Some studies on aromatic nitration

Frank Joseph Modic

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SOME STUDIES ON AROMATIC NITRATION

by

Frank Joseph Modic

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical-Organic Chemistry

Approved:

Signature was redacted for privacy.
In Charge of Major Work

Signature was redacted for privacy.
Head of Major Department

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Dean of Graduate College

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1951
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Appreciation is also expressed to the Institute for Atomic Research for the use of their spectrophotometers used during the course of this study, and for providing the Aniline Hydrochloride-$^{14}C$.

Appreciation is also expressed to Richard Hedges for his assistance in obtaining the Infra-red spectra.
INTRODUCTION

In an effort to understand the substitution reactions of benzene and its derivatives, the nitration reaction has been extensively studied. This reaction is particularly convenient for examination since it is irreversible and easily controlled, forming relatively stable products. The early work consisted of the determination of the various isomers formed in the nitration of different benzene derivatives and the subsequent classification of the substituents as either ortho-para or meta directing groups.¹ From competitive experiments with benzene, it was found that ortho-para directing substituents were activating groups toward nitration and meta directing substituents were deactivating. It was from such work that the general theories of aromatic substitution were developed, since in nitration, as in all the other common substitution reactions (i.e., sulfonation, halogenation, alkylation, and acylation) the attacking species was shown to be electrophilic and, therefore, attack occurred at centers of high electron density.

In recent years, the mechanism of aromatic nitration has been the subject for numerous studies.\(^2\) Several anomalies, however, still exist, one of these being the ortho-para ratio obtained upon the nitration of the derivatives of benzene. The few theories advanced to account for ortho-para ratios are not sufficient to explain the observed experimental results. It was with the idea of attempting to elucidate these facts that this work was undertaken. The problem is one of general interest since a better understanding of the factors involved in aromatic nitration will necessarily lead to a more complete understanding of substitution reactions in general.

\(^2\) For an extensive review, see: R. J. Gillespie and D. J. Millen, *Quart. Revs.*, 2, 277 (1948).
The Mechanism of Nitration

The mechanism of aromatic nitration came in for a great deal of speculation in the past. For a long time, the "addition - elimination" theory was the most widely accepted. Holleman considered substitution reactions to consist of (1) a preliminary addition of the attacking species to a double bond of benzene and then (2) an elimination of water in nitrations or sulfonations or hydrogen halide in halogenations. \(^3a,b\)

\[ \text{Ph} + \text{HNO}_2 \rightarrow \text{PhOH} \rightarrow \text{PhNO}_2 \]

The work of Michael\(^4\) on the addition of sulfuric acid to olefins indicated that there was no analogy in the chemistry of simple alkenes to support the "addition -

---

3. (a) A. F. Holleman, Rec. trav. chim., 12, 355 (1923); Chem. Revs., 1, 187 (1924); (b) M. Wieland and E. Sakellarios, Ber., 53, 201 (1920).

elimination theory of aromatic substitution. In the case of nitration, it was shown by Martinsen's experiments with phosphorus pentoxide addition to mixed acids that the dehydrating action of sulfuric acid was not involved in the mechanism.

At the present time, nitration is regarded as a typical electrophilic displacement reaction in which the nitronium ion is the attacking species. That the nitronium ion, \( \text{NO}_2^+ \), is the active attacking species was first suggested by Euler\(^6\) in 1922. It would be expected that certain analogies would exist between the mechanism of nitration and other electrophilic substitutions. Benford and Ingold\(^7\) have pointed out that, just as the efficiency of a brominating agent depends upon the affinity of \( X \) for the electrons of the \( X-\text{Br} \) bond, so nitrating agents will be of the form \( X-\text{NO}_2 \) and their efficiency will be dependent upon the electron affinity of \( X \). Therefore, due to the weakly acidic properties of \( \text{H}_2\text{O} \), nitric acid, \( \text{HNO}_2 \) can be expected

\[\text{H}_2\text{O}, \text{HNO}_2 \]

---

to be only a weak nitrating agent. Acetyl nitrate might be expected to be a somewhat stronger nitrating agent because of the greater acid strength of acetic acid, and the nitronium ion would be expected to be the strongest possible nitrating agent. Thus, a list of possible nitrating agents, X-NO₂, can be written in order of increasing nitrating strength as follows:

\[
\begin{align*}
&\text{EtO-NO}_2 \\
&\text{H}_2\text{O-NO}_2 \\
&\text{AcO-NO}_2 \\
&\text{NO}_3\text{-NO}_2 \\
&\text{Nitronium ion} \\
&\text{Nitracidium ion} \\
&\text{Nitryl chloride ion} \\
&\text{Ethyl nitrate acid nitrate pentoxide}
\end{align*}
\]

There was no really good substantiating evidence for this nitronium ion until recently. The nature of the solutions of nitric acid have been the subject of much discussion, mainly because of their nitrating properties, and a number of views about the condition of nitric acid in various solvents has been advanced. Saposchnikow, from determinations of densities, elec-

---

8. A. Saposchnikow, Z. physik. Chem., 51, 609 (1905); 49, 697 (1904); 53, 225 (1905).
trical conductivities, and partial vapor pressures of mixtures of nitric and sulfuric acids, concluded that a reversible hydration and dehydration of nitric acid takes place in sulfuric acid solutions.

\[ \text{HNO}_3, \text{mH}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow \text{HNO}_3, (m-n) \text{H}_2\text{O} + \text{H}_2\text{SO}_4, n\text{H}_2\text{O} \]

Thus, when \( n = m \),

\[ 2\text{HNO}_3 + n\text{H}_2\text{SO}_4 \rightarrow \text{N}_2\text{O}_5 + (\text{H}_2\text{SO}_4)_n, \text{H}_2\text{O} \]

This hypothesis was supported by H. von Halban and J. Eisenbrand, who considered the totally different ultraviolet absorption spectra of anhydrous nitric acid and its solutions in sulfuric acid to be due to the presence of dinitrogen pentoxide in the sulfuric acid.

