$$

$$= \frac{1}{1+I} (\varepsilon^o_S + G_S . H_o + I . \varepsilon^o_{SH^+})$$

where $$I = \frac{[SH^+]}{[S]} .$$

The other method of calculation used assumed that there are no medium effects on the absorption intensity of either form of the ester. This in fact appeared to be true in most cases, and the appropriate equation for fitting the points is

$$\varepsilon_{calc.} = \frac{1}{1+I} \left(\varepsilon_S + I \cdot \varepsilon_{SH^+}\right)$$

The data for methyl o-toluate at 232.6 nm. are shown in Table (4) and the respective sigmoid titration curves calculated by the two methods in Fig. (8). The determination of the best fit was made by comparing the sum of squares (Σd_i^2) of the deviations of the experimental points from the calculated line, as well as from visual inspection. As can be seen, a much better fit was obtained overall for the titration curve calculated by ignoring the medium effects, although the agreement with experiment for the ionisation region is somewhat better for the other curve. Moreover, both methods give excellent agreement of the pK'_{SH^+} values, although the slope of the curves in the ionisation region are different and therefore give rise to different 'm' and pK_{SH^+} values. This type of treatment was repeated for the same ester at 261.5 nm. with similar results being obtained. Consequently, all pK_{SH^+} values were calculated by ignoring medium effects.

TABLE 4: EXTINCTION COEFFICIENTS OF METHYL ORTHO-TOLUATE IN SULPHURIC ACID[a,b]

w/w% H_2SO_4	$-H_o$ [a]	$\varepsilon_{exp.}$	$\varepsilon_{calc.}$ [c]	$\varepsilon_{calc.}$ [d]
50.05	3.54	7561	8136	7823
54.68	4.05	7554	8043	7822
59.56	4.65	7950	7920	7820
62.70	4.98	7960	7841	7817
65.66	5.38	7779	7724	7807
68.55	5.80	7865	7553	7781
70.36	6.08	7785	7395	7742
72.65	6.46	7651	7091	7628
75.73	6.98	7084	6419	7207
78.14	7.37	5603	5665	6474
79.60	7.62	5013	5076	5739
82.42	8.07	4129	3916	4068
84.39	8.39	3621	3140	2972
86.41	8.72	2144	2479	2179
88.40	9.08	1434	1951	1690
90.50	9.42	1548	1620	1461
94.46	10.24	1292	1246	1291
96.50	10.61	1168	1181	1274
97.22	10.74	1323	1166	1270

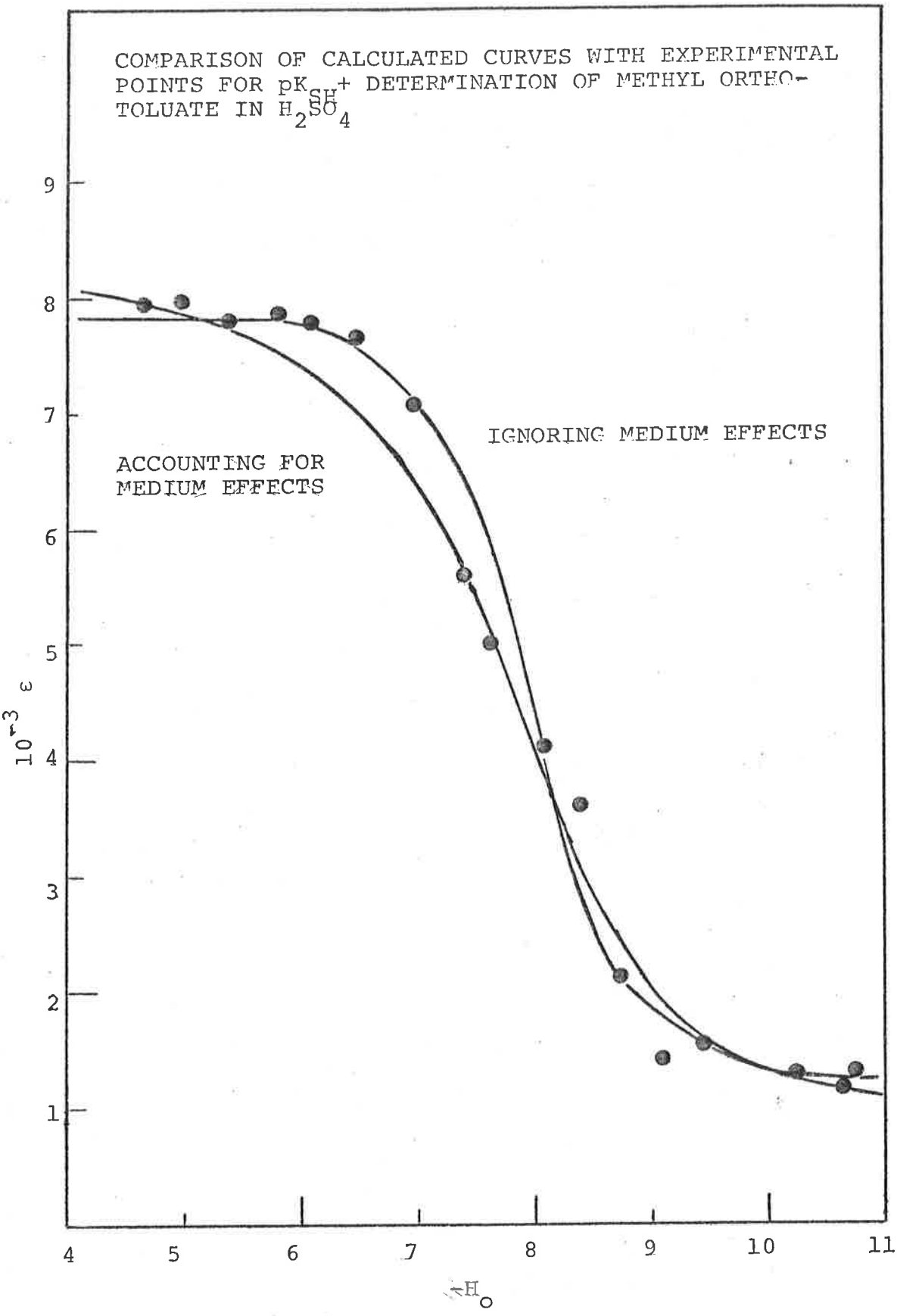
[a] $T = 10^0C$

[b] $\lambda = 232.6$ nm.

