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Decomposition of Meta and Para
Alkylbenzenediazonium Salts

by

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A THESIS
SUBMITTED TO THE FACULTY
IN PARTIAL FULFILLMENT OF THE
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Doctor of Philosophy

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May, 1951
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TO

VIRGINIA
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DEDICATION</strong></td>
<td></td>
</tr>
<tr>
<td><strong>I. INTRODUCTION</strong></td>
<td>1</td>
</tr>
<tr>
<td><strong>II. THEORETICAL SECTION</strong></td>
<td>2</td>
</tr>
<tr>
<td>A. Fundamental Thermodynamic and Mechanical</td>
<td></td>
</tr>
<tr>
<td>Basis for the Detection of Changes in Substi-</td>
<td></td>
</tr>
<tr>
<td>tuent Effects</td>
<td>2</td>
</tr>
<tr>
<td>B. Discussion of the Factors Involved in Pot</td>
<td>4</td>
</tr>
<tr>
<td>tential Energy</td>
<td></td>
</tr>
<tr>
<td>1. Hyperconjugation</td>
<td>4</td>
</tr>
<tr>
<td>2. Dipole Moment and Inductive Effect</td>
<td>9</td>
</tr>
<tr>
<td><strong>III. DISCUSSION</strong></td>
<td>10</td>
</tr>
<tr>
<td>A. Numerical Results Obtained</td>
<td>10</td>
</tr>
<tr>
<td>B. Interpretation of Experimental Results</td>
<td>11</td>
</tr>
<tr>
<td>1. Meta Compounds</td>
<td>11</td>
</tr>
<tr>
<td>2. Para Compounds</td>
<td>12</td>
</tr>
<tr>
<td>C. An Interesting Anomaly</td>
<td>13</td>
</tr>
<tr>
<td><strong>IV. EXPERIMENTAL SECTION</strong></td>
<td>14</td>
</tr>
<tr>
<td>A. Synthesis of Meta and Para Alkylacetanilides</td>
<td>14</td>
</tr>
<tr>
<td>1. General Method Used for the Preparation</td>
<td></td>
</tr>
<tr>
<td>of the Para Alkylacetanilides</td>
<td>14</td>
</tr>
<tr>
<td>2. Preparation of the Meta Alkylacetanilides</td>
<td>19</td>
</tr>
<tr>
<td>a) $m$-Methylacetanilide</td>
<td>19</td>
</tr>
<tr>
<td>b) $m$-Ethylacetanilide</td>
<td>19</td>
</tr>
<tr>
<td>c) $m$-t-Butylacetanilide</td>
<td>21</td>
</tr>
</tbody>
</table>
B. Preparation of the Diazonium Fluoborate Salts 24
   1. General Procedure 24
   2. Modifications 26
C. Kinetic Experiments 28

   Typical Graphs from Kinetic Runs:
   Figure 1, \textit{p-t-}butylbenzenediazonium fluoborate 30
   Figure 2, \textit{m-t-}butylbenzenediazonium fluoborate 31

V. ACKNOWLEDGMENT 32

VI. BIBLIOGRAPHY 33
I.

INTRODUCTION
I. Introduction

This work was undertaken for the purpose of further investigating the effects of alkyl substitution in aromatic compounds at positions remote from the point of substitution, and of learning how these effects vary with the nature of the alkyl group. Previous work in this field has led to no clear-cut explanations, and virtually no work has been done with meta alkyl substituents. The two series of compounds chosen for study were the meta and the para alkylbenzenediazonium fluoborates. The reactions of these substances with water to give the phenols was studied to give some additional information on the effect of alkyl groups. The ortho alkyl compounds were purposely omitted, because extraneous factors enter in, partly because of steric hindrance.
II.

THEORETICAL SECTION
II. Theoretical Section

A. Fundamental Thermodynamic and Mechanical Basis for the Detection of Changes in Substituent Effects

One way to detect the way in which a substituent effect upon a compound varies with the nature of the substituent, is to observe the result of varying the substituent in the compound upon the rate of a reaction of this compound. This method is most significant if the change of kinetic energy terms in the partition functions (i.e., the energy associated with molecular vibrations and rotations) during the reaction of each compound in a series differing only with respect to the substituent is essentially the same for each member of this series. Then any change in the reaction rate, going from one compound to another within this series, is due wholly to a difference between the compounds in the potential energy terms, i.e., the energy due to such internal phenomena as resonance and electrostatic interactions. A good discussion and mathematical proof of this fact may be found in Hammett (1). The result of his derivation is that differences in potential energy are necessarily responsible for observed differences in reaction rate, if the PZ factor in the Arrhenius equation,

$$k = PZ \cdot e^{-E_a/RT},$$

(Eqn. 1)

is the same or nearly the same for the reaction of each compound in the series. In this equation $k$ is the reaction rate constant, $E_a$ is the molar activation energy, i.e., the extra energy a mole of molecules must possess to react, $R$ is the gas constant expressed in calories per mole-degree, and $T$ is the absolute temperature; for first order reactions, such as the decom-
position of diazonium salts, the meaning of P or Z alone is not clear, but
the PZ product always involves the entropy change of the reaction. A suit-
able series of compounds may then be recognized experimentally by using
the above equation to calculate the PZ factor for each compound, after its
rate constant has been determined at two temperatures. It is readily seen
that also the activation energy may be calculated for comparison, after
the rate of the reaction has been determined at more than one temperature.

Let us at this point consider the application of this method to the de-
composition of diazonium compounds. There is strong evidence (2) that in
hydroxylic solvents such as water the mechanism of the decomposition of
diazonium ion, whatever the anion may be, is as follows:

\[ \text{ArN}_2^+ \rightarrow \text{Ar}^+ + \text{N}_2 \text{ (rate determining)} \]  \hspace{1cm} \text{(Eqn. 2)}

\[ \text{Ar}^+ + \text{HOH} \rightarrow \text{ArOH} + \text{H}^+ \]  \hspace{1cm} \text{(Eqn. 3)}

This implies by the transition state theory (1) that there is an equilibrium
formed between the reactant and a transition state (also called activated com-
plex, and indicated here by *), which is in a position of higher energy, that
this complex may decompose to form products or intermediates:

\[ \text{ArN}_2^+ \leftrightarrow \text{ArN}_2^{+*} \rightarrow \text{Ar}^+ + \text{N}_2 \]  \hspace{1cm} \text{(Eqn. 4)}

and that the overall rate of reaction will be dependent upon this equilibrium.

