THE BASICITY
OF
SOME ALKYL SUBSTITUTED
BENZOPHENONES

A THESIS
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ABSTRACT

Samples of 4-t-butyl-, 2,6 dimethyl-, 2,4,6-trimethyl-, and 2,6-dimethyl-4-t-butyl-benzophenones have been prepared. The dissociation constants of the conjugate acids of these ketones, together with benzophenone and 4-methylbenzophenone, have been measured by a spectrophotometric method. The results cannot be explained by the current concepts for the electronic effects of alkyl groups.
I. INTRODUCTION

The effect of alkyl substituents, or for that matter, any substituent, on organic reactivity may be regarded as the compounding of polar, resonance, and steric effects. For meta and para substituted benzene derivatives it was assumed that the substituents were held rigidly at sufficient distances from the reaction sites that no change in steric interaction occurred between the ground state and the transition state in the non-equilibrium case, or between the two ground states in the equilibrium case.

The polar effects of alkyl groups are separated from any resonance interactions in systems where there is no possibility of conjugation between the alkyl substituent and the reaction centre. Such a case is found in the ionisation of the phenylacetic acids where the dissociation constants in water at 25°C are

\[ \text{Phenylacetic acid, } p-\text{RC}_6H_4CH_2CO_2H. \quad H > p\text{-methyl} > p\text{-ethyl} \]

\[ 10^5 K_{\text{therm}} \]

\[ 4.88 \quad 4.27 \quad 4.24 \]

\[ p\text{-isopropyl} > p\text{-t-butyl} \]

\[ 4.06 \quad 3.82 \]

in accord with the order predicted by the inductive effects of the alkyl groups. The inductive effect, due to the greater electronegativity of H in the H-C bond than that of the methyl group in the CH\textsubscript{3}-C bond, can only be transferred through \( \sigma \) bonds. The order of inductive effects in the alkyl groups is t-Bu > iso-Pr > Et > Me > H, the opposite order to that found for the dissociation constants of the phenylacetic acids, as the electron-donating effect of the alkyl group can, through the inductive mechanism, destabilise the acid more than the anion.

That the alkyl groups could also release electrons by a conjugative mechanism was first suggested by Baker and Nathan in 1935, in order to explain the reactivity order
Me > Et > iso-Pr > t-Bu > H for the Henschelkin reaction between the para-alkylbenzyl bromides and pyridine. They suggested that the bonding electrons of the H-C bond in the alkyl group were less localised than those of a similarly placed C-C bond. In valence bond symbols this "hyperconjugation" was represented

\[
\begin{align*}
&\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H}
\end{array} \\
\Longleftrightarrow & \begin{array}{c}
\text{H} \\
\text{C} \cdots \text{C} \cdots \text{C} \\
\text{H}^+
\end{array} \\
&\begin{array}{c}
\text{H} \\
\text{H}
\end{array}
\end{align*}
\]

etc.

It was pointed out that electron release of this type only took place where there was a high demand for electrons, and where the alkyl group was joined to a conjugated system. Release by this mechanism will decrease Me > Et > iso-Pr > t-Bu as the number of \( \alpha \) C-H bonds decreases. The inductive effect and C-H hyperconjugation are both electron releasing mechanisms, but the order of the effects are in the opposite directions for the alkyl groups. It should therefore be possible to obtain a "jumbled" order of relative reactivity for the alkyl groups for a system where these electronic effects have comparable magnitudes. Such a reaction is the ionisation of the benzoic acids\(^1\) in water.

Benzoic acid \( H \) \( Me \) \( Et \) \( iso-Pr \) \( t-Bu \)

\[
\begin{align*}
10^5 K_{\text{therm}} & \quad \text{6.27} \quad \text{4.24} \quad \text{4.43} \quad \text{4.43} \quad \text{3.98}
\end{align*}
\]

Another system where an unequivocal hyperconjugative order is found is the solvolyses of the \( p \)-alkylphenyldimethylcarbinyl chlorides\(^3\), \( p-NC_6H_4CClMe_2 \).

Relative rates of solvolyses of "t-cumyl chlorides" in 90% acetone, 25\(^\circ\).

\[
\begin{align*}
\text{R} = & \quad H \quad Me \quad Et \quad iso-Pr \quad t-Bu \\
\text{meta} \quad k/k_0 & \quad 1 \quad 2.0 \quad 1.94 \quad 1.87 \quad 1.85 \\
\text{para} \quad k/k_0 & \quad 1 \quad 26.0 \quad 22.0 \quad 18.3 \quad 14.4
\end{align*}
\]

Even for the t-butyl group the rate for the para- substituted chloride is far greater than for the corresponding meta-compound. The increase for the \( p \)-methyl substituted compound has been ascribed to hyperconjugation and it is suggested\(^4\).
that the increase in rate for the \( p-t \)-butyl over the \( meta \)-
can also be ascribed to hyperconjugation, carbon–carbon
hyperconjugation, the transition state being represented as

\[
\text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 \quad \leftrightarrow \quad \text{CH}_3 - \text{C} - \text{C} - \text{CH}_3
\]

etc.

From the relative rates Brown estimated that this C–C hyper-
conjugative effect on the stability of the transition state
is worth 80\% of the corresponding C–H hyperconjugative effect.
Carbon–carbon hyperconjugation had also been invoked earlier
to explain the activating effect of the \( p-t \)-butyl group in
aromatic bromination\(^5\).

It was also pointed out by Brown\(^4\) that the slight
hyperconjugative order found for the \( meta \)-alkyl–\( t \)-cumyl
chlorides could be explained by a small hyperconjugative
interaction increasing the electron density at the ortho
position, from where the effect could be transferred by an
inductive mechanism to the reaction centre. A similar
mechanism had been used earlier to explain the activating
effect of the methoxy group in \( meta \)-bromination\(^6\). The
"shunting effect" has also been used to explain the hyper-
conjugative order found for the solvolyses of the \( p \)-alkyl-
benzyldimethylcarbiniyl chlorides\(^7\). Due to the blocking
methylene group no direct conjugation is possible between
the alkyl group and the reaction centre in the transition
state for the reaction.

The activating effect of the alkyl groups is thus
composed of the three separate effects, the inductive effect,
carbon–carbon hyperconjugation, and carbon–hydrogen hyper-
conjugation, the first two acting in opposition to the last
in giving the relative reactivities of the alkyl groups.
The original molecular orbital calculations\(^8\) did not dis-
tinguish between carbon–carbon and carbon–hydrogen hyper-
conjugation, so the relative effects of these two types of
electron release have only been gauged from experimental
results. There are some indications\(^9\) that the ratio of
the two hyperconjugative effects is constant over a wide series of electron demanding reactions.

All of the three electronic effects of alkyl groups are modified to varying extents by the reaction type, the solvent, and the temperature. It is believed that only in reactions of high electron demand are the hyperconjugative effects working to their fullest extent, but hyperconjugation is also found in reactions of low electron demand, as with the ionisation of the benzoic acids, and also in the ionisation of the anilinium ions and the 2-nitrophenols\(^{10}\). For other comparatively low electron demand reactions a reversal of order has been found with change of solvent, as in the alkaline hydrolysis of the \(\pi\)-alkyl-ethylbenzoates\(^{11}\) (hyperconjugative order in 85% ethanol but inductive order in 56% acetone). The order of reactivity is changed with solvent most commonly for \(meta\)-substituted compounds, not unexpectedly, because the hyperconjugative effects are assumed to be least here. Other changes in order with solvent have been noticed for the protode-de-tritiation reactions of the \(\pi\)-alkyl-phenzenes\(^{12}\).

Electrophilic aromatic substitution reactions cover a considerable range of electron-demand on substituents. The majority of these reactions have a high electron-demand corresponding to the need for stabilisation of the Wheland intermediate,

\[
\begin{align*}
R &= \text{H} & \leftrightarrow & \text{R}\text{H} \\
+ & \text{X} & & \text{etc}
\end{align*}
\]

where \(X\) is the attacking electrophile. It would be expected then, that a hyperconjugative order would be obtained for these reactions. Most of the electrophilic aromatic substitution reactions which have been investigated in detail are given in Table I.
Table I
Partial Rate Factors\(^{(a)}\) for Electrophilic Substitution of
Toluene and t-Butylbenzene\(^{(b)}\).

<table>
<thead>
<tr>
<th>Reaction(^{(c)})</th>
<th>Me</th>
<th>Me</th>
<th>t-Bu</th>
<th>t-Bu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Bromination, Br(_2), 85% HOAc, 25(^{\circ})</td>
<td>5.5</td>
<td>2420</td>
<td>6.09</td>
<td>806</td>
</tr>
<tr>
<td>2 Chlorination, Cl(_2), HOAc, 25(^{\circ})</td>
<td>4.95</td>
<td>820</td>
<td>6.0</td>
<td>401</td>
</tr>
<tr>
<td>3 Chloro-de-t-butylation of\n(\text{ArC} (\text{CH}_3)_3)Cl(_2), HOAc, 25(^{\circ})</td>
<td>610</td>
<td>(\ldots)</td>
<td>(\ldots)</td>
<td>380</td>
</tr>
<tr>
<td>4 Acetylation, CH(_3)COCl, AlCl(_3), C(_2)H(_4)Cl(_2), 25(^{\circ})</td>
<td>4.8</td>
<td>749</td>
<td>13.1</td>
<td>658</td>
</tr>
<tr>
<td>5 Benzoylation, C(_6)H(_5)COCl, AlCl(_3), C(_6)H(_5)NO(_2), 25(^{\circ})</td>
<td>5.0</td>
<td>830</td>
<td>(\ldots)</td>
<td>615</td>
</tr>
<tr>
<td>6 Benzoylation, C(_6)H(_5)COCl, AlCl(_3) C(_2)H(_4)Cl(_2), 25(^{\circ})</td>
<td>4.9</td>
<td>633</td>
<td>11.4</td>
<td>398</td>
</tr>
<tr>
<td>7 Deuteration, D(_2)O, CF(_3)CO(_2)H, 70(^{\circ})</td>
<td>3.8</td>
<td>421</td>
<td>7.0</td>
<td>490</td>
</tr>
<tr>
<td>8 Nitration, HNO(_3), 90% HOAc, 45(^{\circ})</td>
<td>2.5</td>
<td>58</td>
<td>4.0</td>
<td>75</td>
</tr>
<tr>
<td>9 Bromination, HOB(_r), HClO(_4), 50% dioxen 25(^{\circ})</td>
<td>2.5</td>
<td>59</td>
<td>2.60</td>
<td>38.6</td>
</tr>
<tr>
<td>10 Desilylation of ArSiMe(_3), Br(_2) HOAc, 25(^{\circ})</td>
<td>3.2</td>
<td>49</td>
<td>(\ldots)</td>
<td>29</td>
</tr>
<tr>
<td>11 Desilylation of ArSiMe(_3), HClO(_4), 50% MeOH</td>
<td>2.3</td>
<td>21.2</td>
<td>(\ldots)</td>
<td>15.6</td>
</tr>
<tr>
<td>12 Desilylation of ArSiMe(_3), HCl, HOAc(^{(d)})</td>
<td>2.14</td>
<td>20.1</td>
<td>2.98</td>
<td>11.9</td>
</tr>
<tr>
<td>10 Mercuration, Hg(OAc)(_2), HOAc, 25(^{\circ})</td>
<td>1.98</td>
<td>16.8</td>
<td>3.04</td>
<td>15.6</td>
</tr>
<tr>
<td>13 Protodetritiation, H(_2)SO(_4), 25(^{\circ})</td>
<td>4.9</td>
<td>253</td>
<td>(\ldots)</td>
<td>164</td>
</tr>
<tr>
<td>14 Protodetritiation, HOAc(^{(f)})</td>
<td>4.8</td>
<td>304</td>
<td>10.3</td>
<td>223</td>
</tr>
<tr>
<td>15 Protodetritiation, CF(_3)CO(_2)H(^{(g)})</td>
<td>8.8</td>
<td>683</td>
<td>35</td>
<td>835</td>
</tr>
</tbody>
</table>