[c] Calculated from: $\log I = 0.69\ (-H_0 - 7.94)$;
$\varepsilon_S = 8733 + 167\ H_0$, $\varepsilon_{SH^+} = 1100$
$\Sigma d_i^2 = 2210$, where d_i = % deviation = $(\varepsilon_{exp} - \varepsilon_{calc})/(\varepsilon_{exp}) \times 100$

[d] Calculated from: $\log I = 1.02\ (-H_0 - 7.94)$
$\varepsilon_S = 7823$, $\varepsilon_{SH^+} = 1261$
$\Sigma d_i^2 = 1259$

FIGURE 8


COMPARISON OF CALCULATED CURVES WITH EXPERIMENTAL POINTS FOR pK_{SH^+} DETERMINATION OF METHYL ORTHO-TOLUATE IN H_2SO_4
IGNORING MEDIUM EFFECTS
ACCOUNTING FOR MEDIUM EFFECTS
$10^{-3}\ \varepsilon$
$-H_o$
1
2
3
4
5
6
7
8
9
10
11

The protonation behaviour was studied at 10°C to prevent rapid hydrolysis of the esters in the concentrated acid region. To determine the values for pK'_{SH^+} and pK_{SH^+}, it was therefore necessary to calculate H_o values at this temperature. The data were obtained from the equation and tables determined by Johnson et al.[94] in their excellent treatment of the temperature-dependence of the H_o acidity function.

$$H_o^T = H_o^{25^\circ} + \frac{\kappa\Delta T}{298.15\ T}$$

where κ is a constant determined for various sulphuric acid concentrations at different temperatures. When H_o at 10°C was calculated in this manner, it was found that a linear relation exists between $H_o(10^\circ C)$ and $H_o(25^\circ C)$,

$$H_o(10^\circ) = 1{,}052\ H_o(25^\circ C) + 0{,}0388$$

or, alternatively:

$$H_o(25^\circ) = 0{,}951\ H_o(10^\circ) - 0.0373 \quad \ldots (33)$$

The latter equation was used to calculate the pK'_{SH^+} and pK_{SH^+} values for the various esters at 25°C from their values at 10°C. This assumes that the slopes for the ionisation plots at the different temperatures are relatively invariant, and that the temperature dependence of the benzoate ester acidity function, mH_o, is identical

to that for H_o itself. Sample data for each ester at a given wavelength are shown in Table 5. The results are summarised in Table 6.

To test the validity of these two assumptions, the protonation behaviour of methyl benzoate was studied at 25°C, as well as at 10°C. There was no difficulty with respect to hydrolysis for this ester, since even in the most concentrated acid studied, its half-life of hydrolysis is at least 70 min. Therefore, in the minute or so it required to prepare the solution and measure the absorbance, less than 1% reaction would have occurred. The spectral data at 25°C for this ester at 232 nm. is given in Table 5e.

The three values for the pK'_{SH^+} and pK_{SH^+} for each ester were averaged and then were all converted from 10°C to values at 25°C by equation (33). These are shown in Table 7. In comparing the calculated values at 25°C for methyl benzoate with those obtained directly from experimental observation, it can be seen that they agree within experimental error and that both sets of values are in accord with the results obtained by Lane and coworkers,[35]

$$\log \left[SH^+\right]/\left[S\right] = 0,846\ (-H_o - 8,18);\ pK_{SH^+} = -6,92$$

TABLE 5a: EXTINCTION COEFFICIENTS FOR METHYL BENZOATE IN SULPHURIC ACID[a,b]

w/w% H_2SO_4	$-H_o$ [a]	$\varepsilon_{exp.}$	$\varepsilon_{calc.}$ [c]	% dev.[d]
45,46	3,09	11399	11418	-0,2
50,20	3,54	11312	11417	-0,9
54,86	4,05	11543	11416	+1,1
56,69	4,61	11418	11412	+0,1
63.78	5,11	11087	11402	-2,8
66.38	5,49	10810	11385	-5,3
67.96	5,73	11266	11365	-0,9
70,84	6,18	10996	11291	-2.7
77,02	7,21	11419	10554	+7.6
79,44	7,61	9866	9720	+1,5
80.32	7.75	9104	9178	-0,8
80.64	7,81	9068	9111	-0,5
81.70	7,98	8719	8488	+2,7
82,09	8,05	7285	8206	-12,6
83,95	8,36	5496	6840	-24,5
87.59	8.96	5081	4331	+14,8
94,28	10.20	2476	2267	+8,4
96.41	10,57	1997	2131	-6,7

[a] $T = 10^{o}C$

[b] $\lambda = 232,0$ nm,

[c] Calculated from: $\log I = 0,845\ (-H_o - 7,09)$;
$\varepsilon_S = 11418$, $\varepsilon_{SH^+} = 1997$

[d] $\Sigma d_i^2 = 1336$

TABLE 5b: EXTINCTION COEFFICIENTS FOR METHYL PARA-TOLUATE IN SULPHURIC ACID[a,b]

w/w% H_2SO_4	$-H_o$[a]	$\varepsilon_{exp.}$	$\varepsilon_{calc.}$[c]	% dev.[d]
50.05	3.54	13596	13663	-0.5
54.68	4.05	13689	13648	+0.3
59.56	4.65	13739	13601	+1.0
62.70	4.98	13235	13547	-2.4
65.66	5.38	13024	13428	-3.1
68.55	5.80	12550	13183	-5.0
70.36	6.08	12427	12904	-3.8
72.65	6.46	11975	12286	-2.6
75.73	6.98	10887	10780	+1.0
76.47	7.09	10065	10345	-2.8
78.14	7.37	9562	9067	+5.2
79.60	7.62	8104	7778	+4.0
82.42	8.07	5115	5446	-6.5
84.39	8.39	3919	4051	-3.4
86.41	8.72	2858	2969	-3.9
88.40	9.08	1759	2180	-24.0
90.50	9.42	1694	1721	-1.6
92.72	9.88	1441	1379	+4.3
94.46	10.24	1266	1241	+2.0
96.50	10.61	1008	1163	-15.4
97.22	10.74	1136	1145	-0.8

[a] $T = 10^{o}C$

[b] $\lambda = 242.6$ nm.

[c] Calculated from: $\log I = 0.734\ (-H_o - 7.70)$;
$\varepsilon_S = 13764$, $\varepsilon_{SH^+} = 1072$

[d] $\Sigma d_i^2 = 1020$

TABLE 5c: EXTINCTION COEFFICIENTS FOR METHYL ORTHO-TOLUATE IN SULPHURIC ACID[a,b]

w/w% H_2SO_4	$-H_o$[a]	$\varepsilon_{exp.}$	$\varepsilon_{calc.}$[c]	% dev.[d]
50.05	3.54	611	609	+0.3
54.68	4.05	497	610	-22.7
59.56	4.65	543	612	-12.7
62.70	4.98	604	615	-1.8
65.66	5.38	613	623	-1.6
68.55	5.80	684	644	+5.9
70.36	6.08	838	673	+19.7
72.65	6.46	730	757	-3.7
75.73	6.98	1202	1067	+11.3
78.14	7.37	1618	1647	-1.8
79.60	7.62	2236	2318	-3.7
82.42	8.07	5037	4415	+12.3
84.39	8.39	7501	6595	+12.1
86.41	8.72	8246	9011	-9.3
88.40	9.08	11091	11187	-0.9
90.50	9.42	12483	12525	-0.3
94.46	10.24	13236	13764	-4.0
96.50	10.61	14145	13914	+1.6
97.22	10.74	13922	13944	-0.2

[a] $T = 10^{o}C$

[b] $\lambda = 265.6$ nm.

