THESIS

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MASTER OF SCIENCE WITH HONOURS

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- D.I. STEDMAN
THE RATES OF SOLVOLYSIS
OF SOME $p$- AND $m$-SUBSTITUTED
$t$-BUTYLPHENYL CARBENYL CHLORIDES.
## CONTENTS

### INTRODUCTION.
1. Steric effects in aralkyl chlorides.  
2. The Hammett equation.  
3. The present investigation.  

### EXPERIMENTAL.
1. General.  
2. Preparation of the carbinols.  
3. Preparation of the carbinyl chlorides.  
4. Preparation of reagents.  
5. Kinetic procedures.  
6a. Calculation of rate constants.  
6b. Experimental accuracy and probable errors.  

### RESULTS.

### DISCUSSION.
1. Comparison of results.  
2. The mechanism and course of the reaction.  
3. A study of the rates with the Hammett equation.  
4. The role of steric effects.  

### REFERENCES.
Some \( m \)- and \( p \)-substituted \( t \)-butylphenyl carbinyl chlorides have been prepared, and their rates of solvolysis in aqueous ethanol have been determined. By applying the Hammett equation, it has been shown that there is no steric inhibition of mesomerism in the intermediate carbonium ions formed in the reactions. The role of steric effects in the solvolysis has been discussed, and explanations for the slow rates of reaction have been considered.
INTRODUCTION.

1. Steric effects in aralkyl chlorides.

An accepted stereochemical rule is that a conjugated system tends to planarity, so that its mesomeric interaction is maximised and its electronic potential energy thereby minimised. If, for some reason, coplanarity is not achieved, mesomerism will be inhibited. An example of such inhibition is provided in 2,3-benzocyclooctanone (I), where the saturated ring is of such size that it deforms, and the bond marked A twists out of planarity to reduce mesomerism between the carbonyl double bond and the aromatic system. Steric promotion of mesomerism is also readily possible. In 2,2-dimethylindanone (II), the small size of the saturated ring ensures its planarity, whereas for pivalophenone (III), there is sufficient steric interaction to reduce mesomerism, this being deduced from the spectra.

The results of these inhibitions and promotions on chemical reaction rates and processes can be quite complex, for either the initial or the transition state or both may be stabilised or destabilised. A reaction may be aided, hindered or even prevented by such effects. In general, increased stabilisation of the transition state will, if uncomplicated, lead to an increased reaction rate.

\[
\begin{align*}
\text{(I)} & \\
\text{(II)} & \\
\text{(III)} &
\end{align*}
\]

This thesis is concerned largely with a limited branch of nucleophilic substitution of solvolysis type. Two varieties of such substitution have been distinguished in the theory on the basis of mechanistic differences: unimolecular or bimolecular (\(S_N^1\) and \(S_N^2\) respectively). \(S_N^1\) reactions involve a rate-determining heterolysis to form a reactive carbonium ion (which is approximately the transition state), while \(S_N^2\) reactions are pictured as synchronous heterolysis of
expelled group and attack of nucleophilic reagent, both expulsion and attack
being rate-determining.

Where large molecules are concerned, steric hindrance in the
transition state of the $S_N2$ reaction is possible, as space is required for
the entering nucleophile. In the $S_N1$ reaction, steric relief in forming
the transition state may be conceived, when a large and strained tetra-
hedrally-bonded molecule becomes a planar ion with larger bond angles.
Thus, steric hindrance to the bimolecular reaction and steric promotion
of the unimolecular mechanism could be expected in suitable cases, and there
is in fact abundant evidence for both effects.4

Baddeley and Chadwick (1951) pointed out5, however, that the
opposite effects can be observed, i.e. steric promotion of the bimolecular
and steric hindrance to the unimolecular reaction. Aryl systems are
subject to fairly stringent steric and resonance requirements, and for
these some solvolyses rates have been presented as evidence for steric
hindrance to the $S_N1$ reaction. The figures (IV) to (VII) represent the
carbonium ions concerned, with ethanolation rates given for $0^\circ C$. The rate
increase from (IV) to (V) is attributed to steric promotion of mesomerism,
for in (IV) the ionisation is hindered by the energy required to bring the
sidechain into the aromatic ring plane, but in (V) the saturated ring is
already fixed in plane in the initial state. However, the rate decrease
in the trend (V) to (VII) is attributed to increasing steric inhibition
of mesomerism due to increased nonplanarity of the saturated ring (of ketones
(I) and (II) for the same effects.). The slower rate in forming (VIII),
compared with (IX), is explained in a similar way.

Further work (1954)6 on steric retardation in unimolecular
reactions led to an interesting rate sequence in ethanolation of a series of
aryl chloride ROH+Ph: R = Me > Et > i-Pr > t-Bu. The corresponding
activation energies are 20.4, 20.7, 22.9 and 25.4 k.cal/mole. It was
interpreted that if these energy changes are due only to variation in
steric effect, this provides further evidence of steric hindrance to the
$S_N1$ reaction, the hindrance presumably involving reduction of conjugation in
the ions along the series.

\[
\begin{align*}
\text{Me}_2^+ & \quad \text{Me}_2^+ \\
\text{H}^+ & \quad \text{H}^+ \\
\text{Me}_2^+ & \quad \text{Me}_2^+
\end{align*}
\]

(IV) (V) (VI) (VII)

\[10^7 k (\text{min}^{-1}) \quad 66 \quad 4000 \quad 1070 \quad 23.5\]

(VIII) (IX)

More recent work \(^2\) (1958) has, however, cast doubt upon the view that steric hindrance is the main cause of the observed rate trends of 1954. New rate sequences were observed where steric effects on mesomerism were fixed for a given series of chlorides, A and B. The obvious explanation for these sequences is that of decreasing hyperconjugative stabilisation of the transition states along each series. This view was confirmed in observing the \(13\%\) rate reduction in the solvolysis of (XI) compared with (X). It had been recognised \(^2\) that hyperconjugation and solvation effects could account for the 1954 trends, but these had initially been considered insignificant in view of the known comparative insensitivity of the solvolysis rates of the chlorides \(\text{RMe}_2\text{Cl}\) to changes in \(\text{R}\).

To gain a more precise understanding of the role of steric effects in aryl carbonium ions, the unimolecular solvolysis of a set of \(m\)- and \(p\)-substituted \(t\)-butylphenyl carbinyl chlorides has been studied. These were chosen because the ease in attaining planarity in the carbonium ion

Series A

\[
\begin{align*}
&> \\
&> \\
&>
\end{align*}
\]
intermediate (XII) would be expected to be relatively low when R is a t-butyl substituent; i.e. any steric effects would be emphasised. The results were analysed in using the Hammett equation as described below.

2. The Hammett equation.

It was discovered in the 1950's that certain side-chain reactions of \( E \) - and \( p \) -substituted benzene derivatives gave results which empirically fitted a relation now known as the Hammett equation \( \log \frac{k}{k_0} = \sigma \rho \):

\[
\log k/k_0 = \sigma \rho
\]

\( k \) is the rate constant for a substituted compound,
\( k_0 \) is the rate constant for the unsubstituted compound,
\( \rho \) is called the reaction constant, and
\( \sigma \) is the substituent constant.

\( \rho \) is specific for the side-chain reaction being studied and depends on its conditions, whilst \( \sigma \) pertains only to the substituent which gives the rate constant \( k \). In effect, \( \rho \) measures the susceptibility of the reaction to electronic effects of substituents, and \( \sigma \) records the extent to which a given substituent may modify the electronic structure of its host molecule.

Convenience led Hammett to take \( \rho \) as unity for the dissociation constants of benzoic acids in water at 25\(^\circ\)C, and from this standard, \( \sigma \) values were defined for the substituents for which suitable data were available.

Although the equation was empirically developed, a theoretical basis has been proposed by Taft \(^9\), and is summarised below with modified symbolism.
The transition state theory of reaction rates states that rate constants follow an equation which, with thermodynamic theory, leads to the relation,

\[ k = \frac{kT}{h} e^{-\Delta G^+/RT} \]  

Thus, \[ \ln k = \ln \left( \frac{kT}{h} \right) - \frac{\Delta G^+}{RT} \]  

This means that the reaction rate \( k \) is determined only by the free energy of activation \( \Delta G^+ \), and the absolute temperature \( T \), the other symbols being constants. If a substance is arbitrarily chosen for a standard of comparison with reaction rate \( k_0 \), then other reaction rates \( k \) may be compared by means of relative free energies:

\[ -RT \ln \left( \frac{k}{k_0} \right) = \Delta G^+ - \Delta G^+_0 \]  

Fundamental relations in statistical thermodynamics allow the equation,

\[ \Delta G^+ = \Delta \Delta G^+ + RT \ln \Pi Q^* \]  

wherein the relative free energy of activation is related to the relative potential energy of activation, \( \Delta \Delta E^+ \), and a product \( \Pi Q^* \) involving partition functions of the transition complex and reactants. \( \Pi Q^* \) is basically determined by molecular motions, but its value cannot yet be calculated for reactions in solution.

The relative potential energy of activation may be qualitatively resolved into three fundamental contributing effects: polar, mesomeric, and steric,

\[ \Delta \Delta G^+ = \Delta \Delta G^+_\sigma + \Delta \Delta G^+_\psi + \Delta \Delta G^+_s \]  

\[ \therefore \Delta \Delta G^+_\sigma = \Delta \Delta G^+_\psi + \Delta \Delta G^+_s - RT \ln \Pi Q^* \]  

In \( \omega \) - and \( p \)-substituted benzene derivatives, the polar factor alone usually determines reactivity, and this fact permits simplification to the Hammett form:

\[ -RT \ln \left( \frac{k}{k_0} \right) = \Delta \Delta E^+_{\sigma} \]  

This could be expected to apply only if resonance and steric considerations
were approximately constant, so that the Hammett equation is really only a polar equation. It was early recognised that in certain reactions, some substituents failed to obey the empirical equation, and these instances are invariably the result of the assumptions taken in deriving equation (7) becoming incorrect.

When $\Delta \varepsilon^+$ is not constant in reaction series studied, i.e. when steric interactions are variable, the polar equation will not apply. Thus, $\sigma$-substituted benzenes derivatives fail to obey the Hammett relationship. A recent attempt $^\text{12}$ has been made, however, to empirically correlate rates of $\sigma$-substituted benzene derivatives, with fair success.