(a) Partial rate factor is rate of substitution in specified position relative to substitution rate for one position in benzene; (b) Date for reactions 1-10 taken from Table I of Stock and Brown\(^{13}\), wherein all references to the
original work are given. Reactions 13-15 from ref. 12; (c) Reaction, electrophilic reagent, catalyst (where used), solvent, temperature; (d) 1.17 M HCl, 3.6 M H₂O, HOAc; (e) 66.6 moles % H₂O/H₂SO₄; (f) 34 moles % 40% H₂SO₄, 26% HOAc; (g) 3.95 moles % H₂O, 14.47 % H₂SO₄, 82.36% CF₃CO₂H.

A clear hyperconjugative order is followed by all but four of these reactions, the exceptions being nitration in acetic acid, acetylation in ethylene dichloride, deuteration in trifluoroacetic acid, and proto-de-tritiation in a mixed solvent containing trifluoroacetic acid. The order found for meta substitution is the inductive order without exception.

Explanations of the orders found have generally been in terms of the relative powers of the inductive and the two hyperconjugative effects. Other hypotheses have been put forward however, mainly dealing with solvent effects on the inductive order. These theories have been discussed in some detail by Berliner14,15, and the main alternative explanation is discussed in Section V of this work. It might be pointed out here that Brown16 has attempted to explain the essential constancy of \( p_{R}^{f} \) for acetylation of the alkylbenzenes in ethylene dichloride (Me 749, Et 743, iso-Pr 745, t-But 658) in terms of a mechanism involving a pi-complex between the substrate and the electrophile being transformed into a sigma-complex.

\[
\begin{align*}
R & \quad + \quad Z^+ \\
\xrightarrow{K_{R}} & \quad \xrightarrow{K_{\sigma}} \\
(\pi) & \quad \xrightarrow{H} \\
(\sigma^-) & \quad etc.
\end{align*}
\]

The stability of the pi-complex would be expected to be determined mainly by the inductive effects of the substituents, but the sigma-complex stability would be in the hyperconjugative order. However, the pi-complex stability is expected to affect the relative rates only if the pi-complex formation is rate determining, or where not, when the forces responsible for complex formation are also operating in the transition state of the rate determining step17. There is no evidence,
other than this, that pi-complexes are anything other than loose associations near the beginning of the reaction path in electrophilic substitution.

Several attempts have been made to separate the electronic effects involved in these electron-demanding reactions, but little progress has been made in isolating solvent effects. The most successful method for relating structure and reactivity in benzene derivatives is by the Hammett equation \(^{(18)}\)

\[
\log \frac{k}{k_0} = \sigma \rho
\]  

(1)

where \(k_0\) and \(k\) are equilibrium or rate constants for the unsubstituted and substituted benzene derivatives of type I.

![Diagram of benzene derivative](image)

In I, \(X\) is the reacting side-chain and \(R\) the variable substituent. The reaction constant \(\rho\), is constant for given conditions of temperature and solvent, and \(\sigma\) is a constant dependant only on the substituent, and its position in the nucleus. The substituent constants \((\sigma)^{(19)}\) are defined by the thermodynamic ionisation constants of the benzoic acids in water at 25\(^0\), with \(\rho = 1\). Because of this definition the reactivity order predicted for \(p\)-alkyl substituents by the Hammett equation is a "jumbled" order. It was found that the simple Hammett equation failed for electrophilic substitution reactions, and other electron-demanding reactions where there is a possibility of conjugation between an electron-donating (+M) substituent and an electron-withdrawing (-M) side-chain. For these reactions it was found that more negative sigma values where required for the +M groups. Brown and his associates have replaced the original sigma constants for these reactions, by special sigma values, \(\sigma^+\), found from the solvolyses of aryldimethylcarbinyil chlorides in 90% acetone at 25\(^0\) (with \(\rho = -4.54\)). It has been found that these new \(\sigma^+\) values hold for electrophilic substitution reactions.
and other highly electron-demanding reactions. It is to be expected, then, that where the reaction requires $\sigma^+$ values to fit the Hammett equation to the results, the hyperconjugative order will be found, and this is predicted in the substituent constants of the $p$-alkyl groups. The converse is not true however, as the ionisation of the anilinium ions follows the hyperconjugative order, but the reaction requires the special $\sigma^-$ substituent constants for conjugation between $+M$ sidechains and $-M$ substituents.

Actual resolution into inductive and resonance contributions has been carried out by Taft and Lewis using a modified Hammett equation. These workers have assumed that the inductive and resonance contributions are independent and additive,

\begin{align}
\log \frac{k_{\text{para}}}{k_0} &= I + R \\
\log \frac{k_{\text{meta}}}{k_0} &= I + \alpha R
\end{align}

where $I =$ inductive effect and $R =$ resonance effects. Other assumptions are that the inductive effect is the same in the meta and para positions, and that the resonance effect in the meta position is a constant fraction, $\alpha$, of the resonance effect in the para position ($\alpha = .33$ when the substituent is conjugated only with the ring, but $\alpha = .10$ when conjugated with the reacting side-chain). The inductive effects are given by

\begin{equation}
I = \sigma^I \rho \sigma_I \quad \text{(iv)}
\end{equation}

where $\sigma^I$ is the inductive substituent constant found from aliphatic unconjugated systems after correction for steric effects, and $\rho \sigma_I$ is the reaction constant. Alternatively $I$ is obtained by elimination of $R$ between equations (ii) and (iii). The resonance effects, $R$, are also given by combining equations (ii) and (iii), or by use of relation (iv) and equation (ii) or (iii). It has been shown that the
quantitative additive relationship

\[ R = n_H h_H + n_C h_C \]

holds for a wide series of reaction. Here \( n_H \) is the number of \( \alpha - C-H \) bonds, \( n_C \) the number of \( \alpha - C-O \) bonds in the alkyl group, and \( h_H, h_C \) are C-H and C-C hyperconjugation constants, respectively, in log units of rate or equilibrium. The ratio \( h_H/h_C \) was shown to be constant for reaction types corresponding to a wide range of electron demand, and to be independent of solvent and temperature.

Weepster has also attempted to resolve the electronic effects of substituents into resonance and essentially inductive components, again by using a modified Hammett equation. Using substituent constants for a select few substituents believed by him not to be capable of para resonance interactions, other substituent constants are calculated from the regression lines obtained. Weepster's "normal sigma values" \( (\sigma^n) \) are obtained as the mean values of these calculated sigma values for reactions where there were no possible resonance interactions. Quantitative resonance interactions for para substituents were then obtained from the calculated sigma values as

\[ -\Delta \Delta \log \frac{k}{k_o} = \rho (\sigma - \sigma^n) \times 2.303 \text{ RT} \]

obtained from

\[ \log \frac{k}{k_o} = \rho \sigma = \rho \sigma^n + \rho (\sigma - \sigma^n) \]

Thus Weepster's treatment is essentially the same as that of Taft except that the "inductive" substituent constants \( (\sigma^n) \) are obtained from reactions of benzene derivatives rather than from aliphatic reactions, and that the "fall off factors" \( \alpha \), for meta resonance interaction, compared with para, is regarded as being a fully variable "constant" where there are possibilities of para resonance interactions. Taft has
recognised this possibility in a later paper\textsuperscript{25}. At present there is only sufficient data for the alkyl groups to obtain a $\sigma^\text{H}$ value for the $p$-methyl group. In view of this paucity of data, and of indications that reactions Weisner considered as having no resonance interaction (as in the ionisation of the $p$-alkylanilines) do have small resonance contributions, it would seem better to use the original or modified ( $\alpha$-variable) Taft-Lewis equation for resolution of activating powers into polar and resonance effects.

The various sigma values are collected in Table II.

\begin{table}[h]
\centering
\caption{Sigma Values}
\begin{tabular}{|c|c|c|c|c|}
\hline
$R^-$ & $\sigma$ & $\sigma^\text{H}$ & $\sigma^+$ & $\sigma^I$ \\
\hline
H & 0 & 0 & 0 & 0 \\
p-Me & -.069 & -.069 & -.066 & -.05 \\
n-Me & -.170 & -.129 & -.311 & \\
n-St & -.07 & -.064 & \\
n-St & -.151 & -.295 & \\
n-iso-Pr & & & -.060 & \\
n-iso-Pr & -.151 & -.280 & \\
n-t-Bu & -.10 & -.059 & -.07 & \\
p-t-Bu & -.197 & -.256 & \\
Reference & 19 & 24 & 20 & 22 \\
\hline
\end{tabular}
\end{table}

From these values it can be seen that even in the ionisation of the benzoic acids the resonance interactions of alkyl groups are quite considerable.