[c] Calculated from: $\log I = 0.963\ (-H_o - 8.49)$;
$\varepsilon_S = 609$, $\varepsilon_{SH^+} = 14034$

[d] $\Sigma d_i^2 = 1663$

TABLE 5d: EXTINCTION COEFFICIENTS FOR METHYL 2,6-DIMETHYL BENZOATE IN SULPHURIC ACID[a,b]

w/w% H_2SO_4	$-H_o$[a]	$\varepsilon_{exp.}$	$\varepsilon_{calc.}$[c]	% dev.[d]
65.66	5.38	2206	2345	-6.3
68.55	5.80	2378	2335	+1.8
70.36	6.08	2321	2322	0
72.65	6.46	2369	2292	+3.3
75.73	6.98	2247	2208	+1.7
78.14	7.37	2018	2091	-3.6
79.60	7.62	2001	1984	+0.9
82.42	8.07	1466	1726	-17.7
83.49	8.25	1589	1607	-1.1
84.39	8.39	1195	1513	-26.6
86.41	8.72	1296	1303	-0.6
88.40	9.08	1216	1116	+8.2
90.50	9.42	992	990	+0.2
94.46	10.24	881	844	+4.2
96.50	10.61	786	819	-4.2
97.22	10.74	791	813	-2.8

[a] $T = 10^{o}C$

[b] $\lambda = 234.7$ nm.

[c] Calculated from: $\log I = 0.743\ (-H_o - 8.30)$;
$\varepsilon_S = 2356$, $\varepsilon_{SH^+} = 789$

[d] $\Sigma d_i^2 = 1206$

TABLE 5e: EXTINCTION COEFFICIENTS FOR METHYL BENZOATE IN SULPHURIC ACID[a,b]

w/w% H_2SO_4	$-H_o$[a]	$\varepsilon_{exp.}$	$\varepsilon_{calc.}$[c]	% dev.[d]
54.86	3.82	11643	11575	+0.6
63.78	4.92	11769	11560	+1.8
68.67	5.60	11392	11509	-1.0
70.64	5.89	11503	11456	+0.4
72.85	6.22	11289	11346	-0.5
75.94	6.69	11113	11004	+1.0
78.64	7.11	10293	10342	-0.5
79.44	7.24	10662	10032	+5.9
80.64	7.43	9303	9472	-1.8
81.70	7.59	8862	8897	-0.4
82.85	7.78	8154	8103	+0.6
83.61	7.90	7569	7554	+0.2
83.95	7.95	7589	7318	+3.6
84.57	8.05	6960	6839	+1.7
85.54	8.21	6095	6076	+0.3
86.63	8.39	5196	5261	-1.2
88.64	8.73	3924	3893	-1.5
92.78	9.45	2597	2561	+1.4
94.84	9.82	2237	2280	-1.9
96.55	10.14	2156	2154	+0.1
97.74	10.36	2038	2103	-3.2
98.47	10.53	1982	2076	-4.8

[a] $T = 25^{o}C$

[b] $\lambda = 232.0$ nm.

[c] Calculated from: $\log I = 0.873\ (-H_o - 8.06)$;
$\varepsilon_S = 11577$, $\varepsilon_{SH^+} = 2010$

[d] $d_{\Sigma d_i^2} = 103$

TABLE 6: SUMMARY OF RESULTS OF PROTONATION BEHAVIOUR OF BENZOATE ESTERS IN SULPHURIC ACID

ESTER	T(°C)	λ (nm.)	m	pK'_{SH^+}	pK_{SH^+}
METHYL		232.0	0.845	-8.39	-7.09
BENZOATE	10	261.5	0.791	-8.59	-6.79
		$\Delta\lambda$[a]	1.04	-8.39	-8.70
METHYL		232.0	0.873	-8.06	-7.04
BENZOATE	25	261.5	0.934	-8.23	-7.69
		$\Delta\lambda$[a]	0.908	-8.17	-7.42
METHYL		242.6	0.734	-7.70	-5.65
PARA-	10	278.0	0.760	-8.10	-6.15
TOLUATE		$\Delta\lambda$[a]	0.825	-7.85	-6.48
METHYL		232.6	1.019	-7.94	-8.10
ORTHO-	10	265.6	0.963	-8.49	-8.17
TOLUATE		$\Delta\lambda$[a]	0.856	-8.30	-7.10
METHYL		234.7	0.743	-8.30	-6.17
2,6-DIMETHYL	10	269.0	0.819	-8.43	-6.90
BENZOATE		$\Delta\lambda$[a]	0.794	-8.45	-6.70

[a] Log I vs. $-H_o$ plots calculated on the basis of the difference between the extinction coefficients at the other two wavelengths.

TABLE 7: AVERAGE VALUES FOR PROTONATION PARAMETERS OF BENZOATE ESTERS IN SULPHURIC ACID AT 10° AND 25°C

ESTER	T(°C)	m	pK'_{SH^+}	pK_{SH^+}
METHYL	10	0.891	-8.46	-7.53
BENZOATE	25[a]	0.890	-8.08	-7.19
	25[b]	0.905	-8.15	-7.38
METHYL	10	0.773	-7.88	-6.09
PARA-TOLUATE	25[a]	0.774	-7.53	-5.83
	25[c]	0.787	-7.60	-5.99
METHYL	10	0.946	-8.24	-7.79
ORTHO-TOLUATE	25[a]	0.946	-7.87	-7.44
	25[c]	0.962	-7.95	-7.64
METHYL	10	0.785	-8.39	-6.59
2,6-DIMETHYL	25[a]	0.786	-8.02	-6.30
BENZOATE	25[c]	0.800	-8.09	-6.47

[a] pK'_{SH^+}, pK_{SH^+} obtained from equation: $H_o(25^oC) = 0.951\ H_o(10^o) - 0.0373$
'm' calculated from: $pK_{SH^+}(25^o)/pK'_{SH^+}(25^o)$

[b] These values for methyl benzoate were obtained directly at 25°C.

[c] These values are those from (a), corrected for the difference between (a) and (b) for methyl benzoate at 25°C. These results, together with (b) for methyl benzoate, were the ones used for all further calculations.

It is clear, from the values listed in Table 7 that there is a considerable spread in pK_{SH}^+ values obtained from the measurements at different wavelengths. This is mainly due to variation in the 'm' values, the slopes of the ionisation plots of log I vs. $-H_o$. It is of some concern, since it is difficult to understand the reasons for this. In most cases, these ionisation plots gave good straight lines for 8-10 points over the $|\log I| < 1$ range. There is much better internal agreement, for each ester, of the pK'_{SH}^+ values, which differ from one another by no more than 0.4 logarithmic units at worst, and usually it is better than this. Nevertheless, the consequences of this relatively poor agreement of pK_{SH}^+ values are not very serious. The data treatments for which these ionisation parameters are needed - 'r' plots and transition state activity coefficient behaviour - rely on them to only a minor extent, and then only in the very concentrated acid region. The second-order rate constants obtained for these rate-acidity correlations may differ slightly, depending on the 'm' and pK_{SH}^+ values used. But the conclusions concerning the behaviour of the esters in varying acid media and how and when they change mechanisms is unaffected, within limits, by this lack of good agreement. In any case, the possible variation of the experimentally observed values for the ionisation parameters from their "true"

values is reduced by averaging all three values obtained for each ester.