Just as for any other equilibrium, we may write for this one a free energy
expression, which can be divided into separate terms involving potential
energy and kinetic energy (1):

\[ \Delta F^* = -RT \ln K^* = \Delta E_p^* + \Delta E_z^* - RT \ln f^*/f \]  \hspace{1cm} \text{(Eqn. 5)}

where \( \Delta F^* \) is the change in free energy during the formation of the complex,
K* is the equilibrium constant, \( \Delta E_p^* \) is the change in potential energy, \( \Delta E_z^* \) is the change in zero-point energy, and \( f^* \) and \( f \) are the partition functions for complex and reactant, respectively. The result of the equality of the PZ factors for the members of a series of compounds is that the last two terms of this equation are constant for the entire series, and the rate of reaction of each compound is changed only by differences in the potential energy term. We have found the PZ factors to be somewhat closely the same, within each of the homologous series of compounds for which rates of decomposition were measured.

B. Discussion of the Factors Involved in Potential Energy

1. Hyperconjugation

The concept now known as "hyperconjugation" was introduced in 1935 by Baker and Nathan (3), who called it "tautomeric electron release". The terms refer in their most general sense to an interaction between an unsaturated center and a group which is normally regarded as saturated. This interaction takes place within a resonance hybrid for which various contributing structures may be written, each containing a double bond in the saturated group. To illustrate by using an alkylbenzene, such as toluene, we may write forms of the type:

\[
\begin{array}{c}
\text{H}^+ \text{C} \equiv \text{C} \equiv \text{H} \\
\text{H} \text{H}
\end{array}
\quad \longleftrightarrow \quad \begin{array}{c}
\text{H} \text{C} \equiv \text{C} \equiv \text{H} \\
\text{H} \text{H}
\end{array}
\]

For toluene, nine of these forms may be written, since the negative charge may also be written on both the ortho positions, and the positive charge on the other two hydrogen atoms. Because this interaction is over and above
the usual kinds of conjugation, it is called hyperconjugation; since the
structures as written have no bond between a hydrogen and a carbon atom,
hyperconjugation is also called "no bond resonance".

In an article just preceding the reference above, Baker and Nathan
presented data showing that the rate of quaternary salt formation of benzyl
bromides with pyridine was greater for all compounds containing a \( p \)-alkyl
group than for the unsubstituted compound, that the rate was different for
each \( p \)-alkylbenzyl bromide, and that the rate increased as the substituent
was changed from \( p-t \)-butyl to \( p \)-isopropyl to \( p \)-ethyl to \( p \)-methyl. They con-
cluded hyperconjugation must be responsible for this last change, by reason-
ing that a better electron-donating group, which would increase the electron
density of the benzene ring and the carbon atom between the bromine atom
and the ring, should increase the ease of anionization of the bromine and
thus increase the rate of reaction; of all alkyl groups the methyl group has
the largest number of hydrogen atoms on the carbon atom next to the ring,
\( \text{i.e.} \), the largest number of hydrogen atoms by which hyperconjugation can
take place, so the methyl group should have, and it did have, the greatest
accelerating effect of all \( p \)-alkyl substituents upon the rate of this reaction.

To show that the observed tautomeric electron release was mesomeric
(permanent) and not just temporary, another article was presented (4). The
reaction chosen to demonstrate whether the effect was mesomeric was the
prototropic change in the methyleneazomethine system:

\[
P-RC_6H_4-CH=N-CH_2-Ph \rightleftharpoons p-RC_6H_4-CH_2-N=CH-Ph
\]

This reaction, which necessitates the ionization of a hydrogen atom in the
triad system, is one of a type opposite to that of the reaction of benzyl
bromides with pyridine in the sense that the mobility of equilibrium between the two methyleneazomethine isomers would be retarded by the action of better electron-releasing groups, while the latter was accelerated. Therefore, if the electron-release were permanent, the rate of interconversion of the two methyleneazomethine isomers should be decreased as the substituent was changed from p-t-butyl to p-isopropyl to p-ethyl to p-methyl. This was found to be the case.

Hyperconjugation involving bonds between a carbon atom and a hydrogen atom is often called the "Baker-Nathan effect".

The relative rates of chlorination of alkylbenzenes, which takes place by an electrophilic attack on the benzene ring, were observed by dela Mare and Robertson (5), and are given in the first row of Table 1. Similar relative rates of bromination, observed by Berliner and Berliner (6), are given in the second row of the table. The third row gives the relative rates of hydrolysis of p-alkylbenzhydryl chlorides, p-RC₆H₄-CH(Ph)-Cl, as observed by Hughes, Ingold, and Taher (7).

Table 1

<table>
<thead>
<tr>
<th>Alkyl Group</th>
<th>H</th>
<th>Me</th>
<th>Et</th>
<th>Ip</th>
<th>t-Bu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorination</td>
<td>0.29</td>
<td>100</td>
<td>84</td>
<td>51</td>
<td>32</td>
</tr>
<tr>
<td>Bromination</td>
<td>100</td>
<td>76</td>
<td>44</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>3.4</td>
<td>100</td>
<td>75</td>
<td>56</td>
<td>43</td>
</tr>
</tbody>
</table>

In all three cases hyperconjugation was used to explain the increase in reaction rate as the substituent was changed stepwise from t-butyl to methyl: the greater hyperconjugative power of the methyl group increased
the electron density of the ring at the ortho and para positions, facilitating
electrophilic attack, or anionization of the chlorine atom in the case of the
benzhydryl chloride hydrolysis.