To see how far these "resonance interactions" are simple resonance effects, rather than the effects of the solvent on the inductive effect, or all three electronic effects, reaction systems are required where conjugation can be destroyed, or partly destroyed by introduction of a suitable substituent. Such a system exists in the benzophenones. In strong acid solutions the carbonyl group of the benzophenone adds on a proton, and an ionisation
constant can be determined from the spectrophotometrically determined ratio of the conjugate acid to the base.

\[
\text{C-C} + H^+ \iff \text{C=O-H} (\text{H}_3\text{O}^+) + \text{C-C}
\]

This reaction should be highly electron-demanding, as was shown for the analogous ionisation of the substituted acetophenones\(^26\) which required the \(\sigma^+\) constant to fit the Hammett equation to the \(pK_{\text{BH}}\) values. It would be expected, then, that any electron-releasing mechanism through a resonance interaction for the 4-substituted alkyl groups will be largely invoked in the conjugate acid. This does not mean to say there is no hyperconjugation possible in the free base, but that the sacrificial hyperconjugation found here will affect the ionisation constant less than the homodative isovalent hyperconjugation\(^27\) in the conjugate acid. Sacrificial hyperconjugation exists when the pi-electron resonance stabilisation is due mainly to structures which have one less pi-bond, or quasi-pi-bond, than the single dominant valence bond structure. In homodative isovalent hyperconjugation there is charge redistribution (equalisation), but no loss of pi-bonds. That sacrificial hyperconjugation is not necessarily small in magnitude in a ground state is shown in the ionisation of the anilinium ions.

The introduction of methyl groups in the 2- and 6-positions in benzophenone would be expected to remove or greatly reduce conjugation between the substituted benzene ring and the carbonyl group.

The dissociation constants of the conjugate acids of two series of benzophenones were measured spectrophotometrically. The first series, benzophenone, 4-methyl and 4-t-butyl-benzophenone, would be expected to show the
hyperconjugative order (Me > t-Bu > H) in the $pK_{BH^+}$ values, and the second series, 2,6-dimethyl, 2, 4, 6-trimethyl, and 2, 6-dimethyl-4-t-butylbenzophenone would be expected to show, if not the inductive order, a reduction in the $pK_{BH^+}$ difference between the methyl and t-butyl para-substituted ketones, if the current concepts of H-C, and C-C hyperconjugation, and the inductive effect are to be believed. As this is an equilibrium study, the full inductomeric and electromeric effects obtained in kinetic studies will not be included, and solvent effects will be limited.
II. 

EXPERIMENTAL

A Preparation of Benzophenones.

Physical constants are uncorrected. Physical constants in parentheses are, unless otherwise stated, the values given in Beilstein's "Handbuch der Organischen Chemie".

(a) Benzophenone

Commercial grade benzophenone was recrystallised three times from methanol, and once from low-boiling petroleum ether. m.p. 48° (48.5°)

(b) 4-Methylbenzophenone.

Commercial grade 4-methylbenzophenone was recrystallised three times from methanol. m.p. 57° (59-60° stable modification)

(c) 4-t-Butylbenzophenone.

4-t-Butylbenzophenone was prepared from t-butylbenzene by the usual Friedel-Crafts benzoylation. t-Butylbenzene (21.5 g) and redistilled benzoyl chloride (24 g) in carbon disulphide (20 ml) were slowly added to an ice-cooled, stirred mixture of aluminium chloride (24 g) and carbon disulphide (100 ml). The reaction mixture was stirred for 15 min. at below 5°, and then allowed to warm upon a water bath for the carbon disulphide to reflux for 45 min. After decomposition with dilute hydrochloric acid-ice, the aqueous layer was separated and extracted twice with ether. The organic layer, after removal of carbon disulphide, was combined with the ether extracts, washed successively with water, 10% sodium hydroxide, water, dried over magnesium sulphate, and distilled to give 19.5 g (62%) slightly blue oil. The ketone was twice distilled, the middle fraction b.p. 189°/4 mm. being collected as a viscous oil. This oil later crystallised, and was recrystallised from methanol, melting range 31.5 - 35°. (reported m.p. 36 - 37.5° 26.

The melting range found could perhaps be explained in part by supercooling, or by the ketone existing in a stable, and a labile form, as does benzophenone, and several other
para substituted benzophenones. Other workers\textsuperscript{29, 37} apparently obtained the ketone only as a viscous oil. A small quantity of the ketone was reduced\textsuperscript{29} to 4-\text{t}-butylbenzhydrol for characterisation purposes. m.p. 82° (reported\textsuperscript{29} 83°).

(d) 2, 4, 6-Trimethylbenzophenone

2, 4, 6-Trimethylbenzophenone was prepared from mesitylene (21.5 g) by the Friedel-Crafts method described above. A colourless viscous oil (21.5 g, 54\%) was obtained after fractionation through a 5 cm. Vigueux column, b.p. 136 - 90°/5 mm. (m.p. 35.5°)

(e) 2, 6-Dimethyl-4-\text{t}-butylbenzophenone

The ketone was prepared from \textit{m}-xylene via 1, 3 dimethyl-5-\text{t}-butylbenzene

(i) 1,3-Dimethyl-5-\text{t}-butylbenzene.

The Friedel-Crafts alkylation method for \textit{m}-xylene was based on that of Norris and Sturgis\textsuperscript{30}. This method was varied in that a much lower molar ratio (1 to 1.3) of aluminium chloride to \text{t}-butyl alcohol was used. \textit{m}-Xylene (420 g) and \text{t}-butyl alcohol (51 g) were added with vigorous stirring to aluminium chloride (70 g) in an ice-salt cooled flask. The reaction mixture was kept below 0° for four hours and then kept at 50 - 55° for 90 min. The decomposition and extraction procedure was the same as that used for 4-\text{t}-butylbenzophenone.

The hydrocarbon was fractionated through a 10 cm. Fenske helix packed column b.p. 101°/25 mm (reported\textsuperscript{31}, 103 - 5°/29 mm) to give 78 g (70\%) 1, 3 dimethyl-5-\text{t}-butylbenzene.

(ii) 2, 6-Dimethyl-4-\text{t}-butylbenzophenone.

1, 3-Dimethyl-5-\text{t}-butylbenzene was benzoylated as above. From \textit{sym}-\text{t}-butyl-xylene (18 g) were obtained plates of
2, 6-dimethyl-4-t-butylbenzophenone (3.5 g, 11%) after distillation, b.p. 171 - 174°/4 mm, and recrystallisation from methanol and low boiling petroleum ether. m.p. 106 - 106.5° (Fusion et al. report 106 - 107.5° for the ketone prepared by this Friedel-Crafts reaction.)

(f) 2, 6-Dimethylbenzophenone

2, 6-Dimethylbenzophenone was prepared from 2, 6-xylidine by the route -

(i) Diazotisation of 2, 6-xylidine

2, 6-xylidine was diazotised, and converted to the iodo-compound by the method of Jacobs.32.

A cooled solution of sodium nitrite (7.8 g in 50 ml) was added over 5 min to a mechanically stirred 2, 6-xylidine hydrochloride suspension in hydrochloric acid (from 13.1 g distilled 2, 6-xylidine and 100 ml. 5N hydrochloric acid), the temperature being kept below -5° during the addition. After further stirring for 15 min., an aqueous solution of potassium iodide (18.8 g in 20 ml) was added to the reaction mixture at such a rate that the temperature remained below 5°. The reaction mixture was left over-night after stirring had been continued for 30 min. on the ice-bath. After warming on a water-bath for one hour, the mixture was made alkaline with 30% sodium hydroxide and steam distilled. The iodo-compound was extracted with ether, washed
successively with 10% sodium hydroxide and water, dried over magnesium sulphate and distilled to give 10.5 g. red
"2, 6-dimethyliodobenzene", boiling range 65 - 70°F/2 mm.,
°D 1.5603. (Jacobs reports 58 - 59°/5 mm., D 1.6003).

No Grignard reagent could be formed from this product,
and when this product, together with that from a diazot-
isation, etc., carried out at 5 - 10°F, was carefully
fractionated through a 15 cm. Fenske helix packed column,
as well as pure 2, 6-dimethyliodobenzene, a slightly yellow,
mobile chloro-compound was collected. b.p. 35°F/1 mm.,
186 - 7°F/768 mm. (reported for 2, 6-dimethylchlorobenzene,
C₈H₉Cl, b.p. 185 - 7°F) D 1.5255.

Analytical - Calculated for C₈H₉Cl C, 63.33; H, 6.45;
Cl, 25.22. Found - C, 68.43; H, 6.45; Cl, 24.83.

Using the above diazotisation, etc., procedures except
that the crude product was washed with dilute hydrochloric
acid, 2, 6-dimethyl-iodobenzene (7.5 g) was obtained in
30% yield. b.p. 46°F/2 mm., D 1.5969 (reported
D 1.6003).

In a separate preparation 2, 6-xylydine hydrochloride
(7 g) in 30 ml. 10 N hydrochloric acid was diazotised by
sodium nitrite (3.25 g) at less than 0°F. The reaction
mixture, after addition of a further 30 ml. 10 N hydrochloric
acid, was heated on a water bath for one hour. The crude
product from steam distillation of the reaction mixture
was extracted with ether, washed with water and dilute
sodium hydroxide, taken up in petroleum ether, and passed
through an alumina column to give slightly yellow
2, 6-dimethylchlorobenzene (3.8 g, 60%). Acidification
of the alkaline washings gave only traces of acidic compounds.
Hantsch reported a 60% yield of chlorobenzene from the
decomposition of phenyldiazonium chloride in concentrated
hydrochloric acid. No Grignard reagent could be prepared
from the 2, 6-dimethylchlorobenzene.

(ii) 2, 6-Dimethylbenzophenone.

The 2, 6-dimethylphenyl magnesium iodide was formed
by the usual Grignard reaction taking all necessary precautions against entry of moisture. Freshly distilled
2, 6-dimethyliodobenzene (10 g) in dry ether was slowly added with mechanical stirring to washed, dried magnesium
(1 g) in dry ether (75 ml). The reaction mixture was warmed for the ether to reflux for 30 min. after the last
addition of the iodoxyylene. From a separate Grignard reaction,
2, 6-dimethylphenyl magnesium iodide (from 5 g. iodoxylene)
was carbonated by dry ice to give 2, 6 dimethylbenzoic acid
(0.9 g, 28%) m.p. 116° after recrystallisation from water.
(m.p. 116°).

The Grignard reagent was reacted with benzoyl chloride
under optimum conditions for this low yield process, that
is, using reverse addition of the Grignard reagent to excess
benzoyl chloride. Low temperatures were not required here
as, due to steric interactions, there is little chance of
further reaction of the Grignard reagent with the ketone formed.