One further adjustment was made. There was a wider range of acid concentration giving linear ionisation plots for the measurements with methyl benzoate at 25°C than at 10°C. It was therefore felt that the former should be given greater weight, in terms of its reliability. As a result, after first converting the parameters obtained for all the esters at 10°C to 25°C, they were corrected by the same small variation as was found between the two sets of values for methyl benzoate at 25°C. These final values, shown in Table 7, were the ones used for further calculations in the rate-acidity correlations.

Finally, Bunnett and Olsen[30a] derived a different linear-free-energy relationship between log I and H_o,

$$\log I + H_o = \phi(\log [H^+] + H_o) + pK_{SH}^+$$

wherein ϕ expresses the response of the protonation equilibrium to changing acid concentration, and pK_{SH}^+ refers to the true thermodynamic equilibrium constant for the reaction at infinite dilution in water. Positive values of ϕ imply that the 'm' value from the log I vs. H_o plot are less than 1, and negative ϕ values mean m > 1. Their treatment on many different sets of data provide no clear distinction as to which method is

preferred. Nevertheless, the data for methyl benzoate at both temperatures were treated by this method, and the results are shown as follows:

T(°C)	λ(nm.)	ϕ	m	pK_{SH}^+ (B-O)[a]	pK_{SH}^+ (A.F.)[b]
10	232.0	0.162	0.845	-7.22	-7.09
	261.5	0.219	0.791	-6.96	-6.79
	Δλ	-0.039	1.037	-8.67	-8.70
25	232.0	0.151	0.873	-7.02	-7.04
	261.5	0.070	0.934	-7.71	-7.69
	Δλ	0.096	0.908	-7.49	-7.42

[a]Calculated from the Bunnett-Olsen treatment

[b]Calculated from the Acidity Function treatment.

There is, in general, very good agreement between the two methods, and the most serious difference, for 10°C at 261.5 nm., is less than 3%, within experimental error. It may also be noted that there is a linear relationship between the ϕ and m values obtained, a result that probably is valid for a given class of organic base, but unlikely to be true in comparing compounds from different classes. Since there is no obvious improvement from the Bunnett-Olsen treatment, further pK_{SH}^+ calculations using their relation were not determined, and the data used were those obtained via the acidity-function method (Table 7).

II. KINETICS OF HYDROLYSIS OF THE BENZOATE ESTERS

The rates of hydrolysis of the four esters - methyl benzoate (MB), methyl para-toluate (MPT), methyl ortho-toluate (MOT) and methyl 2,6-dimethyl benzoate (2,6-MDMB) - were measured at a number of different temperatures over as wide a range of acid concentration as possible. At 25°C, the reaction rates of none of the esters could be conveniently studied in <60% H_2SO_4. The half-lives of hydrolysis were extremely long, and the absorbance changes were usually very small, making accurate rate determinations very difficult. In the more concentrated acid region, the hydrolysis of MOT and 2,6-MDMB posed their own special problems, which will be discussed later.

Pseudo-first order kinetics were observed in all cases, the acid concentration being essentially constant throughout the course of each ester hydrolysis. The rate constants for each ester, at the temperatures studied, are listed in Table 8(a-d), together with the data of Lane and co-workers[35] for methyl benzoate at 25°C. These represent, in general, the mean of at least two independent kinetic runs, and in many cases, especially at the maxima and minima in the rate profiles, at least 5 or 6 independent runs. This was due to there not always being good agreement for multiple runs in a

given acid. As a result, once all the data were collected for each substrate at various temperatures, the rate constants were fitted to give a smooth curve over the acid range studied and linear behaviour in the Arrhenius-type activation plots. The data thus obtained for acid regions where the reaction rate was too slow to be easily measured are included in the tables.

All the data were plotted (cf. Fig. 9 (a-d)) using 6 + log k_ψ (k_ψ, in $min.^{-1}$) as the ordinate, rather than k_ψ itself,* since there is a wide variation in rate constants over the whole acid range, especially for the ortho-substituted esters, MOT and 2,6-MDMB. The rate profiles for the four esters at 25°C are shown in Fig. (10), with the data being given in Table (9). A common feature of A-2 reactions is a maximum in their rate-acidity profiles. This is the net result of an increase in rate as the reactive species, the protonated substrate, increases in concentration, and a rate retardation caused by the decreasing activity of water. There are many examples of A-2 reactions which do not exhibit this behaviour, usually for reasons of substrate structure, but its presence is a good indication of a bimolecular acid-catalysed reaction.

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*The data in Table 8 (a-d) is given in both k_ψ and log k_ψ. The data, plotted using k_ψ at 25°C, will be given for each ester as they are discussed in turn.

TABLE 8a: RATE DATA FOR METHYL BENZOATE HYDROLYSIS IN H_2SO_4

w/w% H_2SO_4	25.0°C		37.0°C		45.0°C	
	10^3k_ψ [a]	$\log k_\psi$ [b]	10^3k_ψ [a]	$\log k_\psi$ [b]	10^3k_ψ [a]	$\log k_\psi$ [b]
40.88			2.57[e]	1.41	3.75[e]	1.57
42.04	0.341[c]	0.533[d]				
46.0	0.459	0.662[d]	1.83	1.26[d]	4.27	1.63[d]
50.0	0.609	0.785[d]	2.39	1.38[d]	5.62	1.75[d]
51.04			3.43[e]	1.54	6.18[e]	1.79
52.93	0.702[c]	0.846[d]				
54.0	0.724	0.860[d]	2.89	1.46[d]	6.78	1.83[d]
58.0	0.830	0.919[d]	3.24	1.51[d]	7.57	1.88[d]
60.0	0.855	0.932[d]			7.71	1.89[d]
60.46			3.28[e]	1.52[d]		
64.0	0.847	0.928[d]	3.26	1.51[d]	7.52	1.88[d]
65.03	0.813[e]	0.910				
67.39	0.755[e]	0.878	2.91[e]	1.46		
69.76	0.690[e]	0.839				
70.29	0.659[e]	0.819				
70.84			2.98[e]	1.48		
71.60			2.27[e]	1.36[d]		
72.88	0.487[e]	0.688	2.02	1.31[d]		
73.75	0.448[c]	0.651				
75.09	0.374[e]	0.573	1.64	1.22[d]		
77.61	0.270[e]	0.431[d]	1.35	1.13[d]		
80.0	0.269	0.429[d]	1.50	1.18[d]		
81.41	0.289[e]	0.461				
82.09			2.24[e]	1.35		
82.68	0.380[e]	0.579				
83.41			2.50[e]	1.40[d]		
85.16	0.628[e]	0.798	4.07	1.61[d]		
87.67	1.20[e]	1.08[d]	7.94	1.90[d]		
88.0	1.28	1.11[d]	8.81	1.95[d]		
89.63	1.99[e]	1.30[d]				
90.0	2.23	1.35[d]	15.9	2.20[d]		

See Table 8d (p. 144) for footnote explanations.