The Raman spectrum of the solutions of nitric acid in sulfuric acid contains two lines, one approximately at 1050 cm\(^{-1}\) and the other approximately at 1400 cm\(^{-1}\), which are not due to either of the acid molecules. The spectrum of solutions of dinitrogen pentoxide in nitric acid also contains lines at

approximately 1050 cm\(^{-1}\) and 1400 cm\(^{-1}\) in addition to the known frequencies of the nitric acid molecule. These two lines also increase in intensity with increasing dinitrogen pentoxide concentration.\(^{11,12}\)

These same two frequencies were also observed in the spectra of solutions of phosphoric acid in nitric acid.\(^{11}\) Both Chedin and Susz attributed these two frequencies, 1050 cm\(^{-1}\) and 1400 cm\(^{-1}\), on the basis of these results, to dinitrogen pentoxide. Chedin, however, later has shown that this interpretation was not entirely satisfactory. He found no trace of these two lines in spectra of dinitrogen pentoxide in carbon tetrachloride, chloroform, phosphorus oxychloride, and nitromethane.\(^{13}\) Chedin and Pradier\(^{14}\) found the Raman spectrum of solid dinitrogen pentoxide to consist of two sharp lines having frequencies of 1050 cm\(^{-1}\) and 1400 cm\(^{-1}\). Since Walden\(^{15}\) had shown cryoscopically that dinitrogen pentoxide existed in the unimolecular form in phosphorus oxychloride solution,

---


Chedin attributed his observed lines to the dinitrogen pentoxide molecule. He concluded that dinitrogen pentoxide did not exist in the unimolecular form, either in the solid state or in nitric or sulfuric acid solutions.

Another view of the nature of nitric acid solutions in sulfuric acid was advanced by Hantzsch on the basis of his cryoscopic, optical absorption, and electrical conductivity studies. He considered sulfuric acid the stronger of the two acids, thus, it would donate a proton to the nitric acid molecule giving rise to the following ionizations,

\[
\begin{align*}
\text{NO}_2\cdot\text{OH} + \text{H}_2\text{SO}_4 & \rightarrow \text{H}_2\text{NO}_3^+ + \text{HSO}_4^- \\
\text{NO}_2\cdot\text{OH} + 2\text{H}_2\text{SO}_4 & \rightarrow \text{H}_3\text{NO}_3^{++} + 2\text{HSO}_4^-
\end{align*}
\]

He found that nitric acid produced an approximately three fold depression of the freezing point (van't Hoff factor, \( i = 3 \)), a result which was subsequently confirmed by Robles and Moles. Hantzsch attempted, but without success, to demonstrate the presence of

\[16. \text{A. Hantzsch, Z. physik. Chem., 65, 41 (1908).} \]
\[17. \text{C. R. deRobles and E. Moles, Anal. Fis. Quim., 32, 474 (1935).}\]
nitric acid in the form of a cation in sulfuric acid solution by means of electrical transference. He attributed this failure to the fact that sulfuric acid alone decomposed upon the electrolysis of these solutions. He was unable to isolate the salts, \((\text{H}_2\text{NO}_3^+)\) (\(\text{HSO}_4^-\)) and \((\text{H}_3\text{NO}_3^{2+})(\text{HSO}_4^-)_2\). He also investigated mixtures of nitric and perchloric acids and claimed to have isolated crystalline perchlorates of both of the suggested cations. The nitracidium salt was recrystallized from anhydrous nitric acid while the hydronitracidium salt from anhydrous perchloric acid, and they both had compositions in agreement with the above formulas. The ionic nature of the salts was confirmed by electrical conductance and transference measurements of their solutions in nitromethane.\(^{18}\)

The technique of cryoscopy in sulfuric acid has recently been greatly improved by Hammett and co-

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workers\(^{19,20}\) and most recently, by Gillespie.\(^{21,22,23}\) Gillespie and coworkers have repeated Hantzsch's work using a more accurate technique and have established that the van't Hoff factor \(i\) for nitric acid in sulfuric solution has the value 3.77.\(^{21}\) They also showed the following ionizations to be taking place in sulfuric acid solutions.

\[
\begin{align*}
\text{HNO}_3 + 2\text{H}_2\text{SO}_4 & \rightarrow \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^- \\
\text{N}_2\text{O}_5 + 3\text{H}_2\text{SO}_4 & \rightarrow 2\text{NO}_2^+ + \text{H}_3\text{O}^+ + 3\text{HSO}_4^- \\
\text{N}_2\text{O}_4 + 3\text{H}_2\text{SO}_4 & \rightarrow \text{NO}_2^+ + \text{NO}^+ + \text{H}_3\text{O}^+ + 3\text{HSO}_4^- \\
\text{N}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 & \rightarrow 2\text{NO}^+ + \text{H}_3\text{O}^+ + 3\text{HSO}_4^- \\
\end{align*}
\]

These conversions are quantitative except that, since water is only a semi-strong base, the ions formed partly

\[\text{20. H. P. Treffers and L. P. Hammett, ibid., 59, 1708 (1937).}\]
\[\text{23. R. J. Gillespie, ibid., 2493 (1950).}\]
recombine as follows:

\[ \text{H}_2\text{O} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_3\text{O}^+ + \text{HSO}_4^- \]

For this reason, the 1 factor for nitric acid is less than the theoretical value of 4.

L. P. Kuhn\(^2\) has confirmed the cryoscopic measurements for solutions of nitric acid in sulfuric acid and has also found an 1 factor of five for the solution of ethyl nitrate in sulfuric acid.

\[ \text{EtO'NO}_2 + 3\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{H}_3\text{O}^+ + \text{EtO'OSO}_3\text{H} + 2\text{HSO}_4^- \]

Hantzsch's results have been reinterpreted by Bennett\(^2\)\(^5\) to give a value of 1 equal to 4, since some of Hantzsch's more satisfactory results were obtained for solutions of potassium nitrate in sulfuric acid. These solutions, after allowing for the potassium acid sulfate formed, give values more nearly equal to 4. Bennett, Brand, and Williams also suggested a simplified explanation of the Raman spectrum of nitric acid in sulfuric acid solutions. They suggested

that Chedin's form might be the ionic form, with the frequency 1400 cm\(^{-1}\) assigned to the nitronium ion and the 1050 cm\(^{-1}\) frequency assigned to the nitrate or bisulfate ion, both of these having a strong frequency in this neighborhood. From spectroscopic selection rules, it could be shown that if the nitronium ion were a linear, centrosymmetrical ion, it would have only one strong Raman frequency. The observation of two Raman lines is then consistent with the ionizations,

\[
\text{(In sulfuric acid) } \text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^-
\]

\[
\text{(In nitric acid) } \text{N}_2\text{O}_5 \rightarrow \text{NO}_2^+ + \text{NO}_3^-
\]

This view has been verified by Millen\(^2^6\) who investigated the Raman spectra of mixtures of nitric acid with other strong acids which have no known frequencies at 1050 cm\(^{-1}\). It was found that the Raman spectra of mixtures of nitric acid with either perchloric or selenic acid contained an intense line at 1400 cm\(^{-1}\) but no corresponding line at 1050 cm\(^{-1}\). Instead, there appeared lines corresponding to the perchlorate or biselenate ions.