Similarly, when $\Delta \varepsilon^+$ varies from reaction to reaction, the simple Hammett relationship breaks down. Reactions where this occurs involve mesomeric transmittance of electronic charge to and from the reaction centre. The earliest recognised examples of this were the reactions of phenols and amines, where electron withdrawing substituents (e.g. $p$-nitro, $p$-cyano) require exalted $\sigma$ constants now known as $\sigma^+$ to allow for mesomeric interactions as in (XIII). Later it was found that aromatic substitution $^\text{13,14}$ and side-chain reactions involving electron-deficient reaction sites $^\text{15,16}$ failed to observe the Hammett relation. This was attributed to mesomeric interactions which are the opposite of those for which $\sigma$ constants are required, as in the intermediate (XIV). It is this type of mesomeric interaction which concerns the present work.

The establishment of a scale of $\sigma^+$ constants for these reactions had been proposed $^\text{17,18,19}$, but the prevailing view was that mesomeric interactions would vary widely between reactions $^\text{13,16,20,21}$ although more favourable views have been expressed. $^\text{15,22,23}$ However, Brown and Okamoto $^\text{24}$ have succeeded in developing a set of these constants from the solvolyses of t-cumyl chlorides, where mesomeric interactions occur with electron-donating $p$-substituents (XV). A plot of log $k$ vs. $\sigma$ was drawn on the $m$-substituents, for which no substantial mesomeric interactions occur, and the value of $\sigma$ for $p$-substituents which provided a fit onto this line was defined as the $\sigma^+$ constant. The remarkable feature of these substituent constants was their extensive applicability, for they satisfactorily correlated a variety of electrophilic reactions and aromatic
substitutions $^{24,25,26}$. The importance of mesomeric considerations can be gauged from the fact that benzyldimethyl carbynyl chlorides fit $\sigma$ constants well $^{27}$, but phenyldimethyl carbynyl chlorides require $\sigma^*$ constants, for good fit.

![Chemical Structures](XIII)

![Chemical Structures](XIV)

More recent studies suggest that the concept of a triad of constituent constants ($\sigma, \sigma^+$, and $\sigma^-$) is questionable. Firstly, the use of electrophilic reaction which $\sigma^+$ constants were not capable of describing was the solvolysis of benzyl tosylates $^{16}$, the partial non-fit of $\sigma^+$ constants being attributed to a change in reaction mechanism $^{25,28}$. Later publications $^{29}$ on these solvolyses have provided evidence not in support of this interpretation, and recently $^{30}$ the persistence of the carbonium ion mechanism has been demonstrated. Hammett concludes $^{30}$, therefore, that there is a breakdown in the $\sigma^-$ treatment, and he has cautioned $^{29}$ against the "indiscriminate assignment of immutable resonance influences to substituents".

Secondly, Taft $^{31}$ has concluded, after statistical survey, that there appears to be a range of $\sigma$ constants rather than a triad, this being attributed to variations in resonance effects. However, a select group of $m$-substituents exhibit precise linearity very generally, and by using these stable values, he recommends the determination of the Hammett line with subsequent evaluation of effective $\sigma$ values ($\bar{\sigma}$) for the other substituents. Resonance interactions may then be assessed by $\bar{\sigma}_R$ values, the effective resonance contribution:

$$\bar{\sigma}_R = \sigma - \sigma^T$$

where $\sigma^T$ is the polar contribution to the overall substituent constant $^9$. $\bar{\sigma}_R$ values would then serve as a basis for comparison of reaction series.
Thirdly, similar conclusions were at about the same time published by Wepster et al. 32 on the basis of statistical studies. The same select group of \( g \)-substituent were found to have fairly constant \( \sigma \) values (called \( \sigma^\circ \) in this thesis and by Taft 31, but \( \sigma^n \) in their review). Wepster's distinctive method of comparing resonance interactions can be developed from equation (6). \( \sigma^\circ \) is the polar constant, and obeys the relation,

\[
-2.303RT \log \frac{k}{k_0} = \Delta \Delta E^+_\sigma
\]

\[= -2.303RT \sigma^\circ \rho \quad (9)
\]

Mesomorphic interactions will require the inclusion of another term,

\[
-2.303RT \sigma \rho = \Delta \Delta E^+_\sigma + \Delta \Delta E^+_\varphi
\]

\[= \Delta \Delta E^+_\varphi = 2.303RT (\sigma - \sigma^\circ) \rho \quad (10)
\]

Here, \( \Delta \Delta E^+_\varphi \), the resonance interaction energy, can be calculated, and its dependence on temperature, on reaction constant, and on deviation of substituent constant will be observed. This more refined treatment has led to a successful understanding of previously anomalous data (e.g. solvolyses of benzyl tosylates) largely because the effect of \( \rho \) is considered. That the resonance contribution to \( \sigma \) is a function of \( \varphi \) was recognised by Okamoto and Brown in their formulation 25,

\[
\sigma = \sigma_{e} + \sigma_{R} f(\varphi)
\]

\[= \sigma_{e} + \sigma_{R} \quad (11)
\]

3. The present investigation.

The solvolysis of \( t \)-butylphenyl carbonyl chlorides could be expected to provide exalted substituent constants for appropriate substituents, but the degree of exaltation is unpredictable. If steric effects were not sufficiently large to force nonplanarity on the intermediate carboxim ion (XII, \( R = \text{OMe}_2 \)), \( \sigma^\circ \), \( \sigma_R \) and \( \Delta \Delta E^+_\varphi \) values would be similar to those in the solvolyses of \( t \)-cumyl chlorides. If, on the other hand, these steric effects were large enough, these quantities would be reduced to values intermediate to those found for \( t \)-cumyl chloride solvolyses and for benzoic acid ionisations. The three treatments (the Brown-Okamoto 25, Taft 31 and Wepster 32 methods) should thus be able to detect if there was significant steric inhibition of conjugation in the intermediate ion.
To enable this, the initially chosen \( \text{m-} \) and \( \text{p-} \) substituted derivatives of \( \text{t-butylphenyl carbaryl chloride were the following:} \)

\[
\begin{align*}
\text{m-Me,} & \quad \text{H,} & \quad \text{m-Cl,} & \quad \text{m-Br,} & \quad \text{m-NO}_2 \\
\text{p-MeO,} & \quad \text{p-Me,} & \quad \text{p-Cl,} & \quad \text{p-Br,} & \quad \text{p-} \text{OH} \\
\end{align*}
\]

The five \( \text{m-} \) points would give a well-defined Hammett plot, and the five \( \text{p-} \) substituents would allow a more than adequate basis for conclusive results. The most useful conclusions would be based on the \( \text{p-methoxy} \) substituent, because of its high mesomeric electron donating powers. However, two difficulties to the original plan were met.

1. The valuable \( \text{m-nitro} \) derivative could not be made, and this strictly limited the range of \( \text{m-} \) points available to define the Hammett line for the Taft and Nenster methods of analysis.

2. The \( \text{p-} \text{naphthyl} \) derivative could not be adequately purified, possibly because the \( \text{p-naphthaldehyde} \) reagent used in its synthesis was too readily reduced by the \( \text{t-butyl Grignard} \) reagent. One preparation, in fact, gave more reduction product that other material, for recrystallisation separated a large amount which was analysed and found to be \( \text{p-naphthyl carbinal.} \)

In addition, it is relevant to point out that steric inhibition of mesomerism in (XVI) would, if present, effectively result in inhibition of hyperconjugation. This is because hyperconjugation is the attributed source of the need for \( \sigma^+ \) constants in \( \text{p-alkyl} \) substituents 35. Carbon-hydrogen hyperconjugation would be inhibited in the \( \text{p-methyl} \) substituent; similarly carbon-carbon hyperconjugation would be inhibited in the \( \text{p-t-butyl} \) substituent, which was prepared by Mr. B.A. Grigor.

![Diagram](XVI)
EXPERIMENTAL.

1. General.

The melting and boiling points, in Centigrade degrees, and the pressures are recorded as observed and uncorrected. Where available, reference values are quoted from the literature; Heilbron and Bunbury is used for the more common chemicals, and is abbreviated HB in the following record. Density measurements used a calibrated pycnometer, and were duplicated. The true density was computed and ethanol-water compositions were determined by interpolation of suitable composition-density tables. Refractive indices were measured in a Hilger Abbé type refractometer, which determines that for the sodium D line within 0.0002. Previously unreported compounds were analysed by Dr. A.D. Campbell of the University of Otago.

Reactions were timed with calibrated watches. All volumetric ware was calibrated in the usual manner, and standard volumetric solutions were made of Analytical grade chemicals.

Thermostatted water baths were used for rate measurements at 40°, 35°, 65° and 95°. To maintain 4°, glycol-water refrigerant was pumped through a coil in the bath. For -23°, a cryostat was employed, whereby A.R. carbon tetrachloride was partially solidified by liquid nitrogen in a Dewar type container sufficiently wide to hold two 25 ml. flasks. Pouring liquid nitrogen when necessary onto the carbon tetrachloride proved more convenient than adding solid carbon dioxide, for gaseous carbon dioxide was too readily absorbed by the cold ethanol-water solvent, leading to enormous titration errors.

Temperatures were checked against standardized thermometers. The intermediate bath temperatures were readily held to within .02° - .03°, and the temperature of the cryostat did not vary by more than .05° provided that it was gently stirred. However, at the upper extreme of 95°, the bath could be kept constant only to within .1°. At this temperature, also, room temperature variations surprisingly necessitated frequent adjustment of the regulator to keep the bath temperature within this limit.

2. Preparation of the carbinols.

The t-butylphenyl carbinols were prepared as intermediates in
the preparation of the chlorides required for the solvolyses reactions. The method of preparation used, in most cases, the reaction between the appropriately substituted benzaldehyde and the Grignard reagent, t-butyl-magnesium chloride. The yields varied from 70% for the p-methoxy derivative to 30% for the p-chloro. The technique was similar in each case, except that there were sometimes experimental modifications to the excess of Grignard used without appreciable increasing effect on yield.

m-Tolualdehyde was not commercially available, but was prepared by reduction of m-tolunitrile with stannous chloride and hydrogen chloride. The preparation of the m-nitro carbinol was attempted, but failed in the last stage. t-Butylphenyl ketone was prepared and nitrated to form t-butyl-m-nitrophenyl ketone. A Meerwein-Ponndorf-Verley reduction did not produce the corresponding alcohol, presumably because of steric hindrance to the formation of the intermediate complexes.