TABLE 8a (CONTINUED)

w/w% H_2SO_4	50.0°C		54.9°C		60.1°C	
	10^3k_ψ [a]	$\log k_\psi$ [b]	10^3k_ψ [a]	$\log k_\psi$ [b]	10^3k_ψ [a]	$\log k_\psi$ [b]
35.27	3.97[e]	1.60				
40.00					12.0[e]	2.08
40.88			9.50[e]	1.98[d]		
42.0	5.21[e]	1.72[d]	8.39	1.92[d]	13.8	2.14[d]
45.38	6.82[e]	1.83[d]				
46.0	7.16	1.86[d]	11.6	2.06[d]	19.1	2.28[d]
50.0			15.3	2.18[d]	25.2	2.40[d]
50.38	9.60[e]	1.98				
51.04			15.1[e]	2.18[d]		
54.0	11.4	2.06[d]	18.5	2.27[d]		
58.0	12.6[e]	2.10[d]	20.5	2.31[d]		
60.16	10.4[e]	2.02[d]				
62.0	12.7[e]	2.10[d]	20.6	2.31[d]		
65.03	12.0[e]	2.08				
67.39	11.2[e]	2.05				
70.29	9.85[e]	1.99				
72.88	8.41[e]	1.93				
75.09	7.61[e]	1.88				
77.61	5.79[e]	1.76[d]				
80.0	8.32	1.92[d]				
82.0	11.9	2.08[d]				
84.0	19.1	2.28[d]				

w/w% H_2SO_4	66.4°C		w/w% H_2SO_4	67.0°C	
	10^3k_ψ [a]	$\log k_\psi$ [b]		10^3k_ψ [a]	$\log k_\psi$ [b]
40.88	21.5[e]	2.33[d]	60.46	64.5[e]	2.81[d]
42.0	24.8	2.39[d]	64.0	61.5[e]	2.79[d]
46.0	34.4	2.54[d]	69.03	53.2[e]	2.73
51.04	41.3[e]	2.62[d]	72.45	46.9[e]	2.67
54.0	55.2	2.74[d]	76.53	39.7[e]	2.60
58.0	60.4	2.78[d]	78.37	47.1[e]	2.67[d]
			80.0	64.4	2.81[d]
			82.97	134[e]	3.13
			85.58	243[e]	3.39[d]
			88.0	598	3.78[d]

FIGURE 9a

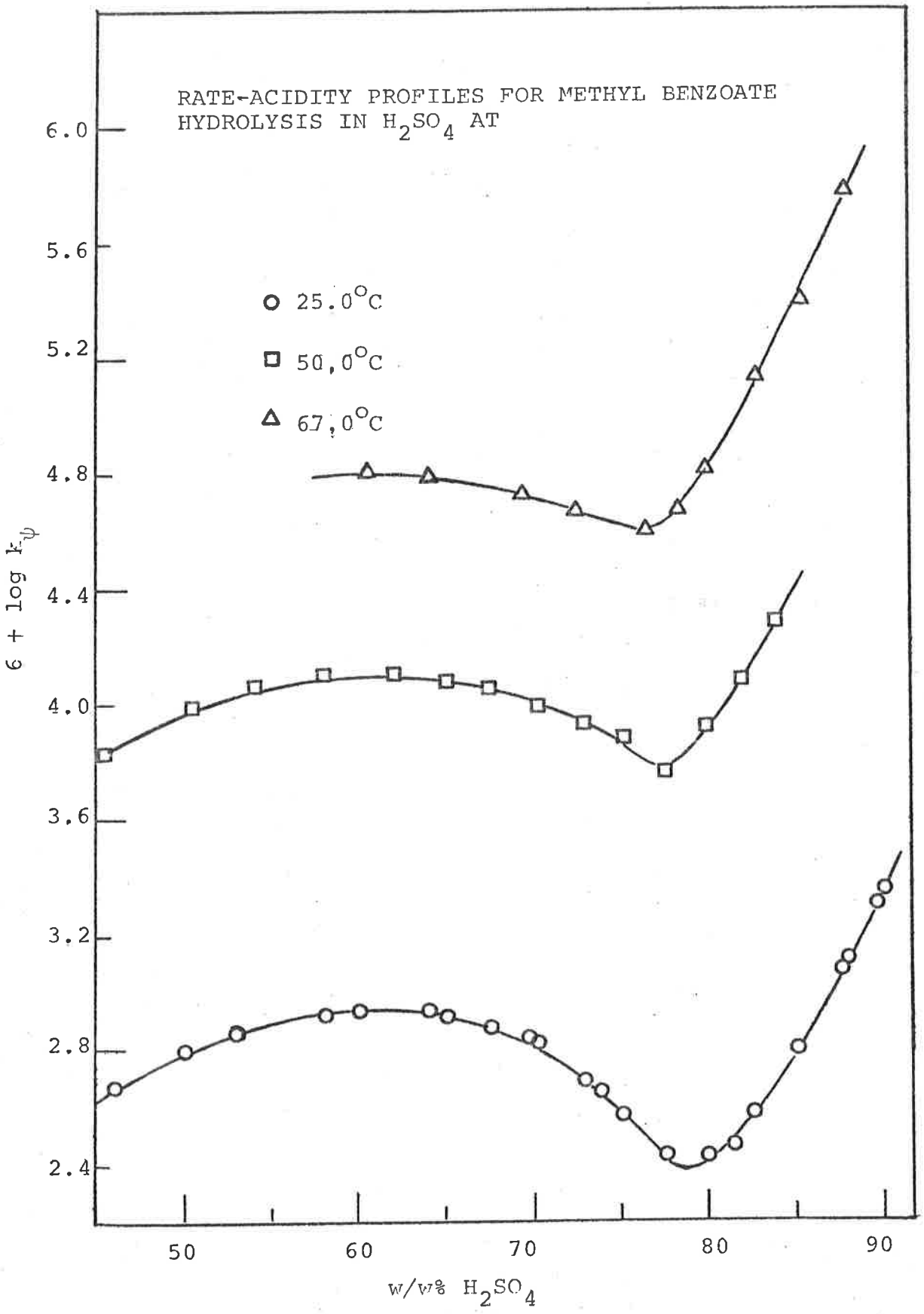
RATE-ACIDITY PROFILES FOR METHYL BENZOATE HYDROLYSIS IN H_2SO_4 AT
25.0°C
50.0°C
67.0°C
6 + log k_ψ
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
50
60
70
80
90
w/w% H_2SO_4