The perchlorates of Hantzsch's assumed ions \( \text{H}_2\text{NO}_3^+ \) and \( \text{H}_3\text{NO}_3^{++} \) have also been reinvestigated. It has been shown by Goddard\(^\text{27}\) that Hantzsch's solid products contained nitronium perchlorate formed as follows:

\[
\text{HNO}_3 + 2\text{HClO}_4 \rightarrow (\text{NO}_2^+)(\text{ClO}_4^-) + (\text{H}_3\text{O}^+)(\text{ClO}_4^-)
\]

Goddard was also able to prepare the following nitronium salts: the perchlorate, the fluorosulfonate, the pyrosulfate, and the bipyrosulfate. Millen has shown by means of his Raman spectroscopic method that these salts have the assigned ionic constitutions. Thus, the evidence assembled certainly substantiates the view that the nitronium ion, \( \text{NO}_2^+ \), actually exists.

The earliest attempted kinetic work was done by Spindler\(^\text{28}\) who examined the nitration of benzene using no solvent, hence, under heterogeneous conditions. He was unable to obtain any rate constants. Giersbach and Kessler\(^\text{29}\) nitrated benzene in nitrobenzene solu-

\begin{itemize}
  \item \text{28.} P. Spindler, \textit{Ann.}, 224, 283 (1884).
  \item \text{29.} J. Giersbach and A. Kessler, \textit{Z. physik. Chem.}, 2, 676 (1888).
\end{itemize}
tion. Their principal observation was that the reaction started very rapidly and ended slowly, probably due to the water formed during the reaction. Holleman and De Bruyn\textsuperscript{30} nitrated nitrobenzene in large excess of the same substance but got no recognizable reaction order. The first real kinetic results were obtained by Martinsen\textsuperscript{5} in 1904. He showed that the nitration of aromatic substances in sulfuric acid was second order:

$$\text{Rate} = k_2 (\text{ArH}) (\text{HNO}_3)$$

This conclusion was verified for several different compounds by other later investigations.\textsuperscript{31,32,33} The variation of the initial solvent composition has a considerable effect upon the rate of nitration. This was first shown by Martinsen\textsuperscript{5} who discovered that the rate of nitration in sulfuric acid - water mixtures

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increased to a maximum at approximately 90 percent sulfuric acid and then decreased. These results have been verified by a number of other investigators including Westheimer and Kharasch, and Bennett and coworkers. In all cases, the maximum nitration rate occurs in the region of 90 percent sulfuric acid, although small variations may appear with change of compound and temperature. Both the above authors suggested that the increase in the initial rate as the concentration of sulfuric acid increased, is due to the increasing formation of the nitronium ion. Bennett et al. explain the decrease in rate by assuming a termolecular process for nitration.

\[ \text{ArH} + \text{NO}_2^+ + \text{HSO}_4^- \rightarrow \text{ArNO}_2 + \text{H}_2\text{SO}_4 \]

This process depends not only upon the attack of the nitronium ion upon the aromatic substance, but also upon the removal of the proton by a base. Westheimer and Kharasch suggest that it might be better to consider the rate of nitration a function of the acidity

---


of the medium instead of the sulfuric acid concentra-
tion. They correlated the rate of nitration with
Hamnett's acidity function,\(^36\)

\[ H_0 = pK_a + \log \frac{C_b}{C_{bh}^+} \]

Westheimer and Kharasch assumed that organic nitro
compounds such as nitrobenzene lowered the acidity of
the medium by acting as bases in the concentrated sul-
furic acid solutions. They calculated the activation
energy for the nitration of nitrobenzene in 90 percent
sulfuric acid as equal to approximately 15,000 cal/mole.
Gillespie and Millen\(^2\) point out that the above views
are not completely satisfactory and suggest that an al-
ternate explanation might be closer to the facts. They
feel that not only the nitrating species, but also the
species being nitrated in solution, is important. They
feel that the decrease in nitration rate can be ex-
plained on the basis of the formation in solution of
hydrogen bonded complexes or in high acid concentra-
tion above 90 percent, the conjugate acid form of the
aromatic substances. Just which form would be present
in any one solution would depend upon the basicity of

\(^{36}\) L. P. Hamnett, "Physical Organic Chemistry,"
the compound and the acidity of the solvent. In a solution of nitrobenzene in sulfuric acid, they assume the following equilibria:

\[
\text{ benzene } + \text{H}_2\text{SO}_4 \rightleftharpoons \text{ benzene} \cdot \text{H}_2\text{SO}_4
\]

The work of L. F. Hammett and R. F. Chapman on the solubility of various aromatic compounds in sulfuric acid - water mixtures provides further evidence for the existence of such hydrogen bonded complexes. The solubility of organic compounds in water is very small. In most cases, on increasing the concentration of sulfuric acid as solvent, the solubility of the compounds undergoes a small decrease in solubility. At acid concentrations of 60-80 percent, a sudden large increase in solubility occurs. In the Table I

<table>
<thead>
<tr>
<th>Compound</th>
<th>$K_b$ (g-mol kg$^{-1}$)</th>
<th>Approx. %Ionization (0.1 molal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{NO}_2$</td>
<td>$5.5 \times 10^{-3}$</td>
<td>21</td>
</tr>
<tr>
<td>$\text{CH}_3\begin{array}{c} \text{NO}_2 \ \text{NO}_2 \end{array}$</td>
<td>$6.7 \times 10^{-3}$</td>
<td>23</td>
</tr>
<tr>
<td>$\text{H}_3\text{N}^+\begin{array}{c} \text{NO}_2 \ \text{NO}_2 \end{array}$</td>
<td>$1.4 \times 10^{-2}$</td>
<td>31</td>
</tr>
<tr>
<td>$\begin{array}{c} \text{NO}_2 \ \end{array}$</td>
<td>$2.9 \times 10^{-2}$</td>
<td>41</td>
</tr>
<tr>
<td>$\text{CH}_3\begin{array}{c} \text{NO}_2 \end{array}$</td>
<td>$2.0 \times 10^{-1}$</td>
<td>73</td>
</tr>
</tbody>
</table>
Gillespie\(^2\) has listed the degree of ionization of several nitro compounds in anhydrous sulfuric acid.