The preparative methods are recorded in detail below. The p-t-butyl derivative of t-butylphenyl carbinol was prepared by Mr. B.A. Grigor in these reactions:

\[
\text{PhCOCH}_3 + \text{Me}_2\text{COOH} \rightarrow \text{PhCOH} + \text{Me}_2\text{COOH} \quad \text{(ref 39)}
\]

\[
\text{C}_6\text{H}_6 + \text{Me}_2\text{COOH} + \text{AlCl}_3 \rightarrow \text{Me}_2\text{C}-\text{O}-\text{CO-COO-Me}_2 \quad \text{(ref 40)}
\]

\[
\text{Me}_2\text{C}-\text{O}-\text{CO-Me}_2 \xrightarrow{\text{LIAIH}_4} \text{Me}_2\text{C}-\text{O}-\text{OHO-Me}_2 \quad \text{(ref 41)}
\]

The following data were determined by Mr. Grigor:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>b.p.</td>
<td>108°/1 mm.</td>
</tr>
<tr>
<td>m.p.</td>
<td>80.5° - 81.5° after three recrystallisations from volatile petroleum ether.</td>
</tr>
</tbody>
</table>

Analysis

<table>
<thead>
<tr>
<th></th>
<th>% calculated</th>
<th>% found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>81.76</td>
<td>81.77</td>
</tr>
<tr>
<td>H</td>
<td>10.98</td>
<td>10.59</td>
</tr>
</tbody>
</table>

The preparation of the carbinol.

Commercial benzaldehyde was washed and distilled at 108° under reduced pressure, (b.p. 179°/751 mm., 62°/10 mm., RB).

This was added (40 g. in 100 ml. dry ether) to the ethereal Grignard
reagent prepared from 25 g. magnesium and 102 g. t-butyl chloride in 300 ml. ether. The Grignard was in excess of, theoretically, 2\textsubscript{2}/3 moles to 1. During the slow addition (2-3 hrs), the reaction mixture was vigorously stirred, and cooled by an ice-salt bath. This procedure was designed to minimise reduction of the benzaldehyde to benzyl alcohol, which is reported to occur only if reaction takes place above room temperature \textsuperscript{43}. Other workers have used solid carbon dioxide-acetone cooling mixtures to keep reaction temperatures to ca. -50\textdegree \textsuperscript{44}. After addition, the reaction mixture was left standing overnight at room temperature.

The green-brown mixture was hydrolysed by pouring slowly onto a vigorously stirred mixture of saturated ammonium chloride solution (400 ml) and crushed ice (200 g.). The aqueous layer was separated and extracted with ether, and the combined ethereal solution was washed successively with water, 5\% sodium bicarbonate solution and water, followed by drying over anhydrous magnesium sulphate. After the ether had been distilled off on a water pump, the remaining lightly coloured mixture was distilled under vacuum at bath temperatures of up to 160\textdegree, to be collected at 100-5\textdegree/6\textsubscript{1}/2 mm. (reported: 95-100\textdegree/10 mm. \textsuperscript{46}, 98-105\textdegree/8 mm. \textsuperscript{47}, 95\textdegree/7 mm. \textsuperscript{48}). Some tarry residue was left. After solidification, it was twice recrystallised from volatile petroleum ether to melt at 44-44\textsubscript{3}/2\textdegree. The yield of grey needles was 20 g. (38\%).

Several workers have prepared this carbinol and contamination with benzyl alcohol \textsuperscript{46} and with pivalophenone \textsuperscript{49} (detected by its 2,4-dinitrophenylhydrazone) have been reported. Saponification of the purified acid phthalate has given products melting at 44-50\textdegree \textsuperscript{46,50,51} where recrystallisation alone had given melting points of 42-44\textsubscript{3}/0 \textsuperscript{51} and 42-3-42-8\textdegree \textsuperscript{46}. Vacuum sublimation of a recrystallised sample (m.p. 45\textdegree) gave a product melting at 44,5\textdegree; the original sample was in this case prepared by lithium aluminium hydride reduction of t-butylphenyl ketone \textsuperscript{41} rather than by the usual Grignard method. Another worker \textsuperscript{47} records a 45\textdegree m.p. on sublimation. Yields, when recorded, were in the 50-60\% range.

t-Butyl-p-tolyl carbinol.

Commercial p-toluic acid was distilled at 180\textdegree under reduced pressure (204-5\textdegree/760 mm., 106\textdegree/10 mm. RB). The carbinol distilled at 99-102\textdegree/5 mm. to form a colourless, viscous liquid which neither thickened
nor crystallised on standing in a refrigerator for several weeks.
Yield, 20 g. (36%), \( n_D^{25} \) 1.5120

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>80.85</td>
<td>10.18</td>
</tr>
<tr>
<td>Found</td>
<td>80.92</td>
<td>9.77</td>
</tr>
</tbody>
</table>

**t-Butyl-p-methoxyphenyl carbinol.**

Anisaldehyde was distilled at 98-100°/4\( \frac{1}{4} \) mm. (124-15°/12 mm., 111-14°/4 mm. HB). The carbinol distilled at 130-135°/5 mm. and solidified on standing. Two recrystallisations from petroleum ether gave white needles melting at 41-2°, 35 g., (70% yield). This carbinol has been previously reported \(^52\) (b.p. 140°/12 mm., m.p. 41-2°, 77%).

**t-Butyl-p-chlorophenyl carbinol.**

p-Chlorobenzaldehyde was recrystallised from petroleum ether melting at 46° (47° HB).

The carbinol was distilled at 118-25°/5 mm. and redistilled at 90-4°/3 mm. (literature: b.p. 90-5°/5 mm., \( n_D^{14} \) 1.5401, yield 55%).

A temperature of 14° was for comparison inaccessible, but an extrapolation based on refractive indices at 17°, 21\( \frac{1}{2} \)° and 25° (1.5340, 1.5238 and 1.5177) gives \( n_D^{14} \) a value of 1.5397.

This carbinol crystallised to needles after several months in a refrigerator. It is molten at room temperature but still solid at 14°. The yield was 15 g. (30%).

**t-Butyl-m-chlorophenyl carbinol.**

m-Chlorobenzaldehyde was distilled at 97°/4\( \frac{1}{2} \) mm. (213-4° HB).

The carbinol was purified in fractional distillations, boiling at 116-9°/5 mm., \( n_D^{25} \) 1.5200, yield 25 g. (51%).

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
</tr>
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<tbody>
<tr>
<td>Calculated</td>
<td>66.49</td>
<td>7.61</td>
</tr>
<tr>
<td>Found</td>
<td>66.31</td>
<td>7.53</td>
</tr>
</tbody>
</table>
p-Bromophenyl-t-butyl carbinol.

p-Bromobenzaldehyde was recrystallised from ethanol-water, m.p. 57° (55-7° HB). The carbinol distilled at 155°/5 mm. and, on fractionation, at 117-8°/5 mm., 15 g. (40%).

This was made late in the study, and could not be crystallised. The yellow oil was fractionated, but analyses demonstrated that successive distillations failed to purify it.

Analysis

<table>
<thead>
<tr>
<th>% calculated</th>
<th>C</th>
<th>H</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>% found</td>
<td>57.26</td>
<td>6.31</td>
<td>27.95</td>
</tr>
</tbody>
</table>

Purification of the solid will probably be successfully achieved after it crystallises. Some of the other solids also took considerable time to form crystals, and were more perfectly purified then.

m-Bromophenyl-t-butyl carbinol.

m-Bromobenzaldehyde was distilled at 80°/5 mm. (215-6°/716 mm. HB), and the carbinol fractionally distilled at 130-3°/5 mm. The yield of 23 g. (46%) had a refractive index nD^20 of 1.5420.

Analysis

<table>
<thead>
<tr>
<th>% calculated</th>
<th>C</th>
<th>H</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>% found</td>
<td>54.04</td>
<td>6.18</td>
<td>33.15</td>
</tr>
</tbody>
</table>

t-Butyl-m-tolyl carbinol.

(a) m-Tolualdehyde.

Anhydrous stannous chloride was prepared by adding commercial stannous chloride dihydrate crystals (520 g.) to vigorously stirred A.R. acetic anhydride (470 g.) (mole ratio 1:2) in a 1½ litre beaker cooled by an ice bath, and the solid was, after 1½ hours, separated in a Buchner funnel, rinsed with dry ether and dried in a vacuum desiccator. m-Tolunitrile was distilled at 82½-83½°/8 mm. to give a lightly coloured liquid (b.p. 84.5°/10 mm., colourless, HB). The following procedure is based on that of a previous study of this Stephen reduction.

To 1000 ml. anhydrous ether, 335 g. anhydrous stannous chloride was added, and dry hydrogen chloride (from a NH₄Cl/H₂SO₄ type gas generator...
followed by a concentrated sulphuric acid bubbler) was passed through for 4-5 hours. The resulting lower viscous layer is described as consisting of stannous chloride dissolved in ethereal HOI, but it appeared to contain a large amount of undissolved crystals as well. m-Tolunitrile (138 g.) was added with vigorous stirring over one hour; stirring and hydrogen chloride bubbling was continued for another two hours and the sealed reaction mixture was kept overnight. Two liquid layers and a solid layer separated out.

The solid, isolated by filtration, consisted of the complex salt formed in the reaction with some of the excess stannous chloride. The liquid layers were ethereal solutions which became homogeneous when washed with sodium carbonate to remove dissolved HOI. After the ether was evacuated off, some excess crystalline stannous chloride and liquid stannic chloride product were deposited.

The solid intermediate complex salt was steam distilled and simultaneously hydrolysed in a continuous distillation apparatus, yielding about 100 ml. of organic layer. Extraction with ether, with subsequent drying, evaporation and distilling, yielded 75 g. colourless m-toluualdehyde, with b.p. 81-83°/10 mm., yield 53% (literature: b.p. 93-94°/17 mm. HB, 198°/756 mm. and 50% \(^{54}\)). The phenylhydrazone melted at 88° after one ethanol-water recrystallisation (m.p. 90°, HB).

\[
\text{RON} + \text{HOI} \rightarrow \text{ROOH} + \text{NH} \quad \text{SnOCl}_2 + 2\text{HOI} \\
\text{RCH} \cdot \text{INH} \quad \text{ROOH} + \text{NH}_2 \quad + \quad \text{SnCl}_4 \quad + \quad \text{warm water} \\
\text{R} \quad \text{H}_2 \text{O}
\]

\( R \) is the \( \text{m-tolyl} \) group.