TABLE 8b: RATE DATA FOR METHYL P-TOLUATE HYDROLYSIS IN H_2SO_4

w/w% H_2SO_4	25.0°C		45.0°C		50.1°C	
	10^3k_ψ [a]	$\log k_\psi$ [b]	10^3k_ψ [a]	$\log k_\psi$ [b]	10^3k_ψ [a]	$\log k_\psi$ [b]
20.39			0.523[e]	0.719[d]		
25.0	0.063	-0.201[d]	0.780	0.892[d]	1.41	1.15[d]
30.97			1.39[e]	1.14[d]		
35.0	0.211	0.324[d]	1.85	1.27[d]	3.13[e]	1.50[d]
40.0	0.358	0.554[d]			4.51[e]	1.65
40.88			3.00[e]	1.48[d]		
44.96	0.562	0.750[d]	3.89	1.59[d]	6.22[e]	1.79
50.05	0.741	0.870[d]	5.01[e]	1.70[d]	7.68[e]	1.89
51.04			5.03[e]	1.70[d]		
54.68	0.789	0.897[d]	5.58	1.75[d]	8.74[e]	1.94[d]
57.5	0.711	0.852[d]	5.57	1.75[d]	9.14[e]	1.96[d]
59.56					9.18[e]	1.96
60.46	0.618[e]	0.791[d]	5.46[e]	1.74[d]		
62.58	0.573[e]	0.758[d]	5.25	1.72[d]	8.91	1.95[d]
65.0	0.467	0.669[d]	5.01	1.70[d]		
65.66					7.89[e]	1.90
66.03	0.393[e]	0.594				
66.27			5.11[e]	1.71		
68.93	0.352[e]	0.547[d]			8.13	1.91[d]
70.0	0.295	0.470[d]	4.27[e]	1.63[d]	8.05	1.91[d]
71.60			4.39[e]	1.64[d]		
72.5	0.270	0.431[d]	4.58	1.66[d]	8.91	1.95[d]
75.0	0.337	0.528[d]	6.10[e]	1.79[d]	12.2[e]	2.09[d]
76.47	0.438[e]	0.641[d]	8.12[e]	1.91[d]	15.7[e]	2.20[d]
77.5	0.557	0.746[d]	10.4	2.02[d]	20.8[e]	2.32[d]
79.60					39.0[e]	2.59
80.19	1.23[e]	1.09	21.9[e]	2.34[d]		
82.97			32.0[e]	2.51	110	3.04[d]
83.13	2.09[e]	1.32				
83.49					127[e]	3.10
85.0			103	3.01[d]		
85.58	4.68[e]	1.67			262[e]	3.42
88.59	8.41[e]	1.92				

TABLE 8b (CONTINUED)

w/w% H_2SO_4	54.6°C		60.1°C		66.5°C	
	$10^3 k_\psi$ [a]	$\log k_\psi$ [b]	$10^3 k_\psi$ [a]	$\log k_\psi$ [b]	$10^3 k_\psi$ [a]	$\log k_\psi$ [b]
20.39	1.69[e]	1.23			7.02[e]	1.85[d]
25.0	2.39	1.38	4.32	1.64[d]	8.45	1.93[d]
30.97	4.52[e]	1.65[d]	6.31	1.80[d]	11.7[e]	2.07
35.0	4.82	1.68[d]	8.11	1.91[d]	14.6	2.16
40.00			11.6[e]	2.06		
40.88	7.34[e]	1.87[d]			19.1[e]	2.28[d]
45.0	8.99	1.95[d]	14.3	2.16[d]	23.9	2.38[d]
50.0			17.8	2.25[d]		
51.04	11.4[e]	2.06[d]			34.9[e]	2.54
52.5	12.2	2.09[d]	19.5	2.29[d]		
54.68			22.6[e]	2.35		
55.0	12.9	2.11[d]			35.9	2.56[d]
57.5	13.6	2.13[d]	22.4	2.35[d]	40.0	2.59[d]
60.0	14.0	2.15[d]	23.5	2.37[d]	41.9	2.62[d]
80.0			162	3.21[d]		
82.5			372	3.57[d]		
85.21			692[e]	3.84		

w/w% H_2SO_4	70.0°C		75.0°C	
	$10^3 k_\psi$ [a]	$\log k_\psi$ [b]	$10^3 k_\psi$ [a]	$\log k_\psi$ [b]
72.5	98.9	3.00[d]	173	3.24[d]
75.0	145	3.16[d]	259	3.41[d]
77.5	251	3.40[d]	449	3.65[d]
79.60	447[e]	3.65[d]	852[e]	3.93[d]
82.5	1340	4.13[d]	2480	4.40[d]
85.0	3450	4.54	6560	4.82[d]

FIGURE 9b

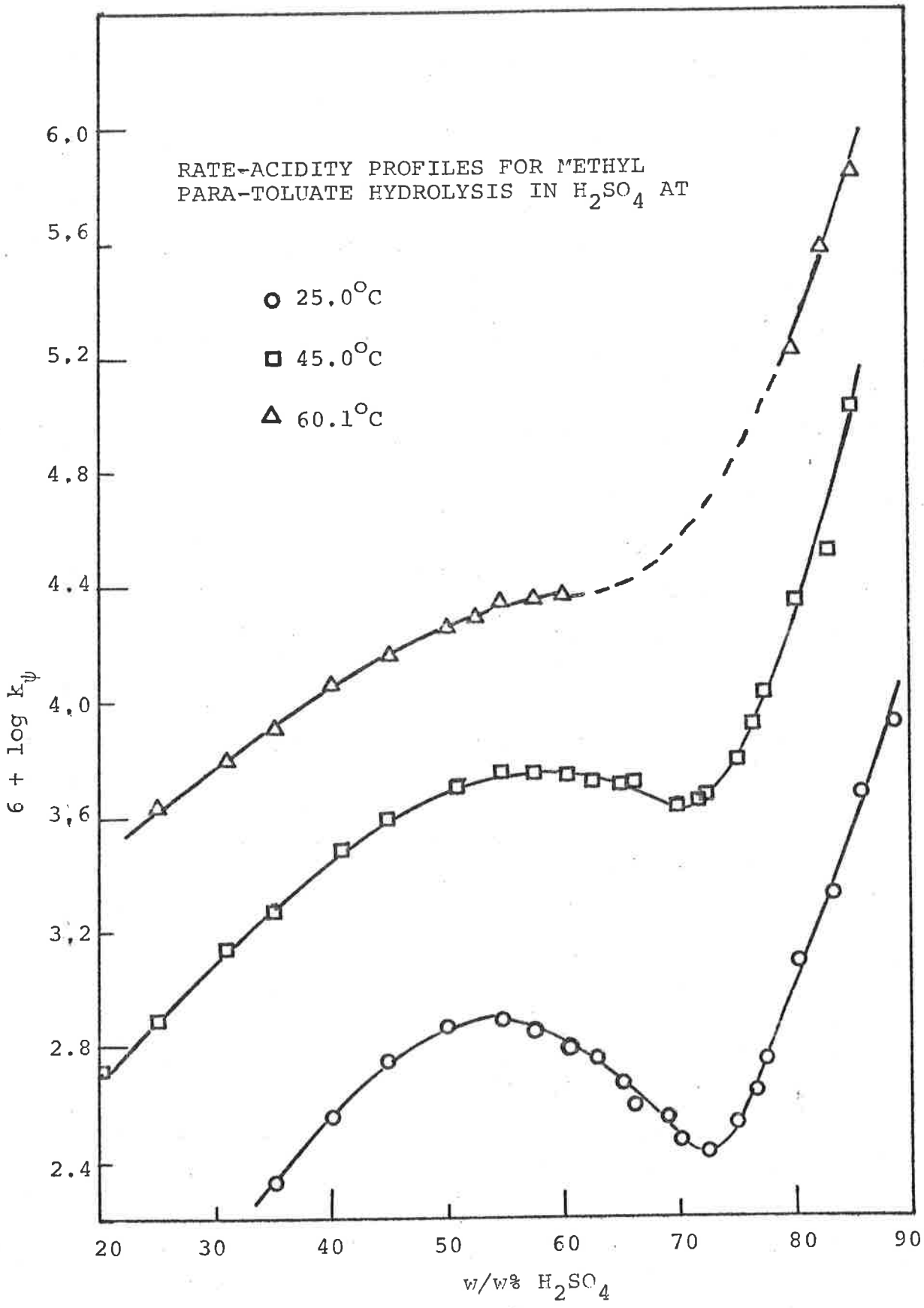
RATE-ACIDITY PROFILES FOR METHYL PARA-TOLUATE HYDROLYSIS IN H_2SO_4 AT
25.0°C
45.0°C
60.1°C
6 + log k_ψ
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
20
30
40
50
60
70
80
90
w/w% H_2SO_4