Benford and Ingold\(^7\) have carried out kinetic investigations in the organic solvent, nitromethane. They used a constant excess of nitric acid and demonstrated zero order kinetics with respect to the aromatic substances. This kinetic law, however, held only for the relatively reactive compounds such as benzene and toluene. Recently it has been shown by

\[
\text{Rate} = k_0 \begin{cases} 
\text{HNO}_3 \text{ in excess} \\
\text{ArH} = \text{PhCH}_3, \text{C}_6\text{H}_6
\end{cases}
\]

Hughes, Ingold and Reed that other organic solvents such as acetic acid will lead to the same kinetic results.\(^3\) They found that with unreactive compounds, such as \(p\)-dichlorobenzene and ethyl benzoate, first order kinetics were obtained. Most aromatic compounds

\[
\text{Rate} = k_1(\text{ArH})
\]

fall into one of these two classes, but some, for example; the phenyl halides, have a critically intermediate reactivity and exhibit intermediate kinetics.

---

Ingold has summarized the kinetic evidence gathered to the present along the following lines. He considered the kinetic experiments in organic solvents which exhibited zero order kinetics and the transition to first order kinetics with diminishing aromatic reactivity to prove without a doubt the formation and effectiveness of the nitronium ion, \( \text{NO}_2^+ \). In these experiments, the kinetically important or rate controlling step is the formation of the nitronium ion. That this is true follows from the fact that sulfuric acid will accelerate the rate of nitration in nitromethane, acetic acid, or in nitric acid. Similarly, nitrates will retard the rate, this being a specific and not a general salt effect. These effects occur alike with zero or first order reactions, always without disturbance of the reaction order. The following ionizations are thought to occur.

\[
2\text{HNO}_3 \rightleftharpoons \text{H}_2\text{NO}_3^+ + \text{NO}_3^- \quad \text{(fast)}
\]

\[
\text{H}_2\text{NO}_3^+ \rightarrow \text{NO}_2^+ + \text{H}_2\text{O} \quad \text{(slow)}
\]

Consistent with the above reactions, the kinetic effect of water in zero order nitration is negligible in comparison to that of the nitrate ion. Thus, gen-
eralizing from the kinetic investigations that have been carried out, acetic acid, nitromethane, nitric acid, and sulfuric acid considered as nitration media form a series in the form of increasing polarity. A replacement, partial or complete, of any of these solvents by a more polar one, increases the nitration rate without increasing the reaction order. From these results, and the well established theory of kinetic solvent effects, it follows that while ionic charges are created in the reactions which form nitronium ion, \( \text{NO}_2^+ \), ionic charges are neither formed nor destroyed in the rate controlling step of the attack by the nitronium ion on the aromatic molecule.

The nitrating attack must be

\[
\text{ArH} + \text{NO}_2^+ \rightarrow \text{ArHNO}_2^+ \quad (\text{slow})
\]

\[
\text{ArHNO}_2^+ \rightarrow \text{ArNO}_2^- + \text{H}^+ \quad (\text{fast})
\]

Thus, the termolecular mechanism postulated by Bennett and coworkers would seem to be eliminated on the basis of the lack of solvent effects upon the reaction order.

\[
\text{ArH} + \text{NO}_2^+ + \text{HSO}_4^- \rightarrow \text{ArNO}_2^- + \text{H}_2\text{SO}_4
\]

These results have been substantiated by the work of
Melander.\textsuperscript{39} He carried out dinitration studies by means of product analyses upon tritium toluenes. It was expected that on dinitration toluene-\textsuperscript{4}-t would lose all, and toluene-\textsuperscript{3}-t none, of its activity. Toluene-\textsuperscript{2}-t, finally would lose an amount corresponding to the relative velocities in the two ortho positions, one containing tritium and the other, protium. He analyzed his reactions by burning the organic molecules and determining the specific activity of the water samples obtained. His results are summarized in Table II.

\begin{table}[h]
\centering
\begin{tabular}{lll}
& \% Tritium Calc. & \% Tritium Found \\
Toluene \textsuperscript{4}-t & 0 & 2.2 \\
\textsuperscript{3}-t & 100 & 99 \\
\textsuperscript{2}-t & (50)* & (51.9)(49.7) \\
\end{tabular}
\caption{Table II}
\end{table}

*This assumes equal nitration velocity in tritium and protium positions.

It was expected in view of the great difference

in mass and therefore, in zero point energy of the original bond that the velocities in nitration should be different if the splitting off of the hydrogen ion takes place in the rate controlling step. The simplest explanation of the observed lack of isotope effect is that the addition of the nitrating agent, the nitronium ion, is the rate controlling step with rapid splitting off of the hydrogen following.
Ortho-Para Ratios

One of the least understood phenomena encountered in aromatic substitution is the theory of ortho-para ratios. It is obvious that, if a given substituent had the same effect upon the ortho and para substitutions,

Table III

Ratio of Para to Ortho Substitution Accompanying Nitration

<table>
<thead>
<tr>
<th>Substance</th>
<th>Ortho (%)</th>
<th>Para (%)</th>
<th>p/o</th>
<th>Substance</th>
<th>Ortho (%)</th>
<th>Para (%)</th>
<th>p/o</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhF</td>
<td>12.4</td>
<td>87.6</td>
<td>7.06</td>
<td>PhCH₂Cl</td>
<td>41</td>
<td>55</td>
<td>1.34</td>
</tr>
<tr>
<td>PhCl</td>
<td>30.1</td>
<td>69.9</td>
<td>2.32</td>
<td>PhCHCl₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PhBr</td>
<td>37.6</td>
<td>62.4</td>
<td>1.66</td>
<td>PhCl₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PhI</td>
<td>41.1</td>
<td>58.7</td>
<td>1.43</td>
<td>PhMe</td>
<td>58</td>
<td>38</td>
<td>0.65</td>
</tr>
</tbody>
</table>

the ratio p/o would be 0.5 since there are two ortho positions and only one para position. Several ideas have been presented to account for the observed experimental results. Table III lists some data presented
by Lapworth and Robinson. These authors point out that most of the data can be explained if it is recognized that substituents showing +I effects (inductive effect directed towards the aromatic ring) activate the neighboring ortho positions more than the remote para positions, whereas substituents showing -I effects deactivate the ortho positions more than the para positions. They also found it necessary to employ the concept of steric hindrance by large substituent groups to explain such observations as the almost complete lack of ortho substitution when diphenyl is nitrated. This idea of steric hindrance has been supported by the work of LePevre who showed that the probability of ortho substitution will be lessened by the size of the substituent group in the order: Me < Et < Pr < Bu. This same sequence would also follow equally well from considerations of hyperconjugation. Ingold postulated the "direct" field effect as an explanation for ortho-para ratios. He proposed this concept to explain

the observed experimental results that Holleman obtained in the nitration of compounds such as o-bromo-chlorobenzene. Thus, for the halogens, besides the +T, tautomeric effect, and -I, inductive effect, there was also a "direct" field effect operating. This effect was also deactivating, -D. This effect is propagated not through the bonds of the benzene ring, but through space, its distribution in the ring being thus in the order: o>m>p. There has been a tendency recently to consider this "direct" field effect to be just a part of the general inductive effect and not a distinct and separate effect. Holleman obtained the data of Table IV for the nitration of nitrobenzene. These results, showing the lack of para nitration, cannot be explained by the original theory of Lapworth and Robinson, nor by considering the steric effects present in the system. Holleman originally proposed a theory to explain the prevalence of ortho nitration on the basis of his "addition - elimination" mechanism of aromatic nitration. He assumed that the effect of the substituent on the aromatic nucleus was felt only in the positions conjugated with the substituent, thus, in the