The slightly yellow ethereal solution of 2, 6-dimethyl-
phenyl magnesium iodide, together with ethereal washings of
the residual magnesium, were transferred to a dropping
funnel protected by a silica gel guard tube, and slowly added
(20 min.) with mechanical stirring to distilled benzoyl
chloride (9 g, i.e. 50% excess) in dry ether (30 ml) to
give a slightly yellow fine precipitate. After addition
of the last of the Grignard reagent the reaction mixture
was refluxed for 14 hours, and then decomposed by refluxing
for 30 min. with 10% acetic acid solution (70 ml). The
ethereal layer was separated, combined with ethereal extracts
from the aqueous layer, washed successively with 5% sodium
hydroxide, dilute hydrochloric acid, water, and dried over
magnesium sulphate. The reaction products were distilled
to give, along with unreacted iodoxylene (1.5 g), crude
2, 6-dimethylbenzophenone, boiling range 150 - 160°/3.5 mm.
The crude product was taken up in low boiling petroleum
ether and passed through an alumina adsorption column to
give white needles of 2, 6-dimethylbenzophenone (0.55 g, 5%) m.p. 63.5 - 64.0. After four recrystallisations from low boiling petroleum ether the melting point was raised to 64 - 64.5.0.

Analysed - Required for C_{15}H_{14}O: C, 85.68; H, 6.71.
Found, C, 85.70; H, 6.75.

Sulphuric Acid Solutions

Sulphuric acid solutions were made covering the range 45 - 95% (by weight) sulphuric acid at about every 5% by dilution of analytical reagent grade concentrated sulphuric acid. A sample of the undiluted acid was weighed from a weight-burette into a calibrated 250 ml. volumetric flask, diluted with water to the volume and titrated from a calibrated burette at constant temperature against weighed samples of analytical reagent grade sodium carbonate which had been dried at 270°C for 90 min. The indicator used was phenol red (pH_in = 8) and the endpoint taken at no colour change on boiling for 5 minutes. The relatively high second dissociation constant of sulphuric acid necessitates the use of an indicator which gives an end-point at a pH of at least 5. Determinations agreed to within ±0.2%.

The concentrated sulphuric acid was diluted by weight by slowly adding distilled water to a known weight of standardised acid in a 1 l. long-necked flat-bottomed flask of borosilicate glass. Standardisation, as above, of a diluted acid agreed to within ±0.1% - i.e. less than the error in standardisation.

20 volume % ethanol - 80 vol. % sulphuric acid-water mixtures were made by a method similar to that of Jaffe. The ethanol had been made low in aldehydes by distilling successively from sulphuric acid and from alkaline silver nitrate (10 g. silver nitrate with 1 g. potassium hydroxide per litre of ethanol). The ethanol was not dried.

Ethanol (20.0 ml) was pipetted into a volumetric flask (100.0 ml), placed in a thermostatted bath at 25.0±0.1°C, and
then diluted to the mark with sulphuric acid of known concentration. There was considerable change of volume on mixing. The density and the concentration by weight of sulphuric acid were obtained from the weights of ethanol and sulphuric acid used.

Dioxan was fractionated off bright sodium using a 60 cm. Fenske helix packed column, the fraction b.p. 101.0°/755 mm. being collected.

C Spectrophotometric Measurements.

Extinction coefficients were measured at two sets of wave-lengths with a Hilger "Unispek" ultra-violet photo-electric spectrophotometer, using the hydrogen discharge tube. The 1 cm. and 4 cm. fused quartz cells were maintained at 25.0±0.2° by a thermostatted cell holder. Solutions required 15 - 20 min. to come to temperature equilibrium as shown by constant optical densities. The cells were matched by comparison when filled with distilled water or potassium chromate solutions. The maximum difference in absorption was .003 density units in the wavelength regions used. Between measurements the cells were rinsed successively with distilled water, methanol and chloroform, and dried in a nitrogen flow.

Extinction coefficients (ε) are defined by the usual relation

\[ D = \log_{10} \frac{I_0}{I} = \varepsilon c l \]

where \( l \) is the thickness of the absorbing layer in cm., and \( c \) the stoichiometric concentration of the solute in moles/l.

Errors in the spectrophotometric determination of extinction coefficients have been discussed comprehensively by Kaplan\textsuperscript{37}, who reached the conclusion that the total errors do not exceed 2 - 3%.

Solutions of the ketones were made in either of several ways, all ketones being recrystallised or redistilled before use.

(a) Where the ketones did not react with the sulphuric acid solvent, a stock solution of the ketone was made in a
sulphuric acid-water mixture of 70 - 80% strength by weight. The ketone (.015 - .02 g) was weighed in a small boat which had been allowed to come to equilibrium with the balance surroundings, transferred to a ground-glass stoppered flask, and sulphuric acid (20 - 40 ml) weighed into the flask to give an about $10^{-3}$ molar solution. The stock solution (.7 to 1.0 g) was diluted with the requisite acid (15 - 20 ml) to give the about $6 \times 10^{-5}$ molar solution required for the 1 cm. cells. Where low solubility prevailed the 4 cm. cells were used and the concentration lowered to as far as $1 \times 10^{-5}$ m. The solvent blank was of the same strength acid as that used to dilute the stock solution. This gave a sulphuric acid concentration difference between blank and test solutions of up to .4% by weight, but as 78% sulphuric acid has a maximum optical density (1 cm. cell) of .110 in the wavelength regions used, the error in optical density is negligible.

(b) With 2, 4, 6-trimethylbenzophenone and 2, 6-dimethyl-4-t-butylbenzophenone, where the ketone reacted with the sulphuric acid solvent, the stock solution of the ketone was made in a 66% dioxan-water mixture. A small amount of this stock solution (.07 to .09 g) was weighed into a ground-glass stoppered flask, and where the solubility permitted the dioxan-water solvent was removed at a vacuum pump before addition of the sulphuric acid solvent.

(c) With the acid concentrations where low solubility prevailed the test solution was made by adding the sulphuric acid-water solvent to the dioxan-water stock solution. The appropriate blank was made by making up approximately the same concentration dioxan-sulphuric acid-water solution. The optical density difference between the blank and the solvent of the test solution was less than .005 optical density units. This method was only used with 2, 4, 6-trimethylbenzophenone in below 60% sulphuric acid solutions, and with 2, 6-dimethyl-4-t-butylbenzophenone in below 80% sulphuric acid solutions. The dioxan concentration in the test solution was always less than 0.08% by weight.
giving a negligible change in pH, and Hₐ.

With these last two methods, cells could be placed in the thermostatted jacket within 4 min. of addition of the sulphuric acid-water solvent.

(d) For 2, 6-dimethyl-4-t-butylbenzophenone in less than 70% sulphuric acid-water a change was made to the 20 volume % ethanol - 80 volume % sulphuric acid - water system. The results in this solvent system were necessary only to define the lower line for the Geissman plot, (see Section III) where the ketone is less than 5% protonated. Any effect of the change in the solvent on the absorption spectra is reduced in the interpretation method, a change of 10% in extinction coefficients resulting in only a .05 pH unit change for this acidity range.

All concentrations were calculated, through the weights of the components of the solutions, from tabulated values of the densities of sulphuric acid - water mixtures at 25°C. For the 20 vol. % ethanol - 80 vol. % sulphuric acid - water system the densities were determined at the time of preparation.

The errors involved in preparation of solutions are estimated to be not greater than 1%, so that the total error in extinction coefficients is less than 4 - 5%, taking into account the difference in optical density between solvent and blank.

The six wavelengths used for each ketone were such that the absorption maxima of the base and acid forms were covered over a 100 Å range, values being taken at every 50 Å. The absorption maxima were found to the nearest 50 Å from scans over the range 2300 - 3300 Å in 85% and 60% sulphuric acid-water solutions. Beer's law was obeyed for all ketones over the small concentration range and the acidity ranges used. Apparent failure of Beer's law in preliminary investigation of 2, 4, 6-trimethyl-, and 2, 6-dimethyl-4-t-butylbenzophenones was due to a slow, presumably proto-de-benzoylation, reaction analogous to the proto-de-acetylation reaction of the acetophenones studied by Schubert. Pseudo-first order kinetics
were followed in 87.7% sulphuric acid - water solution with an observed rate constant of \(1.4 \times 10^{-5}\ \text{sec}^{-1}\). Zero-time spectra for these two ketones were obtained from \(\epsilon -\text{time}\) plots over a 60 min. period, the first value being taken after 15 - 20 min. The linear extrapolation over this, in the majority of cases, much less than one-twentieth half-life, gave zero-time extinction coefficients differing very little from strictly first order extrapolations. For 2, 4, 6-tri-methylbenzophenone the reaction was sufficiently slow in 75% sulphuric acid - water for the extinction coefficients after 20 - 25 min. to be taken as zero-time spectra, but for 2, 6-dimethyl-4-t-butylbenzophenone extrapolation to zero-time had to be carried out to below 55% sulphuric acid.

A solution of 2, 6-dimethylbenzophenone in 74.7% sulphuric acid - water, where it is 67% protonated, showed no change in extinction coefficient after 8 days.
III.

CALCULATION OF BASICITY

For the base, B, we have

\[ B + H^+ \rightarrow BH^+ \]

for which the dissociation constant is

\[ K = \frac{a_{H^+} a_B}{a_{BH^+}} \]

where \( a_{H^+} \), etc., are activities, and

\[ \text{pK}_{BH^+} = \log \frac{c_{BH^+}}{c_B} - \log \frac{a_{H^+} \gamma_B}{\gamma_{BH^+}} \]

where \( c_B \), etc., are molar concentrations, and \( \gamma_B \), etc., activity coefficients, the standard state (i.e. \( \gamma = 1 \)) being an infinitely dilute aqueous solution. For the acidity function, \( H^0 \), defined by

\[ H^0 = -\log \frac{a_{H^+} \gamma_B}{\gamma_{BH^+}} \]

then \( \text{pK}_{BH^+} = H^0 + \log \frac{c_{BH^+}}{c_B} \) (1)

The acidity scale, as defined, is dependent on the base, B, but Hammett and others have shown the constancy of the \( H^0 \) scale using a variety of electrically neutral bases, implying that the ratio \( \gamma_B / \gamma_{BH^+} \) is independent of the base. As the acidity scale has been linked up with the pH scale in dilute aqueous solution the dissociation constants found are thermodynamic constants, i.e. dissociation constants in an infinitely dilute aqueous solution.