\( \text{(b)} \) \( \text{t-Butyl-m-tolyl carbinol} \)

prepared from this aldehyde distilled at 107°-108°/52 mm. after two fractional distillations. \( \rho \text{D}^{25} \) 1.5072, yield 50 g. (50%).

<table>
<thead>
<tr>
<th>Analysis</th>
<th>C</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>% calculated</td>
<td>80.85</td>
<td>10.18</td>
</tr>
<tr>
<td>% found</td>
<td>81.40</td>
<td>10.34</td>
</tr>
</tbody>
</table>
Attempted preparation of t-butyl-m-nitrophenyl carbinol.

1. Trimethylacetyl chloride,

was prepared by Brown’s method 39. Redistilled benzyl chloride, with b.p. 192-4° (197°, HB) (280 g., 2 moles) and trimethylacetic acid (105 g., 1 mole) were placed in a 500 ml. flask fitted with a 25 cm. fractionating side-arm. Trimethylacetyl chloride was distilled over as fast as possible at the recorded temperature of 88-91° (gaseous hydrogen chloride lowers the temperature to below the b.p.) and on fractionation it boiled at 104-5°, with 96 g., yield (82%) (literature: b.p. 102-104° and 105-106° 56; 102-104°, 92% 39).

\[ \text{OMe}_2\text{CO}_2\text{H} + \text{Ph}_2\text{CO}_2\text{H} \rightarrow \text{OMe}_2\text{CO}_2\text{H} + \text{Ph}_2\text{CO}_2\text{H} \]

2. Trimethylacetophenone.

Bromobenzene was distilled at 152-6° (155-6°, HB) and added (210 g.) over 4 hours to magnesium (35 g.) in ether to give a 750 ml. solution approximately 1,6M in concentration of phenylmagnesium bromide. Trimethylacetyl chloride (96 g., 0.8 moles) was dissolved into 300 ml. anhydrous ether in a 2 litre flask fitted with reflux condenser, dropping funnel, stirrer and dry nitrogen inlet, and the solution was cooled by an ice-salt bath. To this, the solution of phenylmagnesium bromide (1.2 moles), prepared as above, was added over 2 2/3 hours with vigorous stirring and in a nitrogen atmosphere. The reaction mixture was hydrolysed with saturated ammonium chloride-ice solution, and the ether solution, after separation and extraction, was washed with water, sodium carbonate and water. Ether was distilled off and trimethylacetophenone distilled over. A further fractional distillation (b.p. 85-7°/5 mm.) yielded about 50 g. (43%) having \( n^\text{D}_{20} 1.5117 \), (literature: b.p. 84-8°/3 mm. 57, 104-6°/13 mm. 58, 78-9°/5 mm. and 84-8°/8 mm. 41, \( n^\text{D}_{20} 1.5102 57 \), \( n^\text{D}_{25} 1.5082 40, n^\text{D}_{20} 1.5094 41, 67\% 57 \).

\[ \text{Ph}_2\text{MgBr} + \text{OMe}_2\text{CO}_2\text{H} \rightarrow \text{Ph}_2\text{CO}_2\text{Me}_2 \]

3. t-Butyl-m-nitrophenyl ketone.

The direct nitration utilised the procedures recommended in an exhaustive study 59 on nitration of acetophenone, where it was concluded that
(a) proportion of m-isomer increases with sulphuric acid concentration,
(b) the cooler and the quicker the reaction is, the greater is the yield, and
(c) manual shaking, rather than mechanical stirring, gave a lighter
product easier to purify.

Tri methylacetophenone (30 g.) was dissolved in concentrated A.R.
sulphuric acid (121 g., density 1.84) to give a dark red solution. A solid
carbon dioxide-acetone bath at -30° cooled this solution to -20°, and some
of the acid crystallised. A mixture of A.R. fuming nitric acid (27.5 g.,
density 1.5) and A.R. concentrated sulphuric acid (84.6 g.) was added
dropwise over 1½ hours with the temperature maintained at around -5°.
Manual shaking was carried out during the addition and after for another
1½ hours. The clear dark-brown reaction mixture was poured onto crushed
ice (600 g.) with stirring, while a pale cream solid separated and was
filtered off. After one recrystallisation from ethanol, colourless plates
melting at 47° were formed, with a yield of 16 g. (42%).

Analysis
% calculated 63.75 6.32 6.76
% found 64.09 6.20 7.08

A further 5 g. was obtained by extraction of the aqueous filtrate with ether
and subsequent distillation at 151-5°/5 mm., but it proved too impure for
successful recrystallisation from ethanol.

The 2,4-dinitrophenylhydrazone was prepared and recrystallised
from ethanol-water, melting at 172-3°.

Nitrogen analysis
% calculated 18.08
% found 17.91

4. Attempted reduction of the ketone.

The mild and specific M.P.V. reduction is the most suited for
a ketone containing a nitro group. For this, commercial isopropanol was
dried by refluxing with lime and, subsequently, magnesium. The reaction
was carried out in the usual manner, whereby a mixture consisting of 7 g.
t-butyl-m-nitrophenyl ketone in a solution of aluminium isopropoxide (6.8 g.)
in dry isopropanol (50 ml.) was heated sufficiently to deliver a few drops
each minute from a side-arm above a short vertical air condenser fitted to
the flask. There was a positive test for acetone for about 3 hours, after
which excess isopropanol was distilled off and the reaction mixture hydrolysed with dilute hydrochloric acid.

An ether solution of the organic layer and the separated aqueous layer was evaporated under vacuum, and the residue crystallised (m.p. 38-42°). After two ethanol recrystallisations, colourless plates were formed (m.p. 45-45.5°).

**Analysis**

<table>
<thead>
<tr>
<th></th>
<th>% calculated for carbinal</th>
<th>% calculated for ketone</th>
<th>% found</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>63.14</td>
<td>63.75</td>
<td>63.97</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>7.23</td>
<td>6.32</td>
<td>6.32</td>
</tr>
<tr>
<td>N</td>
<td>6.69</td>
<td>6.76</td>
<td>6.76</td>
</tr>
</tbody>
</table>

This regeneration of ketone is presumably the result of steric hindrance to the formation of the intermediate complexes of the M.P.V. reaction, as molecular models of these, based on the probable mechanism 61, cannot be constructed. It is inexplicable, however, that there were obtained even weak positive tests for acetone.

3. Preparation of the carbinal chlorides.

**General method.**

The appropriate carbinal was added to freshly distilled purified thionyl chloride (mole ratio 1:2.5) and the mixture was kept overnight. Excess thionyl chloride was evacuated off and the residual chloride dissolved in ether. The solution was washed successively with ice-water and cold sodium bicarbonate solution, and dried over anhydrous potassium carbonate or magnesium sulphate. Ether was distilled off and the product was fractionally distilled. One redistillation invariably gave a sufficiently pure compound.

The only important divergence from this technique occurred with the p-methoxy derivative, when for fear of too rapid hydrolysis, the aqueous washing steps were missed. The p-methyl analogue was twice prepared, once with the washing missed. Similar solvolyses rates, the same refractive indices, but slightly differing analyses were obtained for the two samples. Two other minor differences involved the use of phosphorus pentachloride to chlorinate t-butyl-2-nitrophenyl ketone and the use of ether as solvent in the chlorination of the p-t-butyl derivative.

It was impractical with the small quantities prepared to measure the yields of the chlorides in general, but t-butylphenyl carbinal chloride, of
which the relatively large quantity of \( \frac{3}{2} \) grams were prepared, was obtained in over 70% yield. Refractive indices were obtained on the fresh chlorides at the temperatures recorded. An attempt to obtain the values at a standard temperature about one month later showed that the chlorides had deteriorated, although they had been stored in ground-glass stoppered containers under nitrogen.

**Physical properties.**

t-Butylphenyl carbinyl chloride was distilled at 90-1°/6-7 mm.,

\[ n_D^{24.9} = 1.5144 \] (literature: b.p. 89-90°/6-7 mm. \( 41 \), 89°-90°/6-7 mm. \( 46 \),

\[ n_D^{25} = 1.5142 \] \( \lambda \), \( n_D^{20} = 1.5161 \) \( 41 \)).

The properties of the remaining chlorides are recorded in Table I.

<p>| Physical properties of ( \text{CH}<em>{2} \text{Cl}\text{OCH}</em>{3} ) |
|---|---|---|---|</p>
<table>
<thead>
<tr>
<th>x</th>
<th>b.p.</th>
<th>( n_D^T ) at ( T^0 )</th>
<th>Halogen analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Ne</td>
<td>103-105°/5 mm.</td>
<td>1.5164</td>
<td>18.02</td>
</tr>
<tr>
<td>m-Ne</td>
<td>98-100/2</td>
<td>1.5150</td>
<td>18.02</td>
</tr>
<tr>
<td>p-MeO</td>
<td>113-13/2</td>
<td>1.5260</td>
<td>16.67</td>
</tr>
<tr>
<td>p-Cl</td>
<td>118-2/4</td>
<td>1.5305</td>
<td>32.66</td>
</tr>
<tr>
<td>m-Cl</td>
<td>103-10/5</td>
<td>1.5309</td>
<td>32.66</td>
</tr>
<tr>
<td>p-Br</td>
<td>121-3/2</td>
<td>1.5424</td>
<td>44.10</td>
</tr>
<tr>
<td>m-Br</td>
<td>115-8/2</td>
<td>1.5468</td>
<td>44.10</td>
</tr>
<tr>
<td>p-Bu</td>
<td>105/4</td>
<td>m.p. 57-8</td>
<td>14.65</td>
</tr>
</tbody>
</table>

1,1-dichloro-2,2-dimethyl-m-nitrophenyl propane.

The attempted reduction of t-butyl-m-nitrophenyl ketone yielded a product which could not be chlorinated with thionyl chloride, but phosphorus pentachloride did react, while over a boiling water bath for 4-5 hours, to produce crystals of the above gem dichloride, melting at 106°. These crystals were dissolved in ether, washed and distilled. Ethanol recrystallisation gave a melting point, with sublimation, of 115-116°.