---

model pictured below, carbon atoms two and three are relatively unaffected. Therefore, in the case of nitro-

![Diagram of benzene molecule]

benzene, nitration should occur by means of the addition of elements of HONO₂ to the two, three positions. The major side product, therefore, should be the ortho

**Table IV**

**Nitration of Nitrobenzene**

<table>
<thead>
<tr>
<th>Temp.</th>
<th>% Acid</th>
<th>% Isomers</th>
<th>M</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ortho</td>
<td>Meta</td>
<td>Para</td>
</tr>
<tr>
<td>0°</td>
<td>98.58</td>
<td>6.4</td>
<td>93.2</td>
<td>0.25</td>
</tr>
<tr>
<td>30</td>
<td>94.50</td>
<td>8.1</td>
<td>91.2</td>
<td>0.7</td>
</tr>
<tr>
<td>30</td>
<td>95.90</td>
<td>8.5</td>
<td>91.0</td>
<td>0.5</td>
</tr>
<tr>
<td>30</td>
<td>97.6</td>
<td>8.1</td>
<td>90.9</td>
<td>1.0</td>
</tr>
<tr>
<td>0</td>
<td>H₂SO₄</td>
<td>4.8</td>
<td>93.5</td>
<td>1.7</td>
</tr>
<tr>
<td>30</td>
<td>H₂SO₄</td>
<td>6.8</td>
<td>91.8</td>
<td>1.4</td>
</tr>
</tbody>
</table>
derivative, since carbon atom two is less deactivated than the corresponding para position, carbon atom four, which is part of the conjugated system.

There are quite a few investigations concerning nitration in the chemical literature which report a large ortho-para ratio. Wahl\textsuperscript{44} reports 3,4-dinitro-2,5-dimethylchlorobenzene as the major product of the nitration of 3-nitro-2,5-dimethylchlorobenzene. Also the dinitration of 2,5-dimethylchlorobenzene gave a mixture of 3,4-dinitro-2,5-dimethylchlorobenzene and 4,6-dinitro-2,5-dimethylchlorobenzene. Ingold\textsuperscript{45} also reported that the ortho nitro derivative was the chief by-product of the nitration of benzonitrile. The main product was the meta derivative reported in 81 percent yield. Similarly, Holleman found that the nitration of benzoic acid at -20° gave a mixture of isomers having the following percentages, o:m:p = 14:85:0:6. The methyl ester at -30° yielded, o:m:p = 23:74:2.

Another recent view of ortho-para ratios has been advanced by Waters.\textsuperscript{46} He pointed out that low percent-

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\textsuperscript{44} M. H. Wahl, \textit{Ann. Chim.}, 5, 5 (1936).


\textsuperscript{46} W. A. Waters, \textit{Trans. Faraday Soc.}, 37, 745 (1941).
ages of ortho substitution commonly encountered may be
due, in part, to steric effects, but it is also possible
that it is due to a symmetry factor which affects the
transition states of the possible products. He cor-
relates this transition probability with the stability
of the quinoidal structures that may be formed in the
transition state. As support for this idea, he points
out that it is a well known fact that o-quinones are
less stable than p-quinones; that is, they are more
easily reduced.

Dewar has applied Wheland's molecular orbital
method to an investigation of the relationship between
directive power and electron affinity in electrophilic
substitution. He calculates relative activation en-
ergies for ortho, meta, and para substitution by cal-
culating the differences in total \( \pi \)-electron energy
between PhX and the corresponding transition states
for ortho, meta, and para substitution. For a \( \text{I} \) sub-
stituent, the order of rates should be \( o \succ p \succ m \); for a

47. L. Fieser, "Organic Chemistry," edited by H. Gil-
For a $\text{+E}$ substituent, $m > p > o$. For a $\text{-E}$ substituent, $(o, p) > m$; and with increasing electron affinity, the ratio $o:p$ should fall. For a $\text{+E}$ substituent, $m \gg (o, p)$; and the directive power should increase with increasing electron affinity of the substituent. The ratio $o:p$ should always be considerably greater than unity.

Roberts,\(^{50}\) in his investigation of the electrical effect of the trimethylammonium group, has concluded that the strong meta directing properties of this group towards electrophilic substitution can best be explained on the basis of possible transition states. He feels that the most likely transition states are those which have the least electrical repulsions between like charged centers. For example, structure A below is more stable than B.

\[ \text{A.} \]

\[ \text{B.} \]

---

than structure B. Roberts concludes that the meta directing power of the trimethylammonium group can better be understood on the basis of the possible transition states pictured above than on the basis of the inductive effect of this group.
EXPERIMENTAL

Ultraviolet Absorption Spectra

All the ultraviolet spectrophotometric studies were made with a Cary Recording Spectrophotometer (Model 12). This instrument recorded the optical density of the solution, defined as \( \log \frac{I_o}{I} \), where \( I_o \) and \( I \) represent the incident and transmitted light intensities. The solutions were scanned with the instrument using silica cells. The absorption measurements were made at room temperature. The solvents used were commercial grades without any further purification.

Infra-red Absorption Spectra

All the infra-red studies were made with a Baird Associates Infra-Red Recording Spectrophotometer (Model B). This is a double beam instrument which automatically recorded the percent transmission of the solution. The qualitative work was done using the Nujol mull technique. The analytical work was done using the differential solvent technique. Carbon disulfide was used as the solvent. Potassium bromide cells were used, the reference cell thickness was 0.105 mm. and the sample cell thickness was 0.104 mm.
Nitrobenzene

Nitrobenzene (E.K.C.) was distilled through a 44 plate column and a fraction boiling at 208.2°C was collected and used for the spectrophotometric work.