The measurement of \( \text{pK}_{BH^+} \) now resolves into the measurement
of \( R_0 \), and of \( \frac{c_{BH^+}}{c_B} \). Values for the acidity function in sulpheric acid-water mixtures have recently been revised by Paul and Long.\(^1\)

The ratio \( \frac{c_{BH^+}}{c_B} \) can be found spectrophotometrically. Assuming the species \( B \), \( BH^+ \) absorb independently, then from Beer's law

\[
\epsilon = \frac{\epsilon_B c_B + \epsilon_{BH^+} c_{BH^+}}{c_B + c_{BH^+}}
\]

and hence \( \frac{c_{BH^+}}{c_B} = \frac{\epsilon - \epsilon_B}{\epsilon_{BH^+} - \epsilon} \) \hspace{1cm}(2)

where \( \epsilon \) is the observed extinction coefficient. The extinction coefficients, \( \epsilon_B \), \( \epsilon_{BH^+} \), of the free base and the conjugate acid cannot be taken as those obtained from sulpheric acid-water solutions corresponding to, say 5% and 99.5% ionisation because of the medium effect. This medium effect\(^2\), due to a gradual variation in the nature of the medium in which the absorbing substance is dissolved, has been assumed to be a shift in the reference spectra along the wavelength axis to higher wavelengths with increasing sulpheric acid concentration, without any change in the shape of the curves, or the value of \( \epsilon_{max} \).

Hamnett\(^2\) has developed two methods for correcting for this medium effect. In the first, equations (1), (2) are combined in either of the two forms

\[
K_{BH^+} + \frac{\epsilon_{BH^+} h_B}{\epsilon_B - \epsilon} - \frac{h_B \epsilon}{\epsilon_B - \epsilon} = 0 \hspace{1cm}(3)
\]
\[
\text{or } \frac{1}{K_{BH^+}} + \frac{\varepsilon_B}{h_0 (\varepsilon_{BH^+} - \varepsilon)} \left( \frac{1}{h_0 (\varepsilon_{BH^+} - \varepsilon)} \right) = 0 \quad (4)
\]

where \( h_0 \equiv \text{antilog} (-K_0) \)

The first of these two equations is used where the reference curve of the free base has the least slope, and so is least affected by the medium effect. The value of \( \varepsilon_B \) is taken for the substance at 5% ionisation, and the dissociation constant and \( \varepsilon_{BH^+} \) calculated by least squares, using equation (3), from extinction coefficients found in a range of sulphuric acid-water mixtures. For the least squares analysis the data should be treated as if both the variables \( \frac{h_0}{(\varepsilon_B - \varepsilon)} \) and \( \frac{h_0 \varepsilon}{(\varepsilon_B - \varepsilon)} \) were liable to error\(^{13}\). This treatment weights the data as if each of the variables had equal probable errors in the derived function throughout the range in values, but this is not so. It would appear rather difficult to obtain a satisfactory method to find parameters \( K, \varepsilon_{BH^+} \) for fitting the data to the form of equation (3). In most cases it is doubtful whether an analysis of this type has been made when correcting for the medium effect by using this first method of Hammett.

The second method of Hammett\(^{12}\) involves the creation of an isobestic point on the assumption that the medium effect causes only a lateral shift in the absorption curves. For accurate measurements using this method, a large number of experimental values would appear necessary.

Gold and Hawes\(^{14}\) have developed a method for correction of the medium effect for substances for which the more weakly-absorbing form does not absorb at all at the wavelengths used. For the 2, 6-dimethylbenzophenones there is no wavelength in the regions studied where this criterion is obeyed.
The \( pK_{BH^+} \) values in this investigation were determined by the method of Davis and Geissman.\(^4\)

For Beer's law holding,

\[
(\varepsilon)_{\lambda_{HB^+}} = (\varepsilon_B)_{\lambda_{HB^+}} + [(\varepsilon_{HB^+})_{\lambda_{HB^+}} - (\varepsilon_B)_{\lambda_{HB^+}}]I, \tag{5}
\]

\[
(\varepsilon)_{\lambda_B} = (\varepsilon_{HB^+})_{\lambda_B} + [(\varepsilon_B)_{\lambda_B} - (\varepsilon_{HB^+})_{\lambda_B}](1-I), \tag{6}
\]

where \( \varepsilon \), observed molar extinction coefficient;
\( \varepsilon_B \), molar extinction coefficient of the unionised form;
\( \varepsilon_{HB^+} \), molar extinction coefficient of ionised form;
\( \lambda_B \), a wavelength where \( \varepsilon_B >> \varepsilon_{HB^+} \);
\( \lambda_{HB^+} \), a wavelength where \( \varepsilon_{HB^+} >> \varepsilon_B \);
\( I \), the fraction of the compound in the ionised form.

Subtracting (6) from (5) and putting

\[
D = (\varepsilon)_{\lambda_B} - (\varepsilon)_{\lambda_{HB^+}},
\]

\[
D = [(\varepsilon_B)_{\lambda_{HB^+}} - (\varepsilon_B)_{\lambda_B}] + [(\varepsilon_{HB^+})_{\lambda_{HB^+}} - (\varepsilon_B)_{\lambda_{HB^+}}]
+ [(\varepsilon_B)_{\lambda_B} - (\varepsilon_{HB^+})_{\lambda_B}] \times I
\]

The values of \( (\varepsilon_B)_{\lambda_{HB^+}} \), etc., vary with the sulphuric acid concentration, but may be assumed to be nearly constant over a small acid concentration near 50% ionisation. Thus over a small range,

\[
I = K + cD
\]

where \( c = 1/\left[ (\varepsilon_{HB^+})_{\lambda_{HB^+}} - (\varepsilon_B)_{\lambda_{HB^+}} + (\varepsilon_B)_{\lambda_B} - (\varepsilon_{HB^+})_{\lambda_B} \right] \)

and \( K = \left[ (\varepsilon_B)_{\lambda_B} - (\varepsilon_B)_{\lambda_{HB^+}} \right] \times c \)
\[ H_0 = pK_{BH^+} + \log \frac{c_B}{c_{BH^+}} \]

so

\[ H_0 = 4.43 \ln \left( \frac{1 - cD - K}{K + cD} \right) + pK_{BH^+} \]

The curve obtained by plotting D against \( H_0 \) has slope \( \frac{dH_0}{dD} \) and at the inflection point

\[ \frac{d^2H_0}{dD^2} = 0 = -4.43 c^2 \left[ \frac{1}{(1 - cD - K)^2} - \frac{1}{(cD + K)^2} \right] \]

i.e.

\[ 1 - (cD + K) = cD + K \]

or fraction ionised equals the fraction unionised and, therefore, \( H_0 = pK_{BH^+} \)

The wavelengths chosen were close to those for the maximum absorption of the ionised and the unionised forms. The inflection point of the \( H_0 \) vs. D sigmoid curve was taken as the midpoint of the intercept formed on the "straight" portion by extrapolation of the nearly constant D portions. The \( H_0 \) values were obtained by linear interpolation of values revised by Paul and Long\(^{41}\) for the sulphuric acid-water system, or from those of Si-Jung Yeh and Jaffe\(^{35}\) for the 20 vol. % ethanol - 80 vol. % sulphuric acid-water system.
IV

RESULTS

The spectra of two representative ketones in sulphuric acid-water solutions are shown in Figures I, II. The zero-time spectra of 2, 4, 6-trimethyl- and 2, 6-dimethyl-4-tert-butylbenzophenone were only obtained for a limited wavelength range.

Values of \( \lambda_{\text{max}} \) for the free base and the conjugate acid in 50% and 98% sulphuric acid, respectively, are given to the nearest 50 \( \AA \) in Table III.

<table>
<thead>
<tr>
<th>Benzophenone</th>
<th>( \lambda_{\text{max}} ), B(a), ( \AA )</th>
<th>( \lambda_{\text{max}} ), BH(^{+})(b), ( \AA )</th>
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<tbody>
<tr>
<td>H</td>
<td>2600</td>
<td>3400</td>
</tr>
<tr>
<td>4-Methyl</td>
<td>2750</td>
<td>3600</td>
</tr>
<tr>
<td>4-t-Butyl</td>
<td>2750</td>
<td>3650</td>
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<td>3050</td>
</tr>
<tr>
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<td>3000</td>
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<tr>
<td>2, 6-Dimethyl-4-t-butyl</td>
<td>2550(^{(c)})</td>
<td>3050</td>
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</table>

(a) in 50% sulphuric acid-water, (b) 98% sulphuric acid-water, (c) in 20 vol. % ethanol - 80 vol. % (11 N) sulphuric acid-water.
Basicities

An example of the sigmoid curves obtained is shown in Figure III for 2, 6-dimethylbenzophenone with
\[ D = 3000 \beta - 2600 \beta \], giving \( \log K_{BH^+} = 6.10 - 6.58 \)

(a) Benzophenone

<table>
<thead>
<tr>
<th>H°</th>
<th>( \epsilon 2550 \beta )</th>
<th>( \epsilon 2600 \beta )</th>
<th>( \epsilon 2650 \beta )</th>
<th>( \epsilon 3300 \beta )</th>
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<td>15080</td>
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\( \lambda_{BH^+} : 3350 \beta \ 3400 \beta \ 3450 \beta \ 3350 \beta \ 3400 \beta \ 3450 \beta \ 3350 \beta \ 3400 \beta \ 3450 \beta \)

\( \lambda_B : 2550 \beta \ 2550 \beta \ 2600 \beta \ 2600 \beta \ 2650 \beta \ 2650 \beta \ 2650 \beta \ 2650 \beta \)

\( -\log K_{BH^+} : 6.09 \ 6.16 \ 6.21 \ 6.13 \ 6.20 \ 6.20 \ 6.18 \ 6.24 \ 6.25 \)

Mean \( \log K_{BH^+} = 6.18 \)

Standard Deviation = 0.48
(b) \( \text{\textit{d-Methylbenzophenone}} \)

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\(\lambda_B: 2700 \, \AA, 2700, 2700, 2750, 2750, 2750, 2800, 2800, 2800\)

\(-pK_{BH^+} : 5.78, 5.84, 5.92, 5.82, 5.93, 6.02, 5.78, 5.92, 6.03\)

Mean \( pK_{BH^+} = -5.89 \)