**Chlorine analysis**

\% calculated for \( \text{NO}_2 \text{CH}_{2} \text{ClOCH}_{3} \) 15.57

\% calculated for \( \text{NO}_2 \text{CH}_{2} \text{ClOCH}_{3} \) 27.05

\% found 27.43
This result confirms previous evidence (p. 18) for the nonsuccess of the M.P.V. reduction.

4. The preparation of reagents.

Ethanol solvent.

Commercial absolute ethanol (10 litres) was distilled off 250 ml. of 12N sulphuric acid (to remove basic materials) collecting 8 litres. This was distilled off solid sodium hydride (to polymerise aldehydes) through a 5 foot fractionating column packed with single turn glass helices. 4 litres of the constant boiling middle fraction was obtained (b.p. 77.5°/749-755 mm. and 78.1°/735 mm.; literature 78.15°/760 mm.). No attempt was made to completely dry the ethanol.

The solvent was made up to the required concentration by measuring the density of the ethanol and adding sufficient distilled water to make the proportion of ethanol about 70% w/w. This was checked by further density determinations to give the actual strength of the solvent. The true density $\rho$ was 0.85466, corresponding to 69.92% ethanol (w/w).

Three preliminary kinetic studies on differing solvent concentrations (40%, 60%, 80%) used solvents prepared and checked in this way.

Standard alkali.

A.R. barium hydroxide has less carbonate impurity that the corresponding sodium hydroxide and, moreover, this impurity is readily filtered off. Accordingly, a solution (4 litres, 0.1N) was prepared and siphoned through a sintered glass filter into a polythene container, from which it was led in polythene tubing to a double-bore stopcock burette, the whole system being kept free of carbon dioxide. This solution was standardised and checked at intervals with standard acid.

Standard hydrochloric acid.

To a weighed sample of constant boiling hydrochloric acid $\Delta$ was added sufficient water to make a solution of 0.1N hydrochloric acid. This primary standard was checked $\Delta$ with weighed samples of recrystallised pure borax, using a mixed bromoresol green-methyl red indicator. This indicator gave a sharp endpoint, appeared to be unaffected by atmospheric carbon dioxide, and required a negligible "blank" titre.
5. Kinetic procedures.

For reactions except those of the p-methoxy carbinyl chloride, the convenient sealed-ampoule technique 6,46 was adopted. The reaction mixture (25 ml. ca. 0.03M) was made up at room temperature, and 7-9 aliquots (2 ml. each) were transferred by pipette into ampoules which were sealed, weighted and placed in the thermostat bath. At selected times, these were withdrawn and cooled in ice-salt. When convenient, the contents were transferred into ethanol-water and titrated against standard alkali, using the same indicator as above.

The more rapid reaction of the p-methoxy carbinyl chloride was followed by the sampling technique 6, where the chloride on a glass boat was added to 25 ml. of solvent which had been in a ground-glass stoppered flask in the bath for at least an hour; 2 ml. aliquots were withdrawn at convenient intervals and transferred into ice-cold absolute ethanol, followed by titration. The ethanol effectively froze the reaction, for the endpoint did not change within 10 minutes. The indicator, also, behaved quite satisfactorily in the ethanol.

The p-methoxy carbinyl chloride was difficult to dissolve at the low temperatures used, so that lower than usual concentrations of reaction mixture were necessary. These averaged 0.03N and 0.02N for the reactions at 4° and -23° respectively, and only in the latter case were the graphs used for rate constant determinations less well-defined (see Graph IX). This can be attributed to increased difficulty in finding the precise endpoint. The p-t-butyl carbinyl chloride was also difficult to dissolve, but the lowest concentration used in this reaction (0.04N) gave a reasonably well-defined rate line (see Graph IV).

These preliminary studies in differing solvents provided details of solvent effect on speed and solubility. Known temperature effects are available from previous works 6,46. The standard conditions chosen in this reaction were for a solvent of 70% ethanol concentration and a temperature of 25°. Most solvolyses were measurable at this temperature, but faster ones were studied at two lower temperatures, their rate constants at 25° being determined by extrapolation of Arrhenius plots.

6a. Calculation of rate constants.

The first-order rate equation was used

\[ k = \frac{1}{t} \ln \frac{a}{a-x} \]  \[---(12)\]
where \( (a) \) is the initial concentration of chlorides, and \( (x) \) is the concentration after a time \( (t) \). These symbols were used in terms of direct titration readings, so that \( (a) \) measured the calculated values of alkali required for the "infinity" titre, and \( (x) \) measured the titre value after a time \( (t) \).

As all aliquots were of the same volume, further complications were avoided. In the solvolyses of the \( p \)-methoxy chlorides, the aliquots were not taken at room temperature, and it was therefore necessary to correct for the different volume and density of the solution. The following are the kinetic data for a typical run on each compound.

\[
\begin{align*}
X &= \text{CH}_{3}CN \\
\text{where } X \text{ is given. The rate constants are recorded in } \text{sec}^{-1}.
\end{align*}
\]

\[
\begin{array}{cccc}
\text{t} & \text{sec} & \text{ml.} & \ln \frac{a}{a-x} \\
760 & 1 & 568 & 0.869 \\
1227 & 1.224 & 2.231 \\
1829 & 1.698 & 3.333 \\
4295 & 2.500 & 4.750 \\
6045 & 2.694 & 5.882 \\
7725 & 3.697 & 7.975 \\
10,225 & 4.599 & 1.062 \\
\end{array}
\]

\[
\text{Reaction followed to 63%.}
\]

\[
\begin{array}{cccc}
\text{t} & \text{sec} & \text{ml.} & \ln \frac{a}{a-x} \\
215 & 1 & 172 & 0.943 \\
765 & 1 & 772 & 1.246 \\
1225 & 1.222 & 2.233 \\
2315 & 1.967 & 3.228 \\
2900 & 2.285 & 5.262 \\
3555 & 2.560 & 7.605 \\
4310 & 2.900 & 9.245 \\
5230 & 2.879 & 1.453 \\
\end{array}
\]

\[
\text{Reaction followed to 68%}.
\]

\[
\begin{array}{cccc}
\text{t} & \text{sec} & \text{ml.} & \ln \frac{a}{a-x} \\
455 & 1 & 150 & 0.861 \\
1275 & 1 & 352 & 1.152 \\
1870 & 2.21 & 1.485 \\
2785 & 3.696 & 2.865 \\
3495 & 4.682 & 3.319 \\
4275 & 5.543 & 2.639 \\
5175 & 7.22 & 2.950 \\
6020 & 6.214 & 3.047 \\
\end{array}
\]

\[
\text{Reaction followed to 27%.}
\]
### \( a = 0.390 \) at 35°C

<table>
<thead>
<tr>
<th>( t )</th>
<th>( a )</th>
<th>( \ln(a/a-x) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>490</td>
<td>0.103</td>
<td>-1.231</td>
</tr>
<tr>
<td>1017</td>
<td>0.123</td>
<td>-1.402</td>
</tr>
<tr>
<td>24120</td>
<td>0.150</td>
<td>-1.847</td>
</tr>
<tr>
<td>38350</td>
<td>0.186</td>
<td>-2.370</td>
</tr>
<tr>
<td>67220</td>
<td>0.235</td>
<td>-2.879</td>
</tr>
<tr>
<td>85870</td>
<td>0.285</td>
<td>-3.014</td>
</tr>
<tr>
<td>105480</td>
<td>0.332</td>
<td>-4.676</td>
</tr>
<tr>
<td>115780</td>
<td>0.382</td>
<td>-6.093</td>
</tr>
</tbody>
</table>

From graph, \( k = 5.275 \times 10^{-5} \)

Reactions followed to 40%.

### \( a = 0.475 \) at 22.3°C

<table>
<thead>
<tr>
<th>( t )</th>
<th>( a )</th>
<th>( \ln(a/a-x) )</th>
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</thead>
<tbody>
<tr>
<td>785</td>
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<tr>
<td>1355</td>
<td>0.055</td>
<td>0.138</td>
</tr>
<tr>
<td>2170</td>
<td>0.092</td>
<td>0.160</td>
</tr>
<tr>
<td>2985</td>
<td>0.147</td>
<td>0.104</td>
</tr>
<tr>
<td>4725</td>
<td>0.265</td>
<td>0.142</td>
</tr>
<tr>
<td>6775</td>
<td>0.483</td>
<td>0.162</td>
</tr>
<tr>
<td>8760</td>
<td>0.699</td>
<td>0.237</td>
</tr>
<tr>
<td>9775</td>
<td>1.012</td>
<td>0.241</td>
</tr>
<tr>
<td>1120</td>
<td>1.113</td>
<td>0.285</td>
</tr>
</tbody>
</table>

From graph, \( k = 2.221 \times 10^{-5} \)

Reactions followed to 25%.

### \( a = 6.225 \) at 95°C

<table>
<thead>
<tr>
<th>( t )</th>
<th>( a )</th>
<th>( \ln(a/a-x) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2280</td>
<td>0.228</td>
<td>0.274</td>
</tr>
<tr>
<td>30600</td>
<td>0.443</td>
<td>0.974</td>
</tr>
<tr>
<td>72240</td>
<td>0.741</td>
<td>1.356</td>
</tr>
<tr>
<td>85320</td>
<td>0.845</td>
<td>1.359</td>
</tr>
<tr>
<td>102900</td>
<td>0.981</td>
<td>1.715</td>
</tr>
<tr>
<td>122100</td>
<td>1.070</td>
<td>1.347</td>
</tr>
<tr>
<td>159900</td>
<td>1.571</td>
<td>2.220</td>
</tr>
<tr>
<td>188040</td>
<td>2.222</td>
<td>3.067</td>
</tr>
</tbody>
</table>

From graph, \( k = 1.232 \times 10^{-6} \)

Reactions followed to 95%.

### \( a = 6.356 \) at 95°C

<table>
<thead>
<tr>
<th>( t+1,005 )</th>
<th>( a )</th>
<th>( \ln(a/a-x) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>915</td>
<td>0.499</td>
<td>0.551</td>
</tr>
<tr>
<td>1657</td>
<td>0.791</td>
<td>0.298</td>
</tr>
<tr>
<td>5625</td>
<td>1.191</td>
<td>0.207</td>
</tr>
<tr>
<td>5498</td>
<td>1.601</td>
<td>0.290</td>
</tr>
<tr>
<td>7668</td>
<td>1.855</td>
<td>0.315</td>
</tr>
<tr>
<td>8748</td>
<td>2.054</td>
<td>0.350</td>
</tr>
<tr>
<td>9612</td>
<td>2.305</td>
<td>0.430</td>
</tr>
<tr>
<td>16290</td>
<td>3.126</td>
<td>0.525</td>
</tr>
</tbody>
</table>

From graph, \( k = 4.09 \times 10^{-6} \)

Reactions followed to 75%. 