Berliner and Bondhus (8) noticed that there was a surprisingly large
change in the rate of halogenation between benzene and t-butylbenzene (factor
of about 110) compared to the change between t-butylbenzene and toluene
(factor of about 3 or 4). They proposed that for alkyl groups which are more
highly substituted on the carbon atom adjacent to the ring another kind of
hyperconjugation assumes importance, namely that which involves bonds
between two carbon atoms. In an attempt to represent the resonance hybrid
for a compound like t-butylbenzene, one can write various contributing
structures of the type with no bond between two carbon atoms in the alkyl
group:

\[
\begin{align*}
\text{CH}_3 \text{C} \text{CH}_3 \\
\text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 \text{C} \text{CH}_3 \\
\text{CH}_3
\end{align*}
\]

The relative importance of this kind of hyperconjugation must decrease
stepwise as the alkyl group varies from t-butyl to methyl, whereas the
relative importance of carbon - hydrogen hyperconjugation increases in
this order. It has been clearly shown by Matsen, Robertson, and Chuoke
(9) by means of ultraviolet absorption measurements that the overall
electron-donating power of alkyl groups decreases in this order, and this
proves that the general effect of carbon - hydrogen hyperconjugation is
more important than that of carbon - carbon hyperconjugation. It is inter-
esting to notice that the effect of the latter is similar to the inductive effect,
which decreases in the above sequence of alkyl groups, and which will be discussed shortly.

Mulliken, Rieke, and Brown (10) have studied hyperconjugation from a quantum mechanical viewpoint. We shall not discuss their considerations at length, except to note that contributions from structures of the type \( H_3C=CH=CH^- \) are commonly included in this approach.

Let us now discuss how hyperconjugation might be expected to affect the stability and consequently the rate of decomposition of diazonium compounds. Since the two nitrogen atoms must acquire an extra electron to become a nitrogen molecule:

\[
\begin{align*}
\text{N=N} & \quad \longrightarrow \quad \text{N=N}^+ + \text{N=N}^+ \quad \text{(Eqn. 6)}
\end{align*}
\]

any effect which tends to increase the electron density of the ring should tend to increase the rate of decomposition. Therefore, if this one kind of effect is considered alone, the rate of the reaction should decrease as the alkyl substituent in any position is changed from methyl to ethyl to isopropyl to \( t \)-butyl to hydrogen. However, in the para position (and ortho, if we were to consider it) there is the possibility of resonance stabilization by hyperconjugation:

\[
\begin{align*}
\text{CH}_3\text{-N=N}^- & \quad \longleftrightarrow \quad \text{H}^+\text{CH}_2=\text{N=N}^+ \quad \text{H}^+\text{CH}_2=\text{N=N}^- \\
\end{align*}
\]

This effect would be expected to be largest for the methyl group, since all other alkyl groups have a smaller number of hydrogen atoms available for hyperconjugation; accordingly, from this effect alone, one would expect the rate of reaction of the \( p \)-alkyldiazonium compounds to decrease as the para substituent varies from hydrogen to \( t \)-butyl to isopropyl to ethyl to methyl, opposite to the sequence above. The differences in the rate were small, but
this last order is the one we observed for the p-compounds. In the case of the meta compounds, there is no possibility of resonance stabilization, because there can be no conjugation between the alkyl group and the diazo group.

2. Dipole Moment and Inductive Effect

Baker and Groves (11) found the dipole moments of alkylbenzenes to be: toluene, .37; ethylbenzene, .58; cumene (isopropylbenzene), .65; t-butylbenzene, .70. Matsen, Robertson, and Chuoke (9) estimated by the method of Sklar (12) the electron affinities in electron-volts of alkyl groups to be: methyl, 1.8; ethyl, 1.4; isopropyl, 1.0; t-butyl, about 1.0. This migration of electrons, or displacement of charge, increasing from methyl to ethyl to isopropyl to t-butyl has long been recognized as the "inductive effect", or "(+1) effect", but the whole cause of this anomalous effect is still unexplained.

This effect would predict for either meta or para alkyl diazonium compounds that the rate of decomposition would increase as the substituent is changed from hydrogen to methyl to ethyl to isopropyl to t-butyl. This is our observed sequence for the meta compounds.
III.

DISCUSSION
III. Discussion

A. Numerical Results Obtained

Table 2 gives the numerical results of the data obtained in this laboratory:

<table>
<thead>
<tr>
<th>Substituent</th>
<th>( k ) at 29.96°</th>
<th>( k ) at 40.31°</th>
<th>( k ) at 46.76°</th>
<th>( k ) at 52.98°</th>
<th>( k ) at 55.44°</th>
<th>( k ) at 62.23°</th>
<th>( E_a ), cal.</th>
<th>ln PZ Rel.</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-t-Bu</td>
<td>14.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1610</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-Et</td>
<td>6.93</td>
<td>27.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>24,800</td>
<td>33.9</td>
<td>790</td>
</tr>
<tr>
<td>m-Me</td>
<td>3.92</td>
<td>15.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>24,900</td>
<td>33.5</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>(4.1)</td>
<td>(16.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(25,700)</td>
<td>(34.8)</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>.873*</td>
<td>9.39</td>
<td>29.15</td>
<td></td>
<td></td>
<td></td>
<td>27,200</td>
<td>35.9</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>(29.)</td>
<td></td>
<td>(27,200)</td>
<td></td>
<td></td>
<td></td>
<td>(35.8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-t-Bu</td>
<td>1.822</td>
<td></td>
<td>13.25</td>
<td></td>
<td></td>
<td></td>
<td>27,300</td>
<td>34.4</td>
<td>19.5</td>
</tr>
<tr>
<td>p-s-Bu</td>
<td>1.500</td>
<td></td>
<td>11.25</td>
<td></td>
<td></td>
<td></td>
<td>27,700</td>
<td>34.8</td>
<td>16.0</td>
</tr>
<tr>
<td>p-Ipr</td>
<td>1.459</td>
<td>3.27</td>
<td>10.73</td>
<td></td>
<td></td>
<td></td>
<td>27,500</td>
<td>34.5</td>
<td>15.6</td>
</tr>
<tr>
<td>p-Me</td>
<td>2.39</td>
<td>7.79</td>
<td>27,800</td>
<td></td>
<td></td>
<td></td>
<td>34.6</td>
<td>11.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(2.4)</td>
<td>(7.5)</td>
<td>(27,500)</td>
<td></td>
<td></td>
<td></td>
<td>(34.2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Calculated for comparison purposes from data obtained at other temperatures.

Values in parentheses are those of Crossley, Kienle, and Benbrook (13), the rate constants having been read as accurately as possible from an Arrhenius plot (\( \ln k \ versus 1/T \)) in the article. Values of \( k \) are to be multiplied by \( 10^{-4} \).