TABLE 8c: RATE DATA FOR METHYL O-TOLUATE HYDROLYSIS IN H_2SO_4

w/w% H_2SO_4	25.0°C		37.0°C		44.9°C	
	10^3k_ψ [a]	$\log k_\psi$ [b]	10^3k_ψ [a]	$\log k_\psi$ [b]	10^3k_ψ [a]	$\log k_\psi$ [b]
30.97					1.03[e]	1.01
35.25					1.03[e]	1.01
40.00	0.143	0.155[d]	0.535	0.728[d]		
40.88					1.25[e]	1.10[d]
44.0	0.174	0.240[d]	0.634	0.802[d]	1.41	1.15[d]
48.0	0.191	0.282[d]	0.724	0.860[d]	1.66	1.22[d]
52.0	0.187	0.273[d]	0.791	0.898[d]	1.91	1.28[d]
56.0	0.172	0.235[d]	0.828	0.918[d]	2.14	1.33[d]
60.0	0.159	0.202[d]	0.891	0.950[d]		
60.46					3.02[e]	1.48
64.0	0.224	0.350[d]	1.26	1.10[d]	3.80	1.58[d]
65.03	0.328[e]	0.516				
66.27			2.47[e]	1.39		
67.39	0.356[e]	0.551	2.21[e]	1.34[d]		
68.0	0.378	0.578[d]	2.29	1.36[d]	6.92	1.84[d]
69.03	0.717[e]	0.856			7.62[e]	1.88
70.29	0.600[e]	0.778				
70.68					13.3[e]	2.12
71.60			6.08[e]	1.78		
72.0	1.07	1.03[d]	6.92	1.84[d]	21.9	2.34[d]
72.45	1.70[e]	1.23				
74.03			15.7[e]	2.20		
75.09	3.00[e]	1.48				
75.75					125	3.10
77.02			46.8[e]	2.67		
77.61	7.93[e]	1.90				
79.44			120[e]	3.08		
80.28	22.1[e]	2.34	175[e]	3.24		
82.68	74.9[e]	2.87				
83.95			1170[e]	4.07		
85.16	224[e]	3.35				
87.67	453[e]	3.66				

TABLE 8c: (CONTINUED)

w/w% H_2SO_4	50.1°C		54.9°C		57.8°C	
	10^3k_ψ [a]	$\log k_\psi$ [b]	10^3k_ψ [a]	$\log k_\psi$ [b]	10^3k_ψ [a]	$\log k_\psi$ [b]
20.18	0.934[e]	0.970			2.05[e]	1.31[d]
24.0	1.17	1.07[d]	1.95	1.29[e]	2.63	1.42[d]
28.0	1.38[e]	1.14[d]	2.34	1.37[d]	3.16[e]	1.50[d]
30.41	1.73[e]	1.24			3.59[e]	1.56[d]
35.25	1.65[e]	1.22[d]	2.82	1.45[d]	3.80[e]	1.58[d]
40.00	2.00	1.30[d]			3.91[e]	1.59
40.88			3.08[e]	1.49[d]		
44.0	2.34	1.37[d]	3.63	1.56[d]	4.68	1.67[d]
45.38	2.42[e]	1.38[d]				
48.0	2.69	1.43[d]	4.47[e]	1.65[d]	5.89	1.77[d]
51.04			5.41[e]	1.73[d]		
52.0	3.31	1.52[d]	5.50	1.74[d]	7.41	1.87[d]
56.0	3.98	1.60[d]	6.92	1.84[d]	9.55	1.98[d]
68.0	13.8[e]	2.14[d]				
72.88	45.1[e]	2.65				
75.09	87.5[e]	2.94				
77.61	323[e]	3.51				

w/w% H_2SO_4	60.1°C		66.4°C		70.0°C	
	10^3k_ψ [a]	$\log k_\psi$ [b]	10^3k_ψ [a]	$\log k_\psi$ [b]	10^3k_ψ [a]	$\log k_\psi$ [b]
24.0	3.31	1.52[d]	6.17	1.79[d]	8.71	1.94[d]
28.0	3.98	1.60[d]	7.41	1.87[d]	10.5	2.02[d]
30.41	4.53[e]	1.66[d]				
32.0	4.47	1.65[d]	8.32	1.92[d]	11.7	2.07[d]
36.0	4.79	1.68[d]	8.71	1.94[d]	12.0	2.08[d]
40.0	4.36[e]	1.64			12.6	2.10[d]
40.88			9.22[e]	1.96[d]		
44.0			10.5	2.02[d]	14.1	2.15[d]
44.96	6.23[e]	1.79[d]				
48.0	7.19	1.86[d]	12.9	2.11[d]	17.8	2.25[d]
50.05	7.23[e]	1.86			27.1[e]	2.43
51.04			16.4[e]	2.21		
54.68	11.0[e]	2.04[e]				
56.0	12.1	2.08[e]	24.1	2.38[d]	34.7	2.54[d]