---

The table represents data for reaction kinetics at different temperatures, showing the change in concentration over time and the rate constant \( k \) for each set of conditions.
\[ x = m-Br \] at 95°

<table>
<thead>
<tr>
<th>t</th>
<th>x</th>
<th>ln(a/a-x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>700</td>
<td>0.274</td>
</tr>
<tr>
<td>14</td>
<td>195</td>
<td>0.577</td>
</tr>
<tr>
<td>52</td>
<td>320</td>
<td>0.630</td>
</tr>
<tr>
<td>78</td>
<td>944</td>
<td>0.726</td>
</tr>
<tr>
<td>138</td>
<td>340</td>
<td>1.027</td>
</tr>
<tr>
<td>183</td>
<td>720</td>
<td>1.237</td>
</tr>
<tr>
<td>229</td>
<td>560</td>
<td>1.744</td>
</tr>
</tbody>
</table>

\[ a = 4.691 \]

From graph, \( k = 1.69 \times 10^{-6} \)

Reaction followed to 37%.

\[ x = m-Br \] at 95°

<table>
<thead>
<tr>
<th>t+1,005</th>
<th>x</th>
<th>ln(a/a-x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 160</td>
<td>0.982</td>
<td>2.2350</td>
</tr>
<tr>
<td>5 615</td>
<td>1.163</td>
<td>2.844</td>
</tr>
<tr>
<td>5 115</td>
<td>1.304</td>
<td>3.257</td>
</tr>
<tr>
<td>6 720</td>
<td>1.476</td>
<td>3.778</td>
</tr>
<tr>
<td>12 960</td>
<td>1.965</td>
<td>3.5416</td>
</tr>
<tr>
<td>15 120</td>
<td>2.141</td>
<td>5.092</td>
</tr>
</tbody>
</table>

\[ a = 4.694 \]

From graph, \( k = 2.313 \times 10^{-5} \)

Reaction followed to 45%.

\[ x = m-NO_2 \] p-dimethylide at 95°

<table>
<thead>
<tr>
<th>t</th>
<th>x</th>
<th>ln(a/a-x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21 240</td>
<td>0.264</td>
<td>0.2922</td>
</tr>
<tr>
<td>10 290</td>
<td>0.758</td>
<td>1.2911</td>
</tr>
<tr>
<td>195 320</td>
<td>1.615</td>
<td>2.700</td>
</tr>
<tr>
<td>280 560</td>
<td>2.242</td>
<td>3.221</td>
</tr>
<tr>
<td>351 120</td>
<td>2.740</td>
<td>3.5138</td>
</tr>
<tr>
<td>449 460</td>
<td>2.981</td>
<td>3.739</td>
</tr>
<tr>
<td>540 480</td>
<td>3.828</td>
<td>5.225</td>
</tr>
<tr>
<td>540 600</td>
<td>5.625</td>
<td>7.796</td>
</tr>
</tbody>
</table>

\[ a = 6.829 \]

From graph, \( k = 1.364 \times 10^{-6} \)

Reaction followed to 53%.

6b. Experimental accuracy and probable errors.

Error in t.

The sealed ampoule technique rendered accurate knowledge of the starting time of the reactions impossible, so that the rate graphs did not necessarily go through the origin. This could not error into the rate constant, however. Starting times were uncertain in the sampled runs (for the \( p \)-methoxy carbaryl chloride) because of solubility difficulties.

The time recorded as aliquots were removed corresponded for all titrations. Any error should be small and constant, not affecting the rate constant significantly.

Error in a,

would modify the slope of the rate line and thus the rate constant.
GRAPH 1.

Solvency of t-butylphenyl carbinyll chloride, at 95°.
GRAPH II.
Solvolysis of t-butyl-m-tolyl carbinyl chloride, at 95 °.
GRAPH III.

Solvolyis of t-butyl-$\beta$-tolyl carbinyl chloride, at 65°.
GRAPH IV.

Solvolysis of t-butyl-g-t-butyl-phenyl carbinyi chloride, at 35°.
GRAPH V.
Solvolysis of t-butyl-M-chloro-phenyl carbiny1 chloride, at 95°.
GRAPH VI.
Solvolysis of t-butyl-\(p\)-chloro-phenyl carbinyll chloride, at 95°.
GRAPH VII.

Solvolysis of \( t \)-butyl-\( m \)-bromo-phenyl carbinyl chloride, at 95°
GRAPH VIII.
Solvolysis of $t$-butyl-$p$-bromo-phenyl carbinyl chloride, at $95^\circ$ C.
Graph IX.

Solvolyis of t-butyl-p-methoxy-phenyl carbinyl chloride, at -23°.
GRAPH X.

Solvolyis of 1,1-dichloro-2,2-dimethyl-m-nitrophenyl propane, 95°C.
They are likely to be very slight, as weighing errors (less than \( \frac{1}{1000} \)) are involved and as in general pure compounds were used. In theory these initial concentrations may be checked by "infinity" titres, and this has been done in previous studies \(^6\, ^{46}\), and in fact Brown and Okamoto \(^2\) base their rate constants on this titration. In the present studies, however, they proved to be usually very different and they were always unreliable and irreproducible, so that the calculated value was universally used.

**Errors in \( x \).**

Burette reading error will cause \( x \) to have a diminishing percentage error as it increases, and this is likely to be significant only in the runs where the minimum of chloride was used, where it would make the earlier titres haphazard (see Graph \( x \)).

**Errors in \( a/a-x \).**

As \( x \) increases, these errors will also increase with the constant error in \( x \) ( \( .006 \) ml.). This would imply that the earlier points in the graphs should be given greater weight. Only in the slower reactions was this sometimes found necessary, as illustrated in the graphs chosen for the \( p \)-bromo, \( m \)-chloro- and \( m \)-nitro chlorides (Graphs \( m \), \( v \), and \( x \)). The cause of these deviations toward the end of the runs is likely to be related to the cause of the unreliable "infinity" titres. It appears that the actual time taken in the reaction is significant in this respect, rather than the percentage of reaction followed (p. 22 ff.).

**Error in \( k \).**

is commonly estimated \( 6 \, 24, \, ^{46} \) to be about \( \frac{1}{2} \). However, the inexplicable curvature of the graphs for the \( p \)-methyl carbonyl chloride (Graph \( m \)) and the less definite line of one graph for the \( p \)-methoxy carbonyl chloride (Graph \( x \)), together with extrapolation errors in the Arrhenius plots, will make these rate constants more uncertain.

It should be noted that the apparent curvature in Graph \( m \) is not found in the other two rate lines for this compound. This demonstrates the truly haphazard nature of the scatter towards the end of some runs.
RESULTS.

The rate constants obtained as described in the previous section are tabulated below.

TABLE II

Rate constants obtained from solvolyses of PhOHClOMe₂ in differing solvents, at 65°.

<table>
<thead>
<tr>
<th>Ethanol concentration in EtOH/H₂O (w/v)</th>
<th>Rate constants ( k ) (sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80%</td>
<td>( 1.61 \times 10^{-6} )</td>
</tr>
<tr>
<td>60%</td>
<td>( 1.47 \times 10^{-5} )</td>
</tr>
<tr>
<td>40%</td>
<td>( 1.25 \times 10^{-4} )</td>
</tr>
</tbody>
</table>

TABLE III

Rate constants for solvolyses of \( m\text{-NO}_2\text{-C}_6\text{H}_4\text{Cl}_2\text{OMe}_2 \) in 70% EtOH at 95°, \( 10^6 k \) (sec⁻¹).

<table>
<thead>
<tr>
<th>Individual</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.36</td>
<td>1.369</td>
</tr>
<tr>
<td>1.363</td>
<td></td>
</tr>
<tr>
<td>1.364</td>
<td></td>
</tr>
</tbody>
</table>
TABLE IV
Rate constants for solvolyses of $\text{XO}_2\text{H}_3\text{OH}{\text{Me}}_3$ in 70% EtOH (w/w).

<table>
<thead>
<tr>
<th>X</th>
<th>$10^5 k$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$94.7^\circ$</td>
</tr>
<tr>
<td>H</td>
<td>10.30</td>
</tr>
<tr>
<td>m-NO$_2$</td>
<td>20.71</td>
</tr>
<tr>
<td>p-MeO</td>
<td></td>
</tr>
<tr>
<td>m-Cl</td>
<td>.1294</td>
</tr>
<tr>
<td>p-Cl</td>
<td>4.068</td>
</tr>
<tr>
<td>m-Br</td>
<td>.169</td>
</tr>
<tr>
<td>p-Br</td>
<td>2.806</td>
</tr>
<tr>
<td>p-t-Bu</td>
<td>13.98</td>
</tr>
</tbody>
</table>
### TABLE V

Mean rate constants, from Table IV.

<table>
<thead>
<tr>
<th></th>
<th>$10^5 k$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>94.7°</td>
</tr>
<tr>
<td>H</td>
<td>10.29</td>
</tr>
<tr>
<td>m-Me</td>
<td>20.78</td>
</tr>
<tr>
<td>p-Me</td>
<td>13.2</td>
</tr>
<tr>
<td>p-MeO</td>
<td>66070</td>
</tr>
<tr>
<td>p-t-Bu</td>
<td>269.7</td>
</tr>
<tr>
<td>m-Cl</td>
<td>.1217</td>
</tr>
<tr>
<td>p-Cl</td>
<td>4.091</td>
</tr>
<tr>
<td>m-Br</td>
<td>.1723</td>
</tr>
<tr>
<td>p-Br</td>
<td>2.859</td>
</tr>
</tbody>
</table>

* Extrapolated from Arrhenius plots.

### TABLE VI

Arrhenius parameters and derived data.