Our rate constant values, which we consider to have been determined within \( \pm 3 \) in the last significant figure given, compare favorably with the values of Crossley, Kienle, and Benbrook (13). The values obtained by Moelwyn-Hughes and Johnson (14) and by Pray (15) for the unsubstituted
compound are several per cent higher than our own. Our principal error
probably lies in not knowing the exact temperatures. Within the agitated
reaction vessel, which was held at an almost constant temperature by water
pumped from the thermostatic bath through Tygon tubing, the temperature
may have been of the order of .1 degree lower than in the bath, especially
at the elevated temperatures. The bath temperature may have been in error
by ± .04°C; the reported temperatures are corrected from a thermometer
calibration by means of the transition points of sodium sulfate and sodium
bromide, which occur at 32.384° and 50.674°C, respectively.

B. Interpretation of Experimental Results

1. Meta Compounds

The energy of activation values for the m-methyl and the m-ethyl
compounds appear to differ by only 100 calories, and are both much smaller
than for the unsubstituted compound; the ln PZ values differ by .4. (Unfortu-
nately we were not successful in obtaining m-isopropylbenzenediazonium
fluoborate, and the very small amount of m-t-butylbenzenediazonium fluo-
borate obtained, approximately 150 mg., was lost by decomposition before
a second run could be made. Thus we cannot at this time calculate the activ-
ation energy and PZ factor for these compounds). Without more accurate
knowledge of the energy of activation values and the PZ factors it would be
incorrect to state definitely that changes in the potential energy term in
Equation 5, as one proceeds along the homologous series of meta compounds,
are responsible for the observed differences in reaction rate, for it appears
from these data that there are large enough changes in the kinetic energy
terms to account largely or wholly for the rate differences. However, the rate constants do show a very definite trend toward higher values, as the substituent is varied from methyl to ethyl to t-butyl; this sequence is opposite to that which would have been predicted by a consideration of hyperconjugation effects, and is the same predicted by dipole moment data and the idea called the inductive effect. This homologous series of compounds comprising the m-alkylenediazonium salts therefore is unusual, because the relative rates of reaction of the compounds in a great many series can be predicted by merely a consideration of hyperconjugation effects.

2. Para Compounds

The energy of activation values for all the para compounds tested appear to be spread a little farther apart than they are for the meta compounds. (We were not successful in obtaining p-ethylbenzenediazonium fluoborate — see Experimental Section). Except for the p- §-butyl compound, which exhibited other anomalies (that may or may not be related — see Experimental Section), the ln PZ values are more nearly the same than for the meta compounds, the variation being .2 between the extremes. While the rate constant values of the para compounds are considered to be more accurate than other rate constants in Table 2, they are quite close together. Therefore, as in the meta series, we again must conclude that it would be incorrect to state definitely that a change in the potential energy term of Equation 5 is responsible for the observed differences in rate. Resonance stabilization resulting from hyperconjugation of carbon-hydrogen bonds is undoubtedly an important reason that all the para compounds are much
more stable than the unsubstituted compound.

C. An Interesting Anomaly

It will be recalled that in the meta series, where resonance stabilization is not possible, the hyperconjugation effect would predict a decrease in reaction rate as the substituent is varied from methyl to ethyl to isopropyl to \textit{t}-butyl, while the dipole moment data would predict an increase in rate for this sequence of alkyl groups. In the para series, where resonance stabilization can exist, both the hyperconjugation and the dipole moment data would predict the \textit{same} trend, namely an increase in reaction rate as the alkyl substituent is varied from methyl to ethyl to isopropyl to \textit{t}-butyl. Therefore the rate constants of the meta compounds would be expected to lie close together, and in comparison the rate constants of the para compounds would be predicted to have a wide spread. Such is not the case, and these results represent an intriguing and unexplained reversal of the anticipated outcome. Perhaps this difference can be attributed to changes in the kinetic energy terms in Equation 5.
IV.

EXPERIMENTAL
SECTION
IV. Experimental Section

A. Synthesis of Meta and Para Alkylacetanilides

The acetyl derivative of each meta and para alkylaniline was prepared for the purpose of purifying and storing the compound.

1. General Method Used for the Preparation of the Para Alkylacetanilides

Except for the p-methyl compound, which was available in the form of Eastman White Label p-toluidine, each synthesis began with nitration of the alkylbenzene to the p-nitroalkylbenzene. The nitration was accomplished by adding a mixture of concentrated nitric and sulfuric acids to the hydrocarbon in a round-bottomed three-necked flask, which was equipped with a dropping funnel, mechanical stirrer, thermometer, and small opening to the atmosphere, and which was surrounded by a trough of water to maintain the desired temperature. After the addition, the reaction mixture was stirred for a length of time, diluted by adding slowly through the dropping funnel a volume of water equal to that of the mixture, and steam-distilled from an ordinary round-bottomed flask till all the nitro compound was collected (usually several liters of distillate). The distillate was placed in a large separatory funnel and the product drawn from beneath the water, which was then extracted with benzene, the extracts being added to the main portion of organic material. This benzene solution was washed once with water, twice with 5 per cent sodium hydroxide solution, and then three times with water. After the solvent was evaporated completely, a twenty-inch fractionating column packed with glass helices was used to distil the product
under vacuum and separate most of the ortho isomer, which boils a little lower than the para. The proportions of reactants, the yields, and other data pertinent to the nitrations are given in Table 3a.