Standard Deviation = 0.089
(c) 4-t-Butylbenzophenone

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$\lambda_{HB^+}$: 3550 Å 3600 3650 3550 3600 3650 3550 3600 3650

$\lambda_B$: 2700 Å 2700 2700 2750 2750 2750 2800 2800 2800

$-pK_{HB^+}$: 5.97 6.01 6.05 5.89 6.02 6.06 5.96 6.03 6.08

Mean $pK_{HB^+} = -6.01$

Standard Deviation = .056
(a) 2, 6-Dimethylbenzophenone

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$\lambda_{\text{BB}^+}$: 2950 Å 3000 3050 2950 3000 3050 2950 3000 3050

$\lambda_{B}$: 2550 Å 2550 2550 2600 2600 2600 2600 2650 2650 2650

$-pK_{\text{BB}^+}$: 6.31 6.50 6.60 6.36 6.56 6.62 6.44 6.64 6.74

Mean $pK_{\text{BB}^+} = -6.53$

Standard Deviation = .13
(e) \textit{2, 4, 6-Trimethylbenzophenone}

\begin{tabular}{|c|c|c|c|c|c|c|}
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2.88 & 13420 & 13510 & 12180 & 4970 & 4220 & 3510 \\
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$\lambda_{\text{HB}^+}$: 2950 2950 3050 3000 3050 2950 3000 3050

$\lambda_{\text{B}}$: 2550 2550 2550 2600 2600 2650 2600 2650 2600

$-\text{pK}_{\text{HB}^+}$: 5.88 6.00 6.08 5.97 6.20 6.24 6.16 6.28 6.38

\begin{align*}
\text{Mean } \text{pK}_{\text{HB}^+} &= -6.13 \\
\text{Standard Deviation} &= .15
\end{align*}
(f) 2, 6-Dimethyl-4-t-butylbenzophenone

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$\lambda_{BH^+}$: 2950 Å 3000 3050 2950 3000 3050 2950 3000 3050

$\lambda_B$: 2550 Å 2550 2550 2600 2600 2600 2650 2650 2650


Mean $pK_{BH^+} = -6.35$

Standard Deviation = .13
Figure I

4-Methylbenzophenone

1 \( H_0 = -7.92 \)
2 \( -5.61 \)
3 \( -3.94 \)
Figure II

2,6-Dimethylbenzophenone

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Wavelength in Angstroms
Figure III
Gaisseman Plot
2,6-Dimethylbenzophenone

\[
(E_{3000} - E_{2600}) \times 10^{-3}
\]

Acidity Function, \(-H_0\)
V.

DISCUSSION

The $pK_{BH^+}$ values determined are collected in Table IV.

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The only value of basicity recorded for the benzophenones is that for benzophenone itself. The value, when corrected to the revised $H_0$ scale used in this investigation, is in agreement with the value found here ($-6.12$).

A  Accuracy of Results

The total error in extinction coefficients was estimated in section II C to be less than $4 - 5\%$. As the value of the function plotted depends on the difference in two extinction coefficients, the maximum error in $D$ varies from $\pm 500$ to $\pm 1000$ extinction units corresponding to $D$ values from 0 to $\pm 20,000$ respectively giving an error of $\pm 0.1$ unit in $pK_{BH^+}$. The error in the absolute $H_0$ values is of the order $\pm 0.05$ unit, so the total error in the absolute $pK_{BH^+}$ values should be less than $0.15$ unit.

The trend in $pK_{BH^+}$ with wavelength is systematic over the wavelength region used, an increase in $\lambda_B$ or $\lambda_{BH^+}$ giving a decrease in $pK_{BH^+}$. A similar trend was found in a reanalysis of Hammett's data for acetophenone, using the Geissman method for correction of the medium effect.
Acetophenone

\[ \lambda_{BH^+} = 2900 \text{ Å} \quad 3000 \quad 2900 \quad 3000 \quad 2900 \quad 3000 \]

\[ \lambda_B = 2400 \text{ Å} \quad 2400 \quad 2500 \quad 2500 \quad 2600 \quad 2600 \]

\[ -pK_{BH^+} = 6.07 \quad 6.53 \quad 6.17 \quad 6.53 \quad 6.42 \quad 6.88 \]

The values of \( pK_{BH^+} \) for acetophenone can only be compared indirectly with the value -6.03 given by Hammett as the mean of values from eleven wavelengths (2400 Å to 3600 Å) using his first method for correction of the medium effect, as the H_o scale used in the reanalysis is on the average .12 unit more negative than that used by Hammett\(^{41}\). However, using this correction of .12 unit, Hammett's mean value of -6.15 compares favourably only with value of -6.17 found by the Geissman method using \( \lambda_B = 2500 \text{ Å} \), \( \lambda_{BH^+} = 2900 \text{ Å} \), the \( \lambda_{max} \) values for 0.8% and 97.6% protonation respectively.

For the benzophenones the change in \( pK_{BH^+} \) with wavelength is regular so the mean value of \( pK_{BH^+} \) obtained from the nine combinations of wavelengths is close to that value found using the wavelengths corresponding to maximum absorption just outside the 1% and 99% ionisation ranges. It is apparent, then, that the basicities within the series of compounds should be compared using \( pK_{BH^+} \) values found by using \( \lambda_{max} \) for the base and the conjugate acid. Previous workers\(^{26}, 47\) have done this, though without apparent investigation of the effect of change of wavelength on \( pK_{BH^+} \). From the systematic trends in \( pK_{BH^+} \) with wavelength and the general similarity in absorption spectra it is also thought that the basicities of two substances may be compared using \( pK_{BH^+} \) values from wavelengths similarly related to the \( \lambda_{max} \) values found for similar ionisation ranges.

Hammett with acetophenone\(^{42}\), and Brand with \( \beta \)-nitrotoluene\(^{48}\), both using Hammett's first method for correction of the medium effect, have shown changes in \( pK_{BH^+} \) with wavelength, and even in dilute aqueous solution Mann\(^{49}\) has noted a change in the
pKₐ of phenol of .010 unit over a wavelength range of 50 Å about the λ_max for the phenoxy ion.

It is the relative pK_BH⁺ values that are of greater interest here and as the range of pK_BH⁺ values is small the error in the H_o values will be considerably less than the .05 unit estimated for the absolute values. The error in the D values appears, from the Geisseman sigmoid plots, to be less than the maximum ± 1000 extinction units mentioned previously, a maximum error of ± 500 extinction unit being now proposed. Allowing an error of ± .02 unit in the H_o scale the maximum error in the relative pK_BH⁺ values is estimated to be ± .06 units.

B The Relative Basicities

The order of the pK_BH⁺ values of the para-substituted benzophenones appears to be in the hyperconjugative order H (mean pK = 6.18) < t-Bu (-6.01) < Me (-5.89), the direction of the order confirming that electron-releasing substituents stabilise the conjugate acid more than the free base. The mean of the differences in pK_BH⁺ between 4-methyl- and 4-t-butylbenzophenone, obtained from wavelengths similarly related to the λ_max value, can be compared with zero difference for no hyperconjugative order, using the Student's "t" test. (λ_max 2750 Å, 3600 Å for 1% and 99% ionisation respectively, for both compounds)

<table>
<thead>
<tr>
<th></th>
<th>4-Methyl-</th>
<th>4-t-Butylbenzophenone</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ_B</td>
<td>2700 Å</td>
<td>2700 2700 2750 2750</td>
</tr>
<tr>
<td>λ_BH⁺</td>
<td>3550 Å</td>
<td>3600 3650 3550 3600</td>
</tr>
<tr>
<td>ΔpK</td>
<td>.19</td>
<td>.17 .13 .07 .09 .04</td>
</tr>
</tbody>
</table>

Mean difference = .114

Estimate of standard deviation of mean = .057 (σ = 8)

This mean difference is significantly different from zero difference at the 99.95% level, with eight degrees of freedom, (see Appendix I) confirming the hyperconjugative order.
The 4-substituted-2, 6-dimethylbenzophenones also appear to be in the hyperconjugative order 4-H (mean pK -6.53) <
4-t-Bu (-6.35) < 4-NMe (-6.13). The mean of the differences between the pK\textsubscript{BH+} values for 2, 4, 6-trimethyl- and 2, 6-di-
dimethyl-4-t-butylobenzophenones from similarly related
wavelengths is again compared with zero difference using the Student's "t" test. (λ\textsubscript{max} 2600 Å, 3600 Å for 2% and 98% ionisation, respectively, for both ketones)

<table>
<thead>
<tr>
<th>ΔpK</th>
<th>2, 4, 6 Trimethyl-</th>
<th>2, 6-dimethyl-4-t-butylobenzophenone</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ\textsubscript{B}</td>
<td>2550 Å</td>
<td>2550</td>
</tr>
<tr>
<td>λ\textsubscript{BH+}</td>
<td>2950 Å</td>
<td>3000</td>
</tr>
<tr>
<td>ΔpK</td>
<td>.28</td>
<td>.24</td>
</tr>
</tbody>
</table>

Mean Difference = .217

Estimate of standard deviation of mean = .045 (ν = 8)

Again this mean difference is significantly different from zero difference at the 99.35% level, with eight degrees of freedom, confirming the hyperconjugative order.

The difference in basicity between 4-methylbenzophenone and benzophenone (.29 pK unit) is less than that found for the similarly substituted acetophenones (68 unit). This is as to be expected as the benzophenones have a levelling effect on their basicity due to the extra unsubstituted benzene ring conjugated to the carbonyl group, whereas the acetophenones have only a relatively weak hyperconjugative interaction between the methyl and carbonyl groups.

That the agreement in pK values between acetophenone (pK = -6.13) and benzophenone (pK = -6.18) is also not unreasonable is brought out in the following.

(a) The second benzene ring in benzophenone would be expected to stabilise, through increased conjugation, the conjugate acid with respect to the free base, more so than the methyl group will through isoalsonant hyperconjugation in acetophenone. This effect can also be seen in the S\textsubscript{N} solvolyses of phenyldimethylcarbinyl chloride and
and t-butyl chloride in ethanol at 25°, where the rates are $3.94 \times 10^{-4}$ sec$^{-1}$ \textsuperscript{50} and $9.70 \times 10^{-8}$ sec$^{-1}$ \textsuperscript{51} respectively. The steric assistance would, if anything, be expected to be greater for the t-butyl chloride solvolysis, so the relative electronic effects of phenyl and methyl groups attached to an electron-deficient centre may be even greater than the rates indicate.