<table>
<thead>
<tr>
<th></th>
<th>E (kcal/mole)</th>
<th>log A (kcal/mole)</th>
<th>$\Delta H^\dagger$ (kcal/mole)</th>
<th>$\Delta S^\dagger$ (cal °K$^{-1}$ mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Is</td>
<td>25.0</td>
<td>11.96</td>
<td>24.3</td>
<td>-4.2</td>
</tr>
<tr>
<td>p-t-Bu</td>
<td>25.4</td>
<td>12.54</td>
<td>24.7</td>
<td>-1.6</td>
</tr>
<tr>
<td>p-MeO</td>
<td>16.0</td>
<td>9.50</td>
<td>15.5</td>
<td>-16.4</td>
</tr>
</tbody>
</table>

These quantities were calculated in the equations:

\[ k = A e^{-\frac{E}{RT}} \]

\[ \Delta H^\dagger = E - RT \]

\[ A = \frac{kT}{h} e^{\frac{\Delta S^\dagger}{R}} \]
DISCUSSION

1. Comparison of results.

For the complete reaction series studied in the present work, there are no directly comparable values in the literature. However, t-butylphenyl carbinyl chloride has been solvolyzed by Baddeley 6 and by Einstein 46 and their coworkers, but with a different solvent. Using the preliminary studies in Table II, therefore, the comparison in Table VII has been enabled.

TABLE VII
Rate constants for solvolysis of PhCH=OCHMe₂ in 80% EtOH (v/v), 10⁻⁶k (sec⁻¹).

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Baddeley</th>
<th>Einstein</th>
<th>Present work</th>
</tr>
</thead>
<tbody>
<tr>
<td>49°</td>
<td>0.218</td>
<td>*326</td>
<td>2.4</td>
</tr>
<tr>
<td>50°</td>
<td>2.35 *</td>
<td>2.07 †</td>
<td></td>
</tr>
<tr>
<td>69°</td>
<td>7.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>79°</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The literature here contains a misprint because k = 2.35 x 10⁻⁶, but not 2.35 x 10⁻⁷ as repeated, agrees with the Arrhenius parameters given.
† Calculated from the other two values given by Einstein.
‡ Interpolated from w/w concentrations as given in Table II.
80% EtOH v/v = 75.9% EtOH w/w.

There is satisfying agreement between the rate constants of Baddeley and of the present work, but there is quite a significant difference between those of Baddeley and Einstein. This may be attributed, in part at least, to slight differences in solvent concentrations, particularly with the v/v compositions employed. Brown et al. 65 commented that the rates of some t-cumyl chloride solvolyzes were highly sensitive to minor changes in water content in the 90% aqueous acetone solvent. Less explicable, however, are the differences between these workers' Arrhenius parameters and derived activation values, in Table VIII.
TABLE VII

Arrhenius parameters and derived data for solvolyses of PhCH(OMe)₂ in 80% EtOH (v/v).

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>log A</th>
<th>ΔH⁺</th>
<th>ΔS⁺</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.4</td>
<td>10.7</td>
<td>24.8</td>
<td>-9.8</td>
<td>Baddeley</td>
<td></td>
</tr>
<tr>
<td>28.1</td>
<td>12.2</td>
<td>27.5</td>
<td>-3.1</td>
<td>Wainstein</td>
<td></td>
</tr>
</tbody>
</table>

* Calculated for 50°C from the other parameters given by each reference.

These conflicting results make it impossible to evaluate further data (e.g. $TΔΔS$ and $ΔΔH^+$) for the three substituents for which the Arrhenius data have been derived. The differences in reaction conditions are, in any case, too great to allow any use of other data to extend the results of the present work. A general similarity between the solvolyses of the t-cumyl chlorides $^{24}$ and t-butylyphenyl carbiny1 chlorides $^{39}$ demonstrated later (p. 332 ff.). In the meantime, it may be observed that the general trends in the Arrhenius parameters agree quite reasonably (cf. Tables VI, VII and Table IX.).

TABLE IX

Arrhenius parameters for solvolysis of substituted t-cumyl chlorides.

<table>
<thead>
<tr>
<th>X</th>
<th>E</th>
<th>log A</th>
<th>ΔH⁺</th>
<th>ΔS⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>19.5</td>
<td>10.4</td>
<td>18.8</td>
<td>-12.4</td>
</tr>
<tr>
<td>p-Me</td>
<td>17.8</td>
<td>10.6</td>
<td>17.3</td>
<td>-12.0</td>
</tr>
<tr>
<td>p-t-Bu</td>
<td>17.9</td>
<td>10.3</td>
<td>17.3</td>
<td>-15.3</td>
</tr>
<tr>
<td>p-NO₂</td>
<td>13.4</td>
<td>8.52</td>
<td>12.9</td>
<td>-21.1</td>
</tr>
</tbody>
</table>

In neither reaction series, however, is there the constancy in activation entropy which is often regarded as a prerequisite to Hammett equation treatment. Brown has been questioned on this recently, and he doubts $^{66}$ that constant entropy is essential for conformity to the empirical Hammett relationship. He states that even Hammett's benzoic acids exhibit wide variations in this quantity.
2. The mechanism and course of the reaction.

It has been demonstrated that neopentyl bromide solvolyzes in aqueous ethanol according to the $S_N1$ mechanism, the $S_N2$ being sterically retarded. An $\alpha$-phenyl group would be expected to stabilise the carbonium ion by mesomerism and so increase the unimolecular rate, but the bimolecular mechanism would probably be further sterically retarded. The rearrangement of neopentyl systems requires a carbonium ion ($S_N1$) mechanism, but $\alpha$-phenyl derivatives do not rearrange under similar conditions (see p. 32). The reason attributed is increased stability of the unarranged carbonium ion rather than any bimolecular mechanism.

It is therefore not surprising that solvent and salt effects typical of unimolecular solvolyses have been observed in the solvolysis of $t$-butylphenyl carbonyl chloride ($\alpha$-phenylneopentyl chloride). This reaction has been followed to 68% of the reaction and is stated to have a very steady unimolecular rate constant; one measurement in the present work followed the same reaction to 94%, the rate constant being steady to 62% and thereafter falling in the typical unimolecular manner. The pronounced effect of a changed solvent dielectric constant (see Table II) is also typical of the unimolecular reaction.

The reaction has been demonstrated to be unequivocally unimolecular. Dostrovsky and Samuel have solvolyzed the bromide in 40% ethanol-water and in 99% formic acid-water. These two solvents, of about equal ionising power, gave about equal first-order rate constants. This observation is consistent with the unimolecular mechanism in both media, for damp formic acid promotes the $S_N1$ and represses the $S_N2$ mechanism. Furthermore, rearrangement was detected only in the formic acid medium, and as rearrangement is known to require a carbonium ion intermediate, this observation also strongly hints at an $S_N1$ mechanism in both media. For the solvolysis of the corresponding chloride, Einstein and Morse have studied optical activity changes, and they found that between 12% and 10% inversion takes place in aqueous ethanolysis. This is evidence for the unimolecularity of the reaction.

It was considered possible, however, that for the less reactive compounds studied in the present work, the unimolecular rate might be reduced to such an extent that a bimolecular contribution could become significant. Accordingly, the reaction of the $p$-chloro carbonyl chloride
was further investigated. In this, a powerful nucleophile (sodium hydroxide) was dissolved in the solvent in low concentration, (0.01 M) and the rate decreased by 20% rather than increased. Had there been a significant bimolecular contribution, the rate would have increased markedly, for the nucleophilic concentration was markedly greater. We may be confident that all the faster chlorides reacted by the unimolecular mechanism, as this mechanism is more susceptible to changes of substituent than the bimolecular.

The rearrangement of neopentyl systems to t-butyl derivatives does not apparently occur when an α-phenyl substituent is present. Thus for the reaction,

\[
\text{PhOBrMe}_3 + \text{aq. AgNO}_3 \rightarrow \text{PhOHMe}_3
\]

freezing point depression studies have led to estimations of 30%, 4%, and 0% rearrangement by three workers \[49,46,50\] using successively more refined techniques. Aqueous ethanolation of the bromide leads to unarranged products, but formic and acetic acid solvolyses give some rearrangement \[50\].

The reaction

\[
\text{PhOBrMe}_3 \rightarrow \text{PhOHMe}_3
\]

also gives no unarranged products if thioclyl chloride is the reagent, this being deduced both from optical activity measurements and from scrutiny of the carbinyl chloride's solvolysis rate \[46\]. General lack of rearrangement is attributed \[49\] to mesomeric stabilisation of the intermediate carbonium ion compared with the simpler neopentyl cation. Rearrangement in formic and acetic acids is attributed \[50\] to a longer lifetime of the α-phenylnecopentyl cation in these less nucleophilic solvents, with consequent greater likelihood of rearrangement.

The solvolysis products for the bromide have been identified \[50\], and consist of the alcohol and/or the ether, depending on the aqueous content of the ethanolic solvent. The mechanism of the studied solvolysis reaction may be expressed, therefore, in the following scheme.
3. A study of the rates with the Hammett equation.

As indicated earlier (p. 8), the results may be treated by comparing the fit of \( \sigma^+ \) with that of \( \sigma \) constants, or by determining \( \sigma_R \) values, or by evaluating mesomeric interaction energies. In each case, data from t-butylphenyl carbonyl chloride solvolyses are compared with those from other reaction series. The \( \sigma^+ \) treatment has an advantage in that a least squares line is drawn on 6-9 points, whereas the other two methods have regression lines based on the only four \( \sigma \)-points available. This advantage is magnified somewhat in view of Taft's recommended procedure \(^{31}\) requiring a minimum of five \( \sigma \)-substituents. However, the four points available are otherwise within the recommended tolerances, and other workers have carried out statistical studies on four points \(^{72}\) and fewer \(^{32}\).

(a) Comparison of fit with \( \sigma^+ \) and \( \sigma \) \(^{25}\).

Better fit is achieved with \( \sigma^+ \) constants than with the polar \( \sigma \) constants (see Graphs X and XI). The good fit is expressed also in the appropriate correlation coefficients and standard errors (Table X a, c). Therefore, there are similar resonance interactions of the type

\[
\begin{align*}
\text{Mes} & \leftrightarrow \text{Mes} \\
\begin{array}{c}
\text{Mes} \quad \text{Ph} \\
\begin{array}{c}
\text{Mes} \quad \text{Ph} \\
\end{array}
\end{array}
\end{align*}
\]

in the two reaction series in effect compared (i.e., t-cumyl and t-butylphenyl carbonyl chloride solvolyses). The greatest effect is exhibited in the \( \rho \)-methoxy derivatives, lesser effects being observed for the \( \rho \)-substituents whose mesomeric electron-donating powers are smaller.