Table 3a

Nitration of Alkylbenzenes

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Ethyl</th>
<th>Isopropyl</th>
<th>s-Butyl</th>
<th>t-Butyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles hydrocarbon</td>
<td>.58</td>
<td>.86</td>
<td>.71</td>
<td>1.62</td>
</tr>
<tr>
<td>Moles nitric acid</td>
<td>.63</td>
<td>.93</td>
<td>.76</td>
<td>1.75</td>
</tr>
<tr>
<td>Ml. sulfuric acid</td>
<td>47</td>
<td>68</td>
<td>56</td>
<td>128</td>
</tr>
<tr>
<td>Addition time, hrs.</td>
<td>2.3</td>
<td>1.5</td>
<td>1.7</td>
<td>2</td>
</tr>
<tr>
<td>Addition temp., °C</td>
<td>10</td>
<td>16</td>
<td>15</td>
<td>11</td>
</tr>
<tr>
<td>Stirring period after addition, hrs.</td>
<td>3</td>
<td>2</td>
<td>3</td>
<td>1.5</td>
</tr>
<tr>
<td>Moles unchanged hydrocarbon</td>
<td>.013</td>
<td>?</td>
<td>.082</td>
<td>none</td>
</tr>
<tr>
<td>Bp. p-cpd., minus bp. o-cpd., literature</td>
<td>18</td>
<td>13</td>
<td>17</td>
<td>27</td>
</tr>
<tr>
<td>Fore-run, g.</td>
<td>?</td>
<td>51</td>
<td>minute</td>
<td>*</td>
</tr>
<tr>
<td>Bp. p-cpd., obs. (McLeod gauge)</td>
<td>64/.45</td>
<td>72/.24</td>
<td>71/.29</td>
<td>*</td>
</tr>
<tr>
<td>Moles p-cpd.</td>
<td>.47</td>
<td>.45</td>
<td>.45</td>
<td>*</td>
</tr>
<tr>
<td>% yield p-cpd.</td>
<td>81</td>
<td>52</td>
<td>63</td>
<td>*</td>
</tr>
</tbody>
</table>

* Organic layer of steam-distillate separated and used in next reaction without fractionation.

The p-nitroalkylbenzene was then reduced according to the general method described by Fieser (16) using granulated tin and concentrated
hydrochloric acid in a large round-bottomed flask equipped with a long reflux condenser. A pan of cold water was held in readiness, in case the reaction should become too violent. The resulting amine hydrochloride solution was neutralized and made basic with concentrated sodium hydroxide to free the amine, which was then steam-distilled under a slow stream of nitrogen into a large Erlenmeyer flask containing enough hydrochloric acid to dissolve the amine. If the hydrochloride solution was at all colored, it was treated with activated charcoal at room temperature for a few minutes and filtered. Except in the case of p-ethylaniline, which is discussed below, acetic anhydride (CP) was stirred into the amine hydrochloride solution, followed immediately by a concentrated solution of sodium acetate (CP) in water. The acetyl derivative, which formed immediately, was collected by filtration after half an hour and purified by activated charcoal treatment and by recrystallization from a mixture of chloroform and petroleum ether (60–90°C boiling range). The proper volume of solvent was determined in each case by letting the solute saturate a fairly large amount of the petroleum ether as it boiled, and then adding enough chloroform to effect solution, plus a little more. Since we were concerned only with pure samples, we did not measure yields of the crude p-alkylacetanilides, but they were all high. It was found impossible to purify the acetyl derivative of p-ethylaniline by recrystallization, because in this singular instance the corresponding ortho compound melts higher than the para, by about fifteen degrees. A successful purification by recrystallization was carried out, after preparing the benzoyl derivative by shaking the amine with benzoyl chloride and sodium hydroxide solution;
N-benzoyl-\(p\)-ethylaniline melts four degrees higher than N-benzoyl-\(o\)-ethylaniline. The proportions of reactants for the reductions of the nitro compounds are given in Table 3b, along with the melting point values of the acetanilides, as an indication of purity.

**Table 3b**

Reduction and Acetylation

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Methyl</th>
<th>Ethyl</th>
<th>Isopropyl</th>
<th>s-Butyl</th>
<th>t-Butyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles nitro cpd.</td>
<td>.23**</td>
<td>.46</td>
<td>.62</td>
<td>.27</td>
<td>ca. 1.5</td>
</tr>
<tr>
<td>Moles tin</td>
<td>-</td>
<td>.72</td>
<td>1.0</td>
<td>.42</td>
<td>2.5</td>
</tr>
<tr>
<td>Ml. conc. HCl</td>
<td>-</td>
<td>195</td>
<td>260</td>
<td>110</td>
<td>680</td>
</tr>
<tr>
<td>NaOH to basify, g.</td>
<td>-</td>
<td>150</td>
<td>180</td>
<td>80</td>
<td>520</td>
</tr>
<tr>
<td>Ml. Ac(_2)O</td>
<td>55</td>
<td>60</td>
<td>70</td>
<td>33</td>
<td>210</td>
</tr>
<tr>
<td>NaAc-3H(_2)O, g.</td>
<td>52</td>
<td>75</td>
<td>100</td>
<td>42</td>
<td>260</td>
</tr>
<tr>
<td>Mp. of our acetanilide</td>
<td>148.0-8.8</td>
<td>151.2-1.7*</td>
<td>104.9-5.9</td>
<td>123.8-4.5</td>
<td>170.0-1.5</td>
</tr>
<tr>
<td>Mp., literature</td>
<td>153</td>
<td>151*</td>
<td>102.5</td>
<td>125</td>
<td>169-71</td>
</tr>
</tbody>
</table>

**p**-Toluidine instead of \(p\)-nitrotoluene.

* Benzoyl derivative, since acetyl derivative could not be purified by re-crystallization.

\# \(p\)-t-Butylacetanilide was obtained in 64 per cent yield, based on \(t\)-butylbenzene.

Because there was no definite fractionation of the nitration product of ethylbenzene and because the melting point of N-benzoyl-\(o\)-ethylaniline is only four degrees lower than that of N-benzoyl-\(p\)-ethylaniline, there was still some doubt about the identity of our \(p\)-nitroethylbenzene. Therefore we oxidized 1.1 g. by refluxing it for three hours in a 250-ml. round-bottomed
flask with 5g. of potassium permanganate, 2 ml. of 10 per cent sodium hydroxide solution, and 60 ml. of water. The mixture was then poured slowly with stirring into a solution of dilute sulfuric acid containing enough sodium bisulfite to reduce the excess permanganate and the manganese dioxide, and the resulting yellow mixture was extracted twice with benzene. After the light yellow benzene solution was washed with water and filtered to remove solid material, it was extracted twice with 5 per cent sodium hydroxide solution, which left the benzene almost colorless. After the basic solution was acidified with dilute sulfuric acid, the fine, yellow precipitate was collected, rinsed, dried, and found to melt at 238–40° without recrystallization. The melting points of the three nitrobenzoic acids are: ortho, 147.5°; meta, 140–1°; para, 240–2°. Clearly we have p-nitrobenzoic acid, which proves that practically all of our nitroethylbenzene was the para compound.