2,5-Dichloronitrobenzene

This compound (E.K.C.) was used without further purification. m. pt. = 54°C.

2,5-Dibromonitrobenzene

A good yield of this compound was obtained by adding 20 grams of p-dibromobenzene to about 80 ml. of fuming nitric acid and allowing the mixture to stand for about one hour. The solution was then poured into cracked ice and the crude product recovered by suction filtration. The material was recrystallized twice, first from 95 percent ethanol and secondly from Skelly B. m. pt. = 82-82.5°C.

2,3-Dinitro-1,4-dibromobenzene

This compound was prepared using the procedure of Jackson. m. pt. = 157°C.

Fig. 1 Infra-red spectra of 2,5-Dibromonitrobenzene, 2,5-Dichloronitrobenzene, and 2-Chloro-5-Bromonitrobenzene.
Fig. 2 Infra-red spectra of 2,3-Dinitro-1,4-dichlorobenzene, 2,5-Dinitro-1,4-dichlorobenzene, and 2,6-Dinitro-1,4-dichlorobenzene.
2,5-Dinitro-1,4-dibromobenzene

This compound was obtained by Dr. G. S. Hammond using the method of Jackson and also a modified procedure of Sunde. m. pt. = 128-129°.

2,6-Dinitro-1,4-dibromobenzene

Several attempts were made to obtain a pure sample of this compound from the nitration mixtures resulting from using the procedure developed by Jackson. All attempts were unsuccessful, therefore, an alternate synthesis had to be developed. A pure compound was obtained by running a Sandmeyer reaction on 2,6-dinitro-4-bromoaniline which was prepared by Dr. G. S. Hammond. Approximately 1.8 grams of 2,6-dinitro-4-bromoaniline was dissolved in 20 ml. of concentrated sulfuric acid and cooled to 0° in an ice-salt bath. The amine was diazotized by adding it very slowly to a solution of 0.48 grams of sodium nitrite in 20 ml. of concentrated sulfuric acid at 0°. After the amine had been added, the solution was allowed to stand in an ice bath for about one-half hour. The diazonium salt solution was added slowly to a solution of cu-

prous bromide in 48 percent hydrobromic acid, also at 0°. After addition, the reaction mixture was allowed to stand and warm up to room temperature gradually. The crude product was obtained by extracting the reaction mixture with Skelly B. It was recrystallized from cyclohexane, yellowish crystals were obtained. m. pt. = 112-115°. These crystals were recrystallized from Skelly B using a pinch of Norite. m. pt. = 119-119.5°.

2,6-Dinitrobenzobenzene

This compound was prepared from 2,6-dinitroaniline using the same procedure as that above for 2,6-dinitro-1,4-dibromobenzene. It was prepared mainly to make certain that the bromination step had taken place successfully in the synthesis of 2,6-dinitro-4-bromoaniline. The melting point of the pure 2,6-dinitrobenzobenzene was 103-103.5°. The infra-red absorption spectra also showed that these two compounds were different.

2,3-Dinitro-1,4-dichlorobenzene  m. pt. = 101-102°.  
2,5-Dinitro-1,4-dichlorobenzene  m. pt. = 117.5-118.5°  
2,6-Dinitro-1,4-dichlorobenzene  m. pt. = 104.5-105°  

These compounds were obtained from the dinitration
Fig. 3 Infra-red spectra of 2,3-Dinitro-1,4-dibromobenzene, 2,5-Dinitro-1,4-dibromobenzene, and 2,6-Dinitro-1,4-dibromobenzene.
of 2-dichlorobenzene using the procedure of Jackson\textsuperscript{51} and some modifications by Dr. G. S. Hammond.

It might be mentioned here that both the dichloro and dibromo dinitro benzenes can cause severe contact dermatitis. The first indication is a swelling of the affected joints and general itching. This investigator became sensitized to these compounds after about three months contact, thus indicating that the initial resistance was overcome by this time.

2-Nitro-4-chlorobromobenzene

This compound was prepared from 2-nitro-4-chloroaniline by means of a Sandmeyer reaction.

The amine (34.5 grams) was dissolved in 35 ml. of 48 percent hydrobromic acid and 50 ml. of hot water and stirred mechanically. An additional 77 ml. of 48 percent hydrobromic acid was added causing the amine to form a very fine suspension. The mixture was cooled to 0\textdegree\ in an ice-salt bath. An aqueous solution of sodium nitrite, 14.4 grams in 35 ml. of water pre-cooled to 0\textdegree\ was added slowly to the stirred suspension. The clear diazonium salt solution was tested for excess nitrite with starch-iodide paper, the test was negative. Cuprous bromide was prepared according
to an Organic Syntheses procedure.\textsuperscript{53} The clear diazonium salt solution was added to a suspension of 36 grams of cuprous bromide in 50 ml. of 48 percent hydrobromic acid at room temperature. The suspension was mechanically stirred during the addition. After all the salt had been added, a reflux condenser was attached to the system. The reaction mixture was heated over a steam bath to expel nitrogen. Then the reaction mixture was steam distilled, the product collected in about two and one-half liters of distillate. The crude product was dissolved in ether and extracted with a 5 percent sodium hydroxide solution. The ether was removed and the product recrystallized from 95 percent ethanol using Norite. A second recrystallization from ethanol yielded fine yellowish white crystals, m. pt. = 68-68.5\degree.

\textbf{l-Bromo-2-nitrochlorobenzene}

A good yield of this compound was obtained from the bromination of 2-nitrochlorobenzene using an adap-

The reaction was carried out as described by Waters. To a mixture of 17 grams of silver sulfate and six milliliters of bromine in 100 ml. of concentrated sulfuric acid was added 16 grams of 2-nitrochlorobenzene. This mixture was heated under reflux over a steam bath for approximately ten hours. The mixture was poured onto cracked ice, the excess bromine being removed by the addition of solid sodium bisulfite. The crude solid was filtered and extracted with ethanol and ether. The ether was removed. The product was recrystallized twice from ethanol giving fine light yellow crystals. m. pt. = 69-70°.

**p-Dibromobenzene-Cl**

Another method by which the isomer ratios obtained upon the nitration of 2,5-dibromonitrobenzene could be determined is by the use of isotopic dilution analyses. With this view in mind, the synthesis of ring labeled p-dibromobenzene-Cl was carried out. The tracer work is still in progress. The isotopic dilution method should provide an independent check upon the results obtained by means of the infra-red analytical method.