**Table X**

Statistical data \(^{8}\) on lines of regression drawn.

<table>
<thead>
<tr>
<th>Line of regression</th>
<th>Substituents</th>
<th>( n )</th>
<th>( p )</th>
<th>( \sigma )</th>
<th>( \log k_o )</th>
<th>( s )</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>a through ( \sigma^+ )</td>
<td>all</td>
<td>9</td>
<td>-4.82</td>
<td>.994</td>
<td>.199</td>
<td>-5.96</td>
<td>.194</td>
</tr>
<tr>
<td>b through ( \sigma^+ )</td>
<td>all except ( p )-Me</td>
<td>3</td>
<td>-4.88</td>
<td>.998</td>
<td>.127</td>
<td>-5.32</td>
<td>.127</td>
</tr>
<tr>
<td>c through ( \sigma )</td>
<td>all</td>
<td>9</td>
<td>-5.36</td>
<td>.916</td>
<td>.754</td>
<td>-5.40</td>
<td>.754</td>
</tr>
<tr>
<td>d through ( \sigma )</td>
<td>4 ( \rho )-substituents</td>
<td>4</td>
<td>-4.79</td>
<td>.977</td>
<td>.139</td>
<td>-4.60</td>
<td>.896</td>
</tr>
</tbody>
</table>

Corresponding values for solvolysis of t-cumyl chlorides:

<table>
<thead>
<tr>
<th>( n )</th>
<th>( p )</th>
<th>( \sigma )</th>
<th>( \log k_o )</th>
<th>( s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>-4.48</td>
<td>.998</td>
<td>.091</td>
<td>3.953</td>
</tr>
</tbody>
</table>

\(^{32}\)
GRAPH XI.
Hammett plot, for
solvolysis of $X_2\text{C}_6\text{H}_4\text{CHClCMe}_3$;
$\log k$ vs. $\sigma^+$
GRAPH XII.
Hammett plot, for
solvolysis of \( \text{C}_6\text{H}_4\text{CHClMe}_3 \),
\( \log k \) vs. \( \sigma \)
TABLE XI

<table>
<thead>
<tr>
<th>subst.</th>
<th>( \bar{\alpha}_A )</th>
<th>( \bar{\alpha}_B )</th>
<th>( \bar{\alpha}_C )</th>
<th>( \bar{\alpha}_D )</th>
<th>( \bar{\alpha}_E )</th>
<th>( \bar{\alpha}^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-HeO</td>
<td>1.06</td>
<td>2.17</td>
<td>1.54</td>
<td>1.29</td>
<td>1.59</td>
<td>1798</td>
</tr>
<tr>
<td>p-He</td>
<td>.27</td>
<td>.57</td>
<td>.66</td>
<td>.33</td>
<td>.53</td>
<td>.251</td>
</tr>
<tr>
<td>p-t-Bu</td>
<td>.20</td>
<td>.57</td>
<td>.24</td>
<td>.25</td>
<td>.24</td>
<td>.304</td>
</tr>
<tr>
<td>p-Cl</td>
<td>.56</td>
<td>.57</td>
<td>.34</td>
<td>.28</td>
<td>.106</td>
<td>.116</td>
</tr>
<tr>
<td>p-Br</td>
<td>.31</td>
<td>.31</td>
<td>.32</td>
<td>.32</td>
<td>.35</td>
<td>.116</td>
</tr>
</tbody>
</table>

A. Ar\(\text{C}_6\text{H}_4\)\(\text{CH}_3\) \(\rightarrow\) Ar\(\text{C}_6\text{H}_4\) \(\text{CH}_3\) \(\oplus\) \(-\) data derived from\(^{30}\)

B. Ar\(\text{C}_6\text{H}_4\)\(\text{OH}\) \(\rightarrow\) Ar\(\text{C}_6\text{H}_4\) \(\text{OH}\) \(\oplus\) \(-\) \(-\) \(-\)

C. Ar\(\text{C}_6\text{H}_4\)\(\text{Cl}\) \(\rightarrow\) Ar\(\text{C}_6\text{H}_4\) \(\text{Cl}\) \(\oplus\) \(-\) \(-\) \(-\)

D. Ar\(\text{Br}\) \(\oplus\) \(\rightarrow\) Ar\(\text{Br}\) \(\text{OH}\) \(\oplus\) \(-\) \(-\) \(-\)

E. Ar\(\text{C}_6\text{H}_5\)\(\text{OH}\) \(\rightarrow\) Ar\(\text{C}_6\text{H}_5\)\(\text{OH}\) \(\oplus\) \(-\) \(-\) \(-\)

* \(\bar{\alpha}^*\) is the resonance substituent constant applying in the absence of conjugation between substituent and reaction site.

TABLE XII

Mesomeric interaction energies for five reaction series (\(|\Delta\Delta E^*|\)) in k. cal.).

<table>
<thead>
<tr>
<th>subst.</th>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
<th>(D)</th>
<th>(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>p-HeO</td>
<td>4.2</td>
<td>5.6</td>
<td>1.2</td>
<td>1.3</td>
</tr>
<tr>
<td>(b)</td>
<td>p-He</td>
<td>1.2</td>
<td>1.6</td>
<td>1.6</td>
<td>2.2</td>
</tr>
<tr>
<td>(c)</td>
<td>p-t-Bu</td>
<td>.4</td>
<td>.9</td>
<td>.9</td>
<td>.8</td>
</tr>
<tr>
<td>(d)</td>
<td>p-Cl</td>
<td>.5</td>
<td>.7</td>
<td>.7</td>
<td>.8</td>
</tr>
<tr>
<td>(e)</td>
<td>p-Br</td>
<td>.7</td>
<td>.7</td>
<td>.7</td>
<td>.8</td>
</tr>
<tr>
<td>(f)</td>
<td>-4.46</td>
<td>-2.31</td>
<td>-1.31</td>
<td>3.97</td>
<td>-4.79</td>
</tr>
<tr>
<td>(g)</td>
<td>-4.46</td>
<td>-2.31</td>
<td>-1.31</td>
<td>3.97</td>
<td>-4.79</td>
</tr>
</tbody>
</table>

* Taken from\(^{32}\).

(b) Comparison of \(\bar{\alpha}\) parameters\(^{31}\).

"Effective" resonance contributions to the substituent constant (\(\bar{\alpha}\)) are grouped in Table XI. Here, again, it is evident that the resonance interactions in the t-butylphenyl carbinal chloride solvolyses are analogous.
to those occurring in other highly electrophilic reactions, for reaction 3 shares the large deviations between $\tilde{v}_e$ values and $g^*_a$ constants with the other reactions. As in the $\sigma^+$ treatment, however, reaction 3 appears to have unusually large mesomeric interactions.

(c) Comparison of mesomeric interaction energies, $\Delta \Delta E^*$. 

Table XII displays the similarity between these electrophilic reactions in their mesomeric interactions, and this similarity is even more marked with the better agreement between reaction 3 and the others. This closer agreement with Wepster's more refined treatment has been commented on earlier (p. 8).

With each method of treatment, however, the $p$-methyl substituent provides inconsistent results (e.g., the $\sigma^+$ constant does not provide better fit than the $\sigma$ constant). This may be traced to error in the rate constant, for $t$-butyl-$p$-tolyl carbonyl chloride's rate graphs uniquely exhibit a decided curvature (p. 25). Its rejection on the basis of the Pierce-Chauvenet criterion leads to improved statistical data (Table X b).

4. The role of steric effects.

A decreased reaction rate will result from reduced conjugation in the intermediate carbonium ion formed in the unimolecular solvolysis of aralkyl chlorides. It has been noted that such effects are difficult to disentangle from inductomeric and electromeric effects, so that an estimate of the importance of steric hindrance is not easy to obtain. However, the steric interactions in these systems have been resolved into two cumulative and destabilising effects:

A. resistance to form a planar ion, and

B. loss in mesomeric stabilisation if this ion should be nonplanar.

Evidence has been obtained (p. 5) that decreasing carbon-hydrogen hyperconjugation accounts partly for the observed rate order in solvolysis of the aralkyl chlorides, RCH(=O)Ph. The results of the present work have shown that there is no inhibition of mesomerism in the intermediate ion $\text{OMeCH(=O)Ph}$ (i.e., the equilibrium configuration is the planar one) and the same situation should apply for the other chlorides, RCH(=O)Ph. The observed rate sequence cannot, therefore, be attributed to increasing steric inhibition of mesomerism (B above). But there is likely to be increasing steric strain
as R becomes larger (A above) and this would contribute to the observed sequence. Winstead and Morse have attributed the low rate of solvolysis of t-butylphenyl carbiny1 chloride (relative to that of methylphenyl carbiny1 chloride) in part to greater steric hindrance of solvation, and the different entropies of activation support this suggestion:

\[
\text{CH}_2\text{CHDPh}, \Delta S^\dagger = -17.1 \text{ e.u.}
\]

\[
\text{CH}_2\text{OHPh}, \Delta S^\ddagger = -3.1 \text{ e.u.}
\]

Winstead and Morse have also attributed the slow rate to the steric strain associated with the planar arrangement of the intermediate carbonium ion, resulting in a reduced stability even with the best compromise-configuration. The authors present two cases of "closely related steric effects" which, however, are not truly analogous:

1. The spectra of four \(\alpha,\beta\)-unsaturated ketones (XVII - XX) have been examined 75, to show that (XVII) and (XVIII) have similar spectra, and that (XIX) and (XX) have very similar spectra. This is evidence for steric inhibition of conjugation between the phenyl group and the olefinic bond in (XIX), but not in (XVIII). However, four bonds (1,2,3,4) are required to be coplanar in these ketones instead of only one in the t-buty1phenylmethyl carbonium ion (XVI, R = H), and molecular models indicate that these steric requirements are met in (XVI) but not in (XIX). Furthermore, it seems that ketones have not the same need for mesomeric stabilization as carbonium ions of similar structure, for pivalophenone (III) has sterically inhibited mesomeric (p. 1), whereas the t-buty1phenylmethyl carbonium ion has not (result of the present work).

2. The allyl ion (VII) has a rigid unsaturated ring forcing its nonplanarity, but this steric situation also, although quoted as related, is not analogous to that in the comparatively nonrigid t-buty1phenylmethyl carbonium ion.
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