Because we could not find the melting point of o-s-butylacetanilide for comparison, it was thought best to prove the structure of our p-s-butylacetanilide. Into a 250-ml. round-bottomed flask was placed .95g. of our compound, 26 ml. of concentrated hydrochloric acid, and 25 ml. of water. The mixture was refluxed one and one-half hours to obtain an amine hydrochloride solution, which was diluted with 50 ml. of water to make the anilinium ion concentration no greater than .05 M and the acid concentration about 3 M. The solution was cooled to 0°C and diazotized by adding a sodium nitrite solution dropwise until starch-iodide test paper showed a slight excess of nitrous acid. Then .5 g. of cuprous chloride in dilute hydrochloric acid was added with stirring, and the solution was let sit fifteen minutes and steam-distilled. The chloro-s-butylbenzene thus obtained was separated from the water in the steam-distillate and refluxed for two hours with 3 g.
of potassium permanganate, 35 ml. of water, and 1 ml. of 10 per cent sodium hydroxide solution. The cooled reaction mixture was poured into 50 ml. of dilute sulfuric acid containing enough sodium bisulfite to decompose the excess permanganate and the manganese dioxide. A yellow sticky material formed and was extracted with benzene. After the benzene solution was washed once with water, it was extracted with 5 per cent sodium hydroxide solution. This aqueous solution was slowly acidified with dilute sulfuric acid, precipitating a milky white material, which was not sticky. It was collected by filtration and after one crystallization from water melted at 239-40° (sealed tube to hinder sublimation). The melting points of the three chlorobenzoic acids are: ortho, 141-2°; meta, 158°; para, 242-3°. Therefore our s-butylacetanilide is definitely the para compound.

2. Preparation of the Meta Alkylacetanilides

a) m-Methylacetanilide was prepared from Eastman White Label m-toluidine. The latter was steam-distilled and acetylated in the manner described for the para compounds. m-Methylacetanilide, melting point 66.2-7.3° (literature, 65°), was found to crystallize better and purer from water than from a mixture of petroleum ether and chloroform.

b) m-Ethylacetanilide was prepared by acetylating freshly steam-distilled m-ethylaniline, derived from a two step reduction of Matheson m-nitroacetophenone. A one-step Clemmensen reduction was found to be unsatisfactory. Forty-three milliliters of concentrated hydrochloric acid and 17.8 g. (.15 mole) of granulated tin were employed in the usual way (16) to reduce 16.5 g. (.10 mole) of m-nitroacetophenone to m-aminoacetophenone,
which would not steam-distil after the solution was made basic with sodium hydroxide. However, the oil solidified to a light brown floating solid when the mixture was cooled to room temperature. After the water layer was poured off, this solid was mostly removed with a spatula. The white inorganic solid remaining in the flask was leached with ethyl alcohol to dissolve out small pieces of the aminoketone, the alcohol was evaporated, and the residue was added to the main portion of organic material. The crude \textit{m}-aminoacetophenone was crystallized twice from water, in which it is fairly soluble, and the yield of material having a mp. 96.5-97.5° was 7.7 g., or 58 per cent.

All the \textit{m}-aminoacetophenone from the above reduction was reduced to \textit{m}-ethylaniline by the Huang-Minlon (17) modification of the Wolff-Kishner reduction. Into a 250-ml. round-bottomed flask having a standard taper joint fitted with a reflux condenser were placed 10.8 g. (.19 mole) of potassium hydroxide, 7.5 ml. of 100 per cent hydrazine hydrate, 80 ml. of diethylene glycol, and the \textit{m}-aminoacetophenone. After one hour and fifteen minutes' refluxing, the water was drained from the condenser to permit the solution temperature, as measured with a thermometer suspended by a glass hook, to rise to 200° as water and excess hydrazine distilled from the open end of the condenser. The flow of water through the condenser was resumed, and the mixture was refluxed four hours more. The cooled solution was poured into twice its volume of 10 per cent sodium hydroxide solution, and the floating oily amine was steam-distilled and acetylated in the way already described for the para compounds. \textit{m}-Ethylacetanilide is a liquid
at room temperature, and was purified by vacuum distillation. It boiled
at 130°/1mm., and the yield was 6.0 g., or 63 per cent.

c) m-t-Butylacetanilide was obtained in very small yield
from a sequence of reactions beginning with p-t-butylacetanilide:

p-t-Butylacetanilide was nitrated in a manner similar to that of
McGookin and Swift (18), but with less nitric acid. A slurry of 25 g., (13
mole) of the anilide in 80 ml. of acetic anhydride was added through a dropp-
ing funnel over a one and one-fourth hour period with mechanical stirring
to a cautiously prepared mixture of 33 ml. (.52 mole) of concentrated nitric
acid and 49 ml. of acetic anhydride in a 500-ml. round-bottomed three-
necked flask, in which the temperature was kept at 35-40°. The mixture was
stirred twenty minutes more and slowly poured with hand stirring into 500
ml. of cold water, from which the organic material separated as an orange
viscous liquid denser than water. After standing about a day, the mixture
had become bright red, and showed no signs of crystal formation, so it was
neutralized with base and extracted three times with benzene, which was
then evaporated completely.

The dark red liquid residue from the benzene phase, containing an
unknown amount of 2-nitro-4-t-butylacetanilide, was boiled under reflux
in a 500-ml. round-bottomed flask for three hours with 100 ml. of concen-
trated hydrochloric acid to hydrolyze the acetamino group. Although there
was no apparent change, the mixture was steam-distilled till only very small
amounts of red material were coming over. This distillate, approximately
400 ml., contained no p-t-butylaniline or aniline. The residue was extracted
with benzene to remove the dark red, viscous organic material. After complete evaporation of the benzene, the residue of about 20 g. was dissolved in 550 ml. of glacial acetic acid to be used in the next step.