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Acetanilide-\textsuperscript{14C}

Acetanilide-\textsuperscript{14C} was prepared by dissolving 4.78 grams of aniline hydrochloride-\textsuperscript{14C} in 100 ml. of water and heating to 50\textdegree. To this solution was added six milliliters of acetic anhydride rapidly without stirring. Immediately then, five grams of sodium acetate in 15 ml. of water were added. The solution was stirred rapidly and then cooled in an ice bath to 5\textdegree. The white crystals were collected by suction filtration. Model experiments gave yields of about 90-95 percent.

\textbf{p-Bromoacetanilide-\textsuperscript{14C}}

The white crystals from above were dissolved out of the Buchner funnel by approximately 25 ml. of glacial acetic acid. The acetic acid solution was cooled in an ice bath and then about 2.5 ml. of bromine were added slowly in small portions. The slushy suspension was poured onto cracked ice about 100 ml. The excess bromine was removed with solid sodium bisulfite and then the solid was collected by suction filtration. Model experiments gave yields of about 90 percent.

\textbf{p-Bromoaniline-\textsuperscript{14C}}

The solid was transferred to a 150 ml. distilling
flask to which was added 20 ml. of water. The mixture was then refluxed. About eight milliliters of concentrated hydrochloric acid were added in one milliliter portions in about 15 minutes. The solution was then refluxed for about one hour. Then about 45 ml. of the liquid was distilled over to remove the ethyl acetate formed during the hydrolysis. The clear solution was poured onto about 75 ml. of cracked ice and neutralized carefully with a 10 percent potassium hydroxide solution. The white solid was filtered by suction. Model experiments gave yields ranging from 87-97 percent.

**p-Dibromobenzene-14**

The solid amine was dissolved in 20 ml. of hot water and 20 ml. of 48 percent hydrobromic acid. Then an extra 25 ml. of 48 percent hydrobromic acid was added causing a fine suspension to form. This suspension was cooled to -3° in an ice-salt bath and mechanically stirred during diazotization. The diazotization was carried out by the drop-wise addition of an aqueous solution of sodium nitrite, 2.2 grams in 15 ml. of water, precooled to 0°. The clear diazonium salt solution was checked for excess nitrite with starch-iodide paper. The test was negative. In a 3 neck
250 ml. flask equipped for steam distillation was placed five grams of cuprous bromide and 20 ml. of 48 percent hydrobromic acid. The clear dark purplish red solution was heated to boiling and then the cold diazonium salt solution was added through a dropping funnel in 40 ml. portions. After complete addition of the diazonium salt solution, the crude product was recovered by steam distillation. The crude product was a yellowish white solid, weighing 5.3 grams. The crude material was air dried and then dissolved in about 25 ml. of hot Skelly B. The yellow solution was decolorized with about one gram of Norite. The product was then collected by cooling, and then successively reducing the volume of Skelly and cooling in an ice-salt bath. The total weight of product collected in this fashion was 4.6 grams representing an overall yield for the complete synthesis of 55 percent. Model experiments on the Sandmeyer reaction gave about 90-95 percent for the crude yield and about 95 percent for the recrystallization from Skelly B.

Nitration Studies

One typical nitration run will be described in detail and the data concerning the other runs will be found in the Table V for 2,5-dichloronitrobenzene and
Table VI for 2,5-dibromonitrobenzene.

Run No. 10

To a 100 ml. round bottom flask were added two grams of 2,5-dichloronitrobenzene (0.0104 moles) and 4.4 grams of sodium nitrate (0.052 moles). Then 40 ml. of concentrated sulfuric acid were added and the flask connected to a condenser and immersed in a steam bath. The solution was heated for from four to five hours and then poured into cracked ice. The crude solid was recovered by suction filtration and then air dried. The crude solid was used directly for infra-red analysis without any purification.

Identification of High Temperature Reaction Product

When the nitration of 2,5-dibromonitrobenzene was carried out at temperatures above 100°, a new reaction product was isolated. This product was found when the reaction mixtures were analyzed by the infra-red absorption method. It was very slightly soluble in carbon disulfide in the presence of the dinitro isomers but seemed to be completely insoluble when pure. It was also insoluble in the nitration medium and separated out during the course of the reaction as a fine white solid. It was soluble in benzene. The compound seemed to sublime during the course of melting point
Table V
Nitration of 2,5-Dichloronitrobenzene

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp.</th>
<th>Weight of Cmp'd.</th>
<th>Medium</th>
<th>% Acid</th>
<th>Volume Acid</th>
<th>Weight of NaNO₃</th>
<th>Weight of added salts</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100°</td>
<td>5 grams</td>
<td>H₂SO₄</td>
<td>96.2</td>
<td>50 ml.</td>
<td>11 grams</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>2</td>
<td>HNO₃</td>
<td>Fuming</td>
<td>30</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>2</td>
<td>H₂SO₄</td>
<td>Fuming</td>
<td>30</td>
<td>4.4</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>2</td>
<td>H₂SO₄</td>
<td>96.2</td>
<td>40</td>
<td>4.4</td>
<td>9 grams KHSO₄</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>2</td>
<td>HNO₃</td>
<td>Fuming</td>
<td>40</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>2</td>
<td>H₂SO₄</td>
<td>96.2</td>
<td>40</td>
<td>4.4</td>
<td>9 grams KCIO₄</td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>2</td>
<td>HNO₃</td>
<td>96.2</td>
<td>50</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>8</td>
<td>120</td>
<td>2</td>
<td>H₂SO₄</td>
<td>96.2</td>
<td>150</td>
<td>4.4</td>
<td>---</td>
</tr>
<tr>
<td>9</td>
<td>140</td>
<td>2</td>
<td>H₂SO₄</td>
<td>96.2</td>
<td>160</td>
<td>4.4</td>
<td>---</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>2</td>
<td>H₂SO₄</td>
<td>96.2</td>
<td>40</td>
<td>4.4</td>
<td>---</td>
</tr>
<tr>
<td>Run No.</td>
<td>Temp.</td>
<td>Weight of Comp'd.</td>
<td>Medium</td>
<td>% Acid</td>
<td>Volume Acid</td>
<td>Weight of NaNO₃</td>
<td>Weight of added salts</td>
</tr>
<tr>
<td>--------</td>
<td>-------</td>
<td>------------------</td>
<td>--------</td>
<td>--------</td>
<td>-------------</td>
<td>----------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>11</td>
<td>100°</td>
<td>2 grams</td>
<td>H₂SO₄</td>
<td>95.0</td>
<td>40 ml</td>
<td>4.4</td>
<td>---</td>
</tr>
<tr>
<td>12</td>
<td>100</td>
<td>2</td>
<td>H₂SO₄</td>
<td>89.5</td>
<td>40</td>
<td>4.4</td>
<td>---</td>
</tr>
<tr>
<td>13</td>
<td>140°</td>
<td>2</td>
<td>H₂SO₄</td>
<td>Fuming</td>
<td>160</td>
<td>17.6</td>
<td>---</td>
</tr>
<tr>
<td>14</td>
<td>140°</td>
<td>2</td>
<td>H₂SO₄</td>
<td>96.2</td>
<td>160</td>
<td>17.6</td>
<td>---</td>
</tr>
</tbody>
</table>
Table VI
Nitration of 2,5-Dibromonitrobenzene