(b) This electronic effect tending to make acetophenone less basic than benzophenone is countered by the inductive effects of the phenyl (-I) and methyl groups (+I) working in opposite directions.

(c) The phenyl group has a slightly larger steric requirement than the methyl group tending to reduce conjugation by enforcing non-coplanarity. The angle between the planes of the benzene rings in benzophenone has been estimated to be about 135° in the solid state\textsuperscript{52} and 150° in solution\textsuperscript{53}. If the angle between each ring and the C=O bond is taken to be about 20°, then the decrease in energy of resonance between the rings and the carbonyl group may be as much as the 23% found in the homomorphic 1, 1-diphenylethylen\textsuperscript{54}.

(d) Another factor counteracting the simple resonance effect is cross-conjugation\textsuperscript{55} between the benzene rings in the conjugate acid of benzophenone reducing conjugation between the rings and the protonated carbonyl group.

All these effects will be modified to varying extents by solvation in the highly polar medium, and thus the small difference in basicity between acetophenone and benzophenone is not unreasonable.

C. Hyperconjugative Effects

The difference in basicity between benzophenone and 4-methylbenzophenone ( .29 pK unit) is less than that found (.40 unit) between 2, 6-dimethyl- and 2, 4, 6-trimethylbenzophenones, whilst the differences between the 4-t-butyl- and 4-hydrogen in the two series are constant (.17 and .18 unit). If conjugation is reduced on substitution of ortho methyl
groups, and if alkyl groups release electrons by a conjugative mechanism, a decrease in difference would be expected on ortho substitution. This decrease is obviously not found for the 4-methyl substituent.

The benzene rings in the para substituted benzophenones are conjugated with the carbonyl group, and there is sufficient evidence that conjugation between the substituted ring and the carbonyl group is greatly reduced in the 2, 6-dimethylbenzophenones. Braude\textsuperscript{56}, for the similarly substituted acetophenones, calculated from u.v. spectra that the benzene ring in 2, 4, 6-trimethylacetophenone was twisted 63° out of the plane of the carbonyl group, in good agreement with that angle calculated from dipole moments (62°). It has since been suggested\textsuperscript{57}, however, that Braude's mechanism for excitation is unlikely, so that the angle found from u.v. spectra may be in error, even though it agrees with the independent dipole calculations. As the unsubstituted benzene ring in the 2, 6-dimethylbenzophenones will have a larger steric requirement than the methyl group in the corresponding acetophenones, the angle between the planes of the substituted ring and the carbonyl group would be expected to be greater than that found in the acetophenones. That conjugation is reduced is also shown in the difference in the carbonyl stretching frequency* between benzophenone (1672 cm\textsuperscript{-1}) and 2, 6-dimethylbenzophenone (1681 cm\textsuperscript{-1}). As the carbonyl stretching frequency is directly related to the amount of double bond character, decreasing resonance by substitution of ortho methyl groups increases the carbonyl bond order giving a higher stretching frequency. Another indirect indication of loss of conjugation on ortho substitution is seen in the large "orthoh" effect, the substitution

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* Infra-red spectra were determined during this work by a Perkin-Elmer 221 spectrophotometer using 1 mm. cells and NaCl prism. Solutions, in CCl\textsubscript{4} were about .01 molar.
of the 2- and 6-methyl groups decreasing the pK by .35 units. That this is less than the decrease found for the acetophenones (acetophenone pK = -6.13, 2, 6-dimethylacetophenone \(^{39}\) pK = -7.81) is again evidence for the levelling effect of the second conjugated benzene ring in the benzophenones. As the +I effect of the ortho methyl groups tends to increase the basicity the difference in pK between benzophenone and 2, 6-dimethylbenzophenone due to steric effects is even greater than that found.

The decrease in resonance on ortho substitution can perhaps be estimated from that calculated for non-coplanarity in the homomorph 1, 1-diphenylethylene. For an interplanar angle of 60° the decrease in resonance energy in diphenylethylene is 95% \(^{51}\), this figure referring to twisting of both phenyl groups out of the plane of the double bond. For the 2, 6-dimethylbenzophenones a decrease in resonance interaction between the substituted ring and the carbonyl group of more than 90% would not seem unreasonable, as there is no conjugation between the phenyl groups in the diphenylethylene. The decrease in resonance in the conjugate acids of the benzophenones is probably slightly less as the stabilising effect due to conjugation, which balances the steric interactions, is greater.

The anomaly in the basicities of the two series cannot then be explained by there being no loss of conjugation in the di-ortho substituted series. The results now raise the question of whether alkyl groups can supply electrons by a conjugative mechanism, and if so is this their main mode of electron release? For inductive electron release as the main mode for the alkyl groups little or no difference is expected in the basicities, relative to the non-para substituted ketone, on ortho substitution. The increase in relative pK found in the 4-methyl case could be then due, perhaps, to lack of precision in the results. The simple inductive (+I) effect of the t-butyl group is unquestionably greater than that of the methyl group, both groups being less electronegative than hydrogen. Thus if the inductive
effect were the only one, or the main one affecting reactivity in electrophilic reactions the inductive order \( H < Me < t-Bu \) would be expected for reaction rates or equilibrium constants.

Price and Lincoln\(^{58}\) have suggested the "hyperconjugative" order \( H < t-Bu < Me \) is then due to steric hindrance to solvent stabilisation of the transition state, at the reaction site, being greater for the more bulky \( t \)-butyl group. The decrease in rate of electrophilic attack for meta alkyl substituted systems, as compared with the para systems, can be interpreted along the lines of this theory. Assuming a near constancy in the inductive effects for meta and para positions\(^{59}\), the decrease in rate is due to the meta position being closer to the reaction site. However, as pointed out by Berliner\(^{14}\), inhibition of solvation of the reaction site would predict that the relative difference \( Me, t-Bu \) would be much greater for the meta position than the para due to the smaller distances, in contradiction to results found for most electrophilic substitution reactions where the hyperconjugative order is followed in the para position but the inductive order in the meta. (See, e.g. Table I)

Schubert and Sweeney\(^{60}\) have suggested that even in fully electron-demanding reactions the inherent release of electrons by alkyl groups is in the inductive order (but not necessarily only by the inductive mechanism, as the inductive effect, C-C hyperconjugation and internal dispersion forces\(^{61}\) all work in the inductive order). The hyperconjugative orders found are then due to steric hindrance to solvation of electron-deficient sites near the alkyl group in the transition state, for the kinetic case. For the normal electrophilic reactions these electron-deficient sites are the ortho and para positions in the ring. The more bulky \( t \)-butyl group when in the para position will inhibit solvation of the electron-deficient site in the ring at the point of attachment, more than the methyl group,
giving less stabilisation of the transition state, etc., for the butyl case, leading to the hyperconjugative order. For meta alkyl substituents the situation is open to greater speculation 41, as the meta position is flanked by two electron deficient sites in the transition state. Berliner 14 has taken the attitude that the alkyl group and the reacting side chain, or presumably an attacking electrophile in the transition state for aromatic substitution, exert a probably greater solvation shielding influence on the electron deficient site they flank, than the para-alkyl group does on its electron-deficient site. Thus again there would be expected a nearer equal or even greater spacing of the relative rates for \( \text{p-Me} \) and \( \text{p-t-Bu} \) than for \( \text{p-Me} \) and \( \text{p-t-Bu} \), and that the hyperconjugative order would again be expected for meta alkyl substituents. Berliner showed that although a hyperconjugative order was found for the solvolyses of \( \text{meta-alkylbenzylhydroxylchlorides} \) in 80% aqueous ac- tone the spacing was less than in the para series (relative order \( \text{H, Me, Et, isop-Pr, t-Bu} \) is 4.0: 21.4: 17.3: 13.6: 10.9 for the para series 29, but only 1.00: 1.68: 1.53: 1.39: 1.53 in the meta series 14, both at 25°). The relative rates were said to be much better explained through normal C-H and C-C hyperconjugation, together with the "shunting" effect, than through solvent modifications of the inductive order. Schubert, however, takes the opposite view in that solvation hindrance is more important when the alkyl group is attached directly to the electron-deficient site, rather than ortho to this site, i.e. greater in the para position than the meta. It has been shown 62 that the methanolation of the \( \text{p-alkylbenzyl} \) chlorides follows the hyperconjugative order, and that the \( \text{p-t-butyl} \) chloride is less solvated than the \( \text{p-methyl} \) chloride by vapour pressure measurements. It can be seen that there is some doubt whether solvation effects are a true explanation of the relative rates found, though they may well be important contributing factors. That this is so can be seen in the change in order of the relative rates for the \( \text{meta-alkylbenzylhydroxyl chloride solvolysis with temperature and solvent, Shiner and Verbanic} \) 63 having shown that the inductive order is
followed for the solvolyses of the meta-chlorides in 90% ethanol (relative rates, H, 1.00; Me, 1.93; t-Bu, 2.29; at 0°C) as compared with the hyperconjugative order found by Berliner. Similar results have been found by Brown and Okamoto for the solvolyses of meta-alkylphenyldimethylcarbinyl chlorides, a hyperconjugative order being followed in 90% acetone, but an inductive order in ethanol.

Schubert and Sweeney have discussed these results in terms of the solvation modified inductive order using heats and entropies of activation. Results for the solvolyses of alkylbenzhydryl chlorides in 80% acetone are given in Table V.

Table V

<table>
<thead>
<tr>
<th>R(a)</th>
<th>H</th>
<th>p-Me</th>
<th>p-Et</th>
<th>p-iso Pr</th>
<th>p-t-Bu</th>
</tr>
</thead>
<tbody>
<tr>
<td>k x 10^6 sec^-1 (0°C)</td>
<td>2.32</td>
<td>83.5</td>
<td>62.6</td>
<td>46.0</td>
<td>35.9</td>
</tr>
<tr>
<td>ΔH^# (kcal/mole)</td>
<td>20.5</td>
<td>18.3</td>
<td>18.9</td>
<td>19.3</td>
<td>19.5</td>
</tr>
<tr>
<td>ΔS^# (e.u.)</td>
<td>-8.9</td>
<td>-9.8</td>
<td>-8.6</td>
<td>-7.7</td>
<td>-5.6</td>
</tr>
<tr>
<td>R</td>
<td>m-Me</td>
<td>m-Et</td>
<td>m-iso Pr</td>
<td>m-t-Bu</td>
<td>3,5 Me2(b)</td>
</tr>
<tr>
<td>k x 10^6</td>
<td>4.78</td>
<td>4.28</td>
<td>3.93</td>
<td>4.27</td>
<td>9.55</td>
</tr>
<tr>
<td>ΔH^#</td>
<td>20.4</td>
<td>20.5</td>
<td>20.5</td>
<td>20.5</td>
<td>20.0</td>
</tr>
<tr>
<td>ΔS^#</td>
<td>-8.3</td>
<td>-8.1</td>
<td>-8.6</td>
<td>-8.2</td>
<td>-6.3</td>
</tr>
</tbody>
</table>

(a) Reference 29, (b) reference 64, all others reference 14.