Into a 2-l. three-necked flask equipped with a dropping funnel, mechanical stirrer, thermometer, and a small opening to the atmosphere was placed 675 ml. of concentrated sulfuric acid. This was cooled somewhat below room temperature, 28 g. of sodium nitrite was added and dissolved by stirring, and the mixture was further cooled to 0°. The acetic acid solution of the residue from the previous step was added during one hour with vigorous stirring, followed by 135 ml. of 50 per cent hypophosphorous acid in forty-five minutes, while the temperature was kept between 0° and 10°. At this point there was excessive foaming for several hours, and the volume of the flask was not sufficient to contain it. The flask was removed from its accessories and set very loosely stoppered in the refrigerator for about a day. After sitting on the steam bath no more gas was evolved, the reaction mixture was cooled in ice water with the formation of an organic solid material. The mixture was poured slowly with stirring into a liter of ice water, which was then extracted three times with benzene. The benzene solution was washed three times with water, filtered, and heated in a 1-l. round-bottomed flask to remove the solvent completely, the last traces being evaporated under vacuum. Some water was added to this residue, and the mixture was steam-distilled till there was about 4 g. of yellow-orange organic liquid. During three days' standing a sizable amount of an unidentified yellow crystalline solid, mp. 98.5-100.5° after two crystallizations
from water, separated from the large volume of distillate, and it was necessary to use a plug of glass wool as a filter for the yellow-orange organic liquid, as it was drained slowly out the bottom of a 6-l. separatory funnel into a 30-ml. modified Claisen flask; no solvent was used to extract the large volume of water, because probably more impurity (eg., the yellow solid) than desired product would have been taken out. The organic liquid was distilled, and 2.2 g. (.012 mole) of lemon yellow \( m \)-nitro-\( t \)-butylbenzene was collected as it boiled at 88-90\(^\circ\)/imm. This represents a 9.3 per cent yield, based upon \( p \)-\( t \)-butylacetanilide. There was 2-3 g. of a higher-boiling red residue left in the distillation flask.

Most of the above quantity of \( m \)-nitro-\( t \)-butylbenzene was reduced, steam-distilled under nitrogen, and acetylated, using exactly the same procedure as was used for the para compounds. The \( m \)-\( t \)-butylacetanilide first formed as a pale lavender oil, which solidified after about a day, and was crystallized from a large amount of water, mp. 95-97.5\(^\circ\). Since two recrystallizations of a very small amount of the material from petroleum ether (60-90\(^\circ\) boiling range) did not raise the melting point, the solution of the main portion in petroleum ether was filtered rapidly after it was perhaps one-fourth crystallized. The white residue was some not yet identified compound, mp. 85-6\(^\circ\), weighing 93 mg. The white solid that separated from the filtrate was recrystallized several more times from petroleum ether until a constant melting point was obtained, 98.8-99.5\(^\circ\) (literature, 99\(^\circ\)), and the weight of pure \( m \)-\( t \)-butylacetanilide was 250 mg. (.0013 mole), or 10.5 per cent based upon \( m \)-nitro-\( t \)-butylbenzene.
B. Preparation of the Diazonium Fluoborate Salts

1. General Procedure

The diazonium fluoborates were prepared according to and following the proportions of the following general procedure, except for certain important modifications which will be given afterwards.

Approximately .03 mole of the acetylated amine (see Modification e) was placed along with two glass beads in a 125-ml. round-bottomed standard taper flask fitted with a male joint, the tube on which was surrounded by an ice water jacket to make a short vertical reflux condenser. In order to flush out the system with nitrogen, a 3 mm. x 150 mm. glass tube, which had been drawn to a jet at one end and bent in the middle through an angle of about 150° for support, was inserted jet-first into the short condenser and connected at the other end to the nitrogen line. After a few minutes’ nitrogen flow, a mixture of 10 ml. (.12 mole) of concentrated hydrochloric acid and about 15 ml. of water was poured through the top of the condenser, the nitrogen flow was reduced, and the mixture was boiled under reflux, for three or four hours in the case of the p-alkylacetanilides, and for forty-five minutes or less in the case of the m-alkylacetanilides. It was found best to reflux the mixture at least twice the length of time necessary for the acetanilide to dissolve, because in several cases a shorter reflux period led to incomplete hydrolysis. With the nitrogen still flowing slowly the flask was cooled to room temperature (see Modification a), and if the solution had any color at this point, it was treated with activated charcoal at room temperature for a few minutes and filtered into another round-bottomed flask, which had been
flushed out with nitrogen. The solution was then cooled to ice or ice-salt temperature, as measured by a thermometer inserted through the short condenser and into the flask; because of the much lower solubility of the p-alkylaniline hydrochlorides, it was necessary to cool to 0° quite slowly to permit good crystallization and prevent troublesome solidification of the material, but the higher solubility of the m-alkylaniline hydrochlorides permitted rapid cooling to -5° to -10° without lumping. Through the short condenser was then added with some shaking a concentrated solution of sodium nitrite (usually about .035 mole) by increments small enough to cause less than a five degree temperature rise. After most of the compound was diazotized, the nitrogen jet and the short condenser were removed, and sodium nitrite was added until a test with starch-iodide paper showed a slight excess. Since at this point there was always some solid material in the flask, the mixture was filtered at 0° through course paper in a cold funnel into a 125-ml. Erlenmeyer flask partially submerged in ice. Then 25 ml. of cold 42 per cent fluoboric acid was poured into the diazonium solution by small increments, so that the heat of dilution would not cause the temperature to rise more than about five degrees. The m-alkyldiazonium fluoborates precipitated immediately, whereas the p-alkyldiazonium fluoborates are much more soluble, and often separated from solution only after being cooled to -10° to -15° (see Modification b). The solid diazonium salt was collected by filtration in a porous-bottomed crucible (see Modification c), washed twice with successive 3-ml. portions of each of the following liquids (see Modification d): precooled 5 per cent fluoboric acid solution,
cold C.P. methanol to remove water, and C.P. absolute ether to remove the
methanol. The salt was transferred to a weighing bottle, placed in a vacuum
desiccator over phosphorus pentoxide, and completely dried at about 1 mm.
pressure. The salts were obtained in yields varying from 50 to 70 per cent,
they were usually almost pure white, and were stored in the desiccator in
the dark; in addition, the \( m \)-alkyldiazonium salts were kept in the refriger-
ator because of their greater instability.