FIGURE 9c

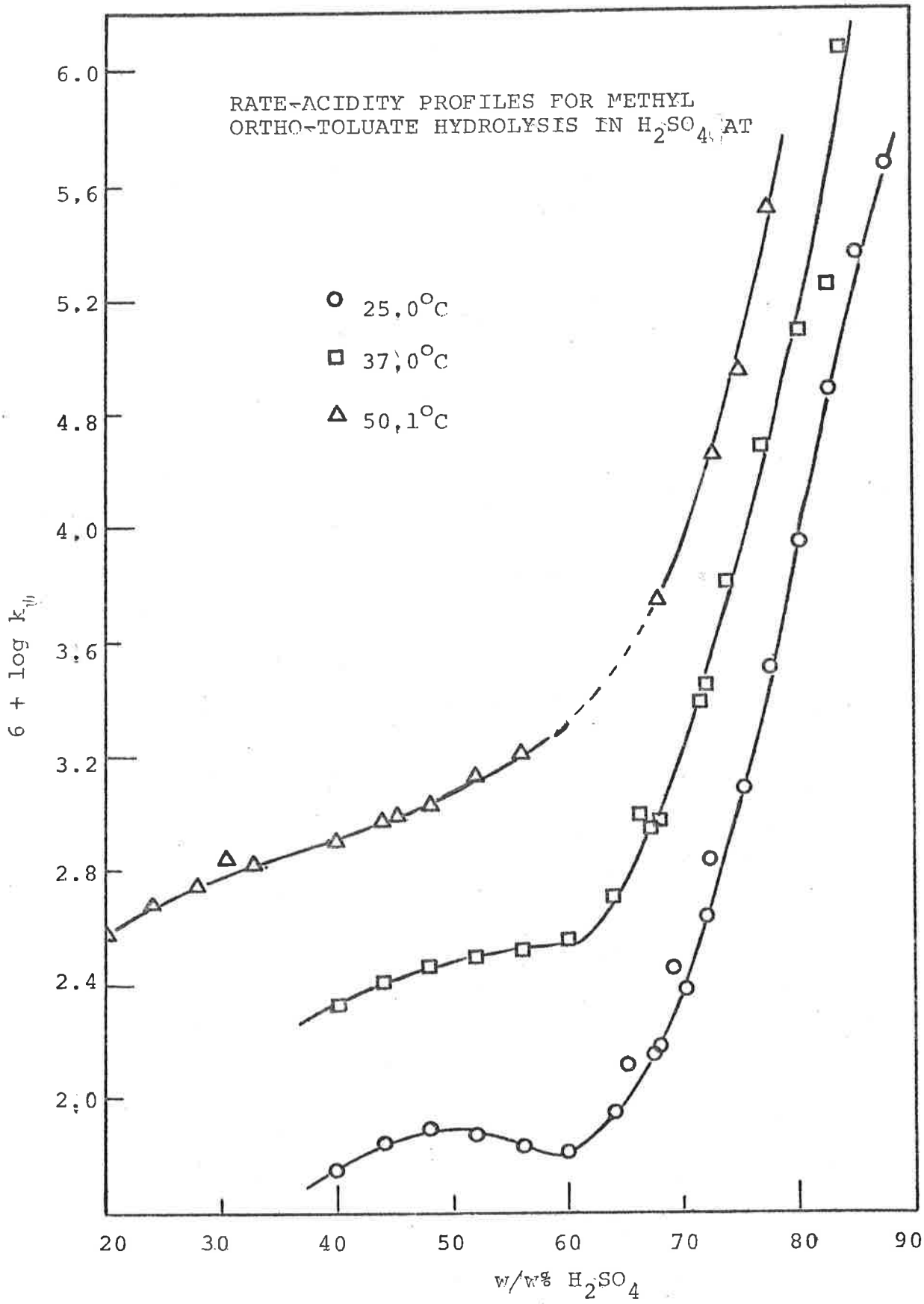
RATE-ACIDITY PROFILES FOR METHYL ORTHO-TOLUATE HYDROLYSIS IN H_2SO_4 AT
25.0°C
37.0°C
50.1°C
6 + log k_ψ
6.0
5.6
5.2
4.8
4.0
3.6
3.2
2.8
2.4
2.0
20
30
40
50
60
70
80
90
w/w% H_2SO_4

TABLE 8d. RATE DATA FOR METHYL 2,6-DIMETHYL BENZOATE HYDROLYSIS IN H_2SO_4

w/w% H_2SO_4	25.0°C		37.0°C		45.0°C	
	10^3k_ψ [a]	$\log k_\psi$ [b]	10^3k_ψ [a]	$\log k_\psi$ [b]	10^3k_ψ [a]	$\log k_\psi$ [b]
54.0	0.033	1.52[2]	0.156	2.19[d]	0.412	2.62[d]
55.02	0.041	1.61[d]	0.195	2.20[d]	0.521	2.72[d]
58.0	0.081	1.91[d]	0.415	2.62[d]	1.20	3.08[d]
60.16	0.154[e]	2.19	1.42[e]	3.15		
60.46					4.18[e]	3.62
62.0	0.235	2.37[d]	1.51	3.18[d]	4.90	3.69[d]
65.03	0.614[e]	2.79				
66.0	0.863	2.94[d]	7.24	3.86[d]		
66.27					3.06[e]	4.49
67.39	2.12[e]	3.33	13.0[e]	4.11		
70.0	3.94	3.60[d]			240	5.38[d]
70.29	5.88[e]	3.77	42.4[e]	4.63		
70.84			72.9[e]	4.86		
72.0	8.24	3.92[d]	145	5.16[d]	902	5.96[d]
72.88	14.3[e]	4.16				
74.0	20.6	4.31[d]	537	5.73[d]	3960	6.60[d]
75.09	36.4[e]	4.56				
76.53	69.9[e]	4.84				
77.61	126[e]	5.10				
80.28	580[e]	5.76				
81.41	1560[e]	6.19				
82.68	1760[e]	6.25				

TABLE 8d (CONTINUED)

w/w% H_2SO_4	50.1°C		60.3°C		75.1°C	
	10^3k_ψ [a]	$\log k_\psi$ [f]	10^3k_ψ [a]	$\log k_\psi$ [f]	10^3k_ψ [a]	$\log k_\psi$ [f]
20.18					0.264 [e]	2.42 [d]
25.0	0.016	1.20 [d]	0.055	1.74 [d]	0.337 [e]	2.53 [d]
30.41					0.499 [e]	2.70 [d]
34.0	0.035	1.54 [d]	0.115	2.06 [d]	0.658	2.82 [d]
38.0	0.053	1.72 [d]	0.181 [e]	2.26 [d]	0.946	2.98 [d]
40.0	0.069	1.84 [d]	0.224 [e]	2.35 [d]	1.39 [e]	3.14 [d]
42.0	0.091	1.96 [d]	0.289	2.46 [d]	1.50	3.18 [d]
46.0	0.162 [e]	2.21 [d]	0.501	2.70 [d]	2.50	3.40 [d]
50.05	0.327 [e]	2.51 [d]	1.00 [e]	3.00 [d]	4.68	3.67 [d]
54.0	0.746 [e]	2.87 [d]	2.30	3.36 [d]	10.6	4.03 [d]
55.02	0.918 [e]	2.96 [d]	3.09	3.49 [d]		
58.0	2.29 [e]	3.36 [d]	7.60	3.88 [d]		
60.16	4.83 [e]	3.68 [d]				
62.0	10.0 [e]	4.00 [d]				
65.03	48.6 [e]	4.69 [d]				
68.0	180	5.26 [d]				
70.0	630	5.80 [d]				

[a] Units of $min.^{-1}$

[b] Values given as $(4 + \log k_\psi)$.

[c] Reference 35.

[d] From activation parameter plots.

[e] This study.

[f] Values given as $(6 + \log k_\psi)$.