For the para series, where there is a distinct hyperconjugative order, solvation at the point of attachment of the alkyl group to the ring will be greatest for methyl and least for t-butyl because of the increasing bulk. Solvation will increase the activation energy (ΔH^#) for the solvolysis reaction in the order Me < Et < iso Pr < t-Bu, but, as there would be least solvent orientation in the transition state for the t-butyl substituent, the entropy of activation due to solvation will increase in the same order Me < t-Bu. The entropy and heat of activation are related to the rate constant.
in the Eyring equation
\[ k = \frac{(kT/h) \exp (\Delta S^*/R) \exp (-\Delta H^*/RT)}{h} \] so solvation effects work in opposite directions on the relative rates through the entropy and heat of activation. Schubert suggests that these "rates, heats of activation, and entropies of activation are consistent with the viewpoint that inherent electron release by alkyl groups is in the inductive order and steric hindrance to solvation acts to invert the rate order." 

The meta substituted compounds give heats and entropies of activation too close together for any significance to be attached to their differences. With the 3, 5 dialkyl chlorides, however, there again appear to be significant differences. The second t-butyl group in meta-di-t-butylbenzhydryl chloride shows the expected increase over the similar meta-dimethyl chloride in heats and entropy of activation due to increased solvent shielding of electron-deficient sites in the ring in the transition state with the more bulky substituent, leading to the hyperconjugative order again. The introduction of the second p-methyl group lowers the heat of activation by 0.4 kcal indicating the expected greater stabilisation of the transition state with two +I groups, but with the second t-butyl group there is no change in heat of activation indicating a balancing of the decrease in heat due to increased inductive effect, and the increase due to increased solvation shielding.

Schubert's interpretation, based on the inherent order of electron release, is sufficient to explain the effects found, but it must be remembered that factors contributing to the heat and entropy of activation are complex, and it may well be that these quantities can be explained in terms of inductive and a more important hyperconjugative release of electrons. It should also be remembered that Schubert's explanation is mainly based on solvent effects on the electron release by alkyl groups in molecules undergoing spectral transitions. In the gas phase the energies of these transitions follow the hyperconjugative order for the alkylbenzenes, but the inductive order for the p-alkylnitro-
benzenes and the p-alkylacetophenones. There has been considerable controversy over interpreting the order in the alkylbenzenes as being due to C-H hyperconjugation and some authors have suggested that where the inductive order is found for spectral transitions that this is due to C-C hyperconjugation being more important than C-H hyperconjugation. Schubert has shown that the energy order in the spectral transitions can be changed by solvent. The point has been raised that as yet it has not been established that factors influencing chemical reactivity are related in any simple way to those factors influencing spectra, and it was suggested that caution be used when correlating chemical reactivity with spectral results.

The hyperconjugative order found for both series of ketones in the present work could be explained in terms of Schubert's steric hindrance to solvation affecting the inductive order of electron release, if this inductive order is largely due to effects other than hyperconjugation. This would seem to be unreasonable in that the validity of Schubert's assumption that the inherent order of electron release is the inductive order has not been adequately tested, and that there are more apparently anomalous results left unexplained when using this theory than when using that combining inductive and hyperconjugative effects of some magnitude.

Nucleophilic attack, where the hyperconjugative order is H > t-Bu > Me, has been suggested by Berliner to be a possible stumbling block to the steric hindrance to solvation interpretations. The hyperconjugative order has been found in aromatic nucleophilic substitution reactions as with the Menschutkin reaction between 4-alkyl-2-nitrochromo-benzenes and pyridine, in the alkaline hydrolysis of p-alkylbenzoates in 85% ethanol (but the inductive order in 50% acetone), the methanolysis of 1-methyl-alkyl-benzoates (for both p and m alkyl substituents) and the hydrolysis of both benzoyl chlorides and benzoic anhydrides. For steric hindrance to solvation explanations of these
reactivity orders it appears that additional hypotheses of solvation effects on the transition state must be made. At the present time few results have included heats and entropies of activation for this type of reaction. Thus sufficient pertinent data for supporting the additional postulates may be lacking for some time.

Also requiring modification to the steric hindrance of solvation interpretations are some electron-demanding reactions that follow the inductive order, as does the nitration of alkylenzenes in 90% acetic acid$^{71}$. Nitration in this solvent is believed to involve attack by the positively charged nitronium ion, NO$_2^+$ $^{72}$. Other electron-demanding reactions in this solvent follow the hyperconjugative order, as with bromination and chlorination$^{73}$ which both involve attack by the uncharged halogen molecule, and proto-de-silylation$^{74}$ where there is attack by a positively-charged electrophile. These results would seem to suggest that the reactivity order depends on the electrophile as well as the solvent. The original explanation$^{71}$ of the nitration results was that here the inductive effect was the most important electronic effect. Berliner and Chen$^{14}$ support this and suggest that the dominance of inductive over hyperconjugative effects in this reaction is due to the high electrophilicity and therefore low selectivity$^{75}, 13$ of the attacking species. However, the mercuration reaction in acetic acid also gives a hyperconjugative order, but has a lower selectivity factor and therefore a more electrophilic attacking entity than the nitration reaction. (For p-Me, S$_f$ nitration = 1.36 at 45°, S$_f$ mercuration = .93 at 25°; for p-t-Bu, S$_f$ nitration = 1.27 at 45°, S$_f$ mercuration = .71 at 25°$^{13}$). It may be possible that these results are better explained in terms of varying relative powers of C-C hyperconjugation and C-H hyperconjugation superimposed on the inductive effect. This would also help to explain the ratio of para to meta substitution if we are to assume that the inductive effect falls off gradually ortho $>$ meta $>$ para$^{59}$. But again, there seems to be little correlation between the relative demands on the two types of
hyperconjugation as determined by the reactivity order of the alkyl substituted compounds and the reactivity as measured by the rate of para substitution, which is excellently correlated with selectivity (log $p_i/m_i$) for both toluene and t-butylbenzene in electrophilic reactions.

To this situation can be added the recent results of Saborni, and Lauer and Stadman, who have studied the hydrogen exchange reactions of the p-alkylbenzenes. Saborni found a reversal from the hyperconjugative to the inductive order for proto-de-tritiation on changing the solvent from 33 moles % sulphuric acid - water to 32 moles % trifluoroacetic acid - 4% sulphuric acid - water. The other workers found a slight inductive order for deuteration in the para position in 60 - 80% trifluoroacetic acid - deuterium oxide. Both these reactions have high selectivity and so comparatively low electrophilicity. These results again show that the effects of the solvent cannot be ignored when discussing the electronic effects of alkyl groups, though the results can be explained equally well by the approaches of steric hindrance to solvation affecting inherent electron release in the inductive order, or, a composite of electronic effects - the inductive effect, and C-C and C-H hyperconjugative effects of considerable magnitude compared with the inductive effect.

The Schubert interpretation also appears to be in contradiction to the quantitative analysis of reactivity into inductive and resonance components carried out by Taft and Lewis. As mentioned earlier these workers have shown that the resonance effects of alkyl groups attached to an aromatic nucleus can be resolved into C-H, and C-C hyperconjugative interactions, and that the ratio of these hyperconjugative effects for the para substituents is constant, with very few exceptions, for thirty reactions. Schubert's explanation of the hyperconjugative order is in terms of solvation effects on an inherent electron release in the inductive order, but it is unlikely that solvation effects will be constant for the range of solvents covered by the reactions analysed by Taft and Lewis, leaving the constancy in the ratios of "hyperconjugative" effects unexplained.
by the solvation theory.

At this time it is too early to see whether Schubert's theory is capable of explaining the preliminary observation by Brown\textsuperscript{77} that the hyperconjugative contributions of the 4-methyl substituent to the rate of solvolysis of 4-tolyldimethylcarbinyl chloride are reduced by adding a 2-methyl group to destroy coplanarity in the transition state. This result appears to be at variance with the results found in this work, but no conclusion can be reached until the similar 4-t-butyl compounds are investigated.

In conclusion it would seem that while the results of this work cannot be explained in terms of C-C, C-H hyperconjugation, most results in this field of investigation can be explained in terms of these electronic effects, along with the inductive effect. This does not mean to say that solvation effects are unimportant – on the other hand it has been shown that the study of hyperconjugation must necessarily include a close study of solvent effects – but that the explanations involving solvation factors are not sufficiently in accord with all the present facts to say that solvation is the dominant effect. Further work is needed before we can be satisfied that the effects of the alkyl groups on reactivity have been satisfactorily resolved into the various electronic and steric components and that solvation effects on these components are known other than qualitatively. The various effects concerned are of such magnitude, and complexity, that it may be considerable time before the problem is solved, and it is possible to predict with precision the order of reactivity to be found in most reactions.
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72. See p.70, reference 17.
77. See p.117, in reference 57.
APPENDIX

Students’ “t” Test

The mean, $\bar{x}$, of the set of differences in $pk$ is compared with an assumed mean of zero for the parent population using Students’ “t” test for the significance of means of small samples.

$$t = \frac{\bar{X} - \mu_0}{s/\sqrt{n}} ; \quad s = \sigma \sqrt{\frac{n}{\nu}}$$

where $n$ is the number in the sample, $s$ is the unbiased estimate of the standard deviation of the mean $\bar{X}$, $\sigma$ the standard deviation of the differences, and $\nu$ the number of degrees of freedom. For this case $\nu = n - 1$ as degrees of freedom are lost by linear constraints (i.e. in taking the mean).

For the para substituted benzophenones

$$t = \frac{.114}{.057/\sqrt{9}} = 6.0$$

with eight degrees of freedom. From tables $t < 5.04$ for the difference in means to be significant at the 99.95% level, i.e. the mean of the differences in $pk$, (.114), is significantly different from zero difference at the 99.95% level.

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2. A. Hald, "Statistical Tables and Formulas", Wiley, New York, 1952, Table IV.