2. Modifications

a) \( p-t \)-Butylaniline hydrochloride seems to have a higher
temperature coefficient of solubility just above room temperature than the
other compounds and had to be cooled to room temperature more slowly to
prevent solidification. The charcoal treatment and filtration had to be per-
formed at about 50\(^\circ\).

b) \( p \)-Methylbenzenediazonium fluoborate crystallized slowly
at -15\(^\circ\), forming thin plate-like crystals, but all the other \( p \)-alkyldiazonium
fluoborate salts separated first as oils, which crystallized sooner or later.
\( p-s \)-Butylbenzenediazonium fluoborate did not crystallize until after about
four hours in the freezing chest of the refrigerator, and was found to be easi-
ly soluble in ether when still liquid.

c) Since \( m-t \)-butylbenzenediazonium fluoborate was prepared
on a very small scale yielding only 150 mg., the salt was collected in a 3-ml.
sintered glass funnel of medium porosity.

d) All the \( p \)-alkyldiazonium fluoborates except the \( p \)-methyl
compound are soluble in methanol, and both \( p \)-butyl compounds are fairly
soluble in dioxane, so these particular washings were omitted. The resulting dried salts were not as white as the others, but gave good kinetic data nevertheless.

e) We did not have at hand the acetyl derivative of p-ethyl-aniline (see Part A of Experimental Section), but instead the benzoyl derivative, which was much more difficult to hydrolyze. Finally 2.4 g. of N-benzoyl-p-ethylaniline was largely hydrolyzed by boiling to reflux under nitrogen with 15 ml. of concentrated hydrochloric and 5 ml. of ethanol for four days, during which more acid and alcohol were added twice or three times a day, and as much ethyl benzoate as possible was permitted to diffuse out the open end of the reflux condenser. The resulting almost colorless liquid was filtered into a 100-ml. round-bottomed standard taper flask through a plug of glass wool to remove some dirty white solid, and was then evaporated to about 10 ml., by means of vacuum applied through a short, uncooled, standard taper reflux condenser in order to prevent loss of solution by bumping. To the resulting solution, which had no odor of either alcohol or ethyl benzoate, was added about 1 ml. of concentrated hydrochloric acid, and the diazotization was carried out in the manner employed for the other compounds, with one exception: even before half the theoretical amount of sodium nitrite had been added, the solution tested for not a small excess of nitrous acid, indicating that there must not have been nearly as much amine present as expected. When 10 ml. of fluoboric acid was added, no separation of salt occurred, even after several hours standing in the freezing chest of the refrigerator. The ice-cold solution, which was about 25 ml. in volume, was placed in an evaporating dish in a vacuum desiccator over a large quantity
of phosphorus pentoxide, and the desiccator was quickly evacuated to about 5 mm pressure and placed in the refrigerator. After one and one-half days, the solution had evaporated to about 8 ml, and had precipitated a sizable amount of snow-white crystalline material. This solid was collected by cold filtration in a 3-ml sintered glass funnel of medium porosity and found to be quite soluble in water and 5 per cent fluoboric acid solution, but only sparingly soluble in methanol and ether. However, no worthwhile kinetic data could be obtained with this material, and it was found not to couple with 2-naphthol. It also was found to melt with decomposition in the range of 330-350° and to give a flame test for fluorine and sodium with only a minute amount of charring. The white crystalline solid must have been sodium fluoborate produced largely as a result of etching the evaporating dish with fluoboric acid, and we were therefore unsuccessful in obtaining p-ethylbenzenediazonium fluoborate.

C. Kinetic Experiments

The kinetic run on m-t-butylbenzenediazonium fluoborate, of which we had only 150 mg, was made with a manometric apparatus, which requires only about 25 mg of sample per run. This apparatus is described by Hinds (19) of this laboratory. The data for all the other compounds were obtained using the volumetric apparatus which is described by Godfrey (2).

Both devices provided a measure of the rate of nitrogen evolution from a dilute solution of the diazonium compound under study and thereby a measure of the rate of decomposition of the diazonium ion. The solvent was .1N hydrochloric acid prepared with doubly deionized water. It is known that certain metal ions, notably cupric ion (19), noticeably affect the
rate of decomposition of the more stable diazonium compounds, but in a test run the rate of decomposition of \( m \)-methylbenzenediazonium fluoborate was not changed by the presence of \( .001 \text{M} \) cupric sulfate. It should be recalled that the rate does not depend upon the nature of the anion present \((2,19)\), especially in dilute solution. Barometric pressures were noted with the kinetic readings, and the data were corrected for barometric changes; this was practicable, since the gas volumes of the systems were known within a few ml., and it was very worthwhile procedure, even when the atmospheric pressure changed by less than one millimeter of mercury. The thermostatic bath was maintained within \( \pm .02^\circ \) of the median temperature by a mercury expansion thermoregulator, and the thermometers were calibrated by means of the transition points of sodium sulfate and sodium bromide, which occur at 32.384\(^\circ\) and 50.674\(^\circ\) respectively.

In order to determine the rate constants, the data were plotted by two independent first-order methods, as shown by each of the typical graphs, Figure 1 and Figure 2. By the conventional method \( \log (V_f - V_t) \) or \( \log (P_f - P_t) \) was plotted as a function of time \( t \); \( V_f \) or \( P_f \) is the final volume or pressure reading, and \( V_t \) or \( P_t \) is the reading at time \( t \). By the method of Guggenheim \((20)\), which is more accurate since it does not depend upon a final reading, \( \log \Delta V \) or \( \log \Delta P \) was plotted as a function of \( t \); \( \Delta V \) or \( \Delta P \) is the volume or pressure reading difference for each of a series of overlapping, equal time intervals. The interval used for Figure 1 was 8000 seconds, and the interval for Figure 2 was 36 minutes.
$p$-t-BuC$_6$H$_4$N$_2$BF$_4$

46.76°

$k = 1.822 \times 10^{-4} \text{ sec}^{-1}$

$t_{1/2} = 3805 \text{ sec.}$
Figure 2

\[ m-t\text{-BuC}_6\text{H}_4\text{N}_2\text{BF}_4 \]

\[ k = 1.41 \times 10^{-3}\text{sec}^{-1} \]

\[ t_{1/2} = 492\text{sec} \]

For \( \Delta P \)  
16  20  24  28  32  36  40  min.

For \( P_f - P_t \)  
4  8  12  16  20  24  28
V.

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VI.

BIBLIOGRAPHY
VI. Bibliography


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