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp.</th>
<th>Weight of Comp'd.</th>
<th>Medium</th>
<th>% Acid</th>
<th>Volume Acid</th>
<th>Weight of NaNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>100°</td>
<td>2</td>
<td>H₂SO₄</td>
<td>96.9</td>
<td>40</td>
<td>3.1</td>
</tr>
<tr>
<td>A-2</td>
<td>100</td>
<td>2.85</td>
<td>H₂SO₄</td>
<td>89.0</td>
<td>40</td>
<td>4.4</td>
</tr>
<tr>
<td>A-3</td>
<td>100</td>
<td>2.85</td>
<td>H₂SO₄</td>
<td>Fuming</td>
<td>40</td>
<td>4.4</td>
</tr>
<tr>
<td>A-4</td>
<td>100</td>
<td>2</td>
<td>HNO₃</td>
<td>Fuming</td>
<td>50</td>
<td>---</td>
</tr>
<tr>
<td>A-6</td>
<td>100</td>
<td>2.85</td>
<td>H₂SO₄</td>
<td>96.9</td>
<td>40</td>
<td>4.4</td>
</tr>
<tr>
<td>A-7</td>
<td>100</td>
<td>2.85</td>
<td>H₂SO₄</td>
<td>96.9</td>
<td>40</td>
<td>6.6</td>
</tr>
<tr>
<td>A-8</td>
<td>140 10</td>
<td>2.85</td>
<td>H₂SO₄</td>
<td>96.9</td>
<td>150</td>
<td>17.6</td>
</tr>
<tr>
<td>A-9</td>
<td>120 5</td>
<td>2.85</td>
<td>H₂SO₄</td>
<td>96.9</td>
<td>160</td>
<td>17.6</td>
</tr>
<tr>
<td>A-10</td>
<td>120 2</td>
<td>2.85</td>
<td>H₂SO₄</td>
<td>90</td>
<td>160</td>
<td>17.6</td>
</tr>
<tr>
<td>A-11</td>
<td>100</td>
<td>2.85</td>
<td>H₂SO₄</td>
<td>96.9</td>
<td>40</td>
<td>4.4</td>
</tr>
<tr>
<td>A-12</td>
<td>100</td>
<td>2.85</td>
<td>H₂SO₄</td>
<td>Fuming</td>
<td>40</td>
<td>4.4</td>
</tr>
</tbody>
</table>
determination upon a melting point block. The compound softened at 209° in a sealed capillary and then seemed to decompose above 215°.

The same product was obtained when 2,5-dinitro-1,4-dibromobenzene was added to the usual nitration medium at 140°. It was identical with the product obtained from the nitration of 2,5-dibromonitrobenzene as shown by infra-red absorption spectra. This compound contained both bromine and nitrogen but no sulfur. It also gave a positive test for the presence of two or three nitro groups in the molecule. A bright red color was obtained when a few milligrams of compound were added to a mixture of acetone and 5 percent sodium hydroxide.

This reaction product is thought to be the trinitro compound; 2,3,5-trinitro-1,4-dibromobenzene.

Analysis: Calcd. N = 11.3 percent; Found N = percent.

Infra-red Spectrophotometric Analytical Methods

The differential solvent technique was employed for the analytical procedure. The solvent used was

analytical grade carbon disulfide since this solvent had good absorption characteristics above the 10 μm range. The spectra of the pure compounds in carbon disulfide was determined and then it was found that each of the products and the starting material had distinctive absorption bonds. Experimental conditions were then determined in such a fashion that the Lambert-Beer Law was followed.

\[ \log \frac{I_0}{I} = kcl \]

Samples of from 0.05 grams to 0.30 grams were weighed directly into 10 ml. volumetric flasks. This concentration range was employed due to the solubility of the compounds in carbon disulfide. This range resulted in readings of percent transmission ranging from 95 to 75 percent. The percent transmission readings obtained were then plotted on semi log paper against the weight of the sample. In all cases, enough samples were used to determine a good straight line correlation which gave results within three percent accuracy when applied to some synthetic mixtures. The accuracy of the method was affected to a large extent by the background or noise level of the machine and the limit of readability of the percent transmission.
due to line thickness. In most cases, the noise level of the machine was no more than a half of a division or 0.5 percent transmission. This would be responsible for the differences between the true values and the calculated values for the synthetic mixtures. In all of the nitration runs on 2,5-dichloronitrobenzene, the reactions were carried to completion so that there was no interference due to unreacted starting material. This fact could easily be ascertained by the absence of the characteristic 2,5-dichloronitrobenzene wavelength at 9.52\(\mu\). This starting material had a band at 12.18\(\mu\) which was identical with the analytical band for 2,3-dinitro-1,4-dichlorobenzene. In the case of the mixtures, the base line technique was employed so as to minimize the background contribution of the other components to the analytical band of component being measured. Since substances following the Lambert-Beer Law, the optical densities are additive, the true absorption maxima were calculated by subtracting the logarithm of the background from the logarithm of the observed percent transmission.

In Table VII are listed the distinctive analytical absorption bands used for the determination of the isomer ratios in this study.
Table VII

Analytical Infra-red Absorption Bands

<table>
<thead>
<tr>
<th>Compound</th>
<th>(microns)</th>
<th>(cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,5 dichloronitrobenzene</td>
<td>9.52</td>
<td>1050</td>
</tr>
<tr>
<td>2,3 dinitro-1,1'-dichlorobenzene</td>
<td>12.18</td>
<td>822</td>
</tr>
<tr>
<td>2,5 dinitro-1,1'-dichlorobenzene</td>
<td>11.88</td>
<td>842</td>
</tr>
<tr>
<td>2,6 dinitro-1,1'-dichlorobenzene</td>
<td>13.95</td>
<td>718</td>
</tr>
<tr>
<td>2,5 dibromonitrobenzene</td>
<td>9.68</td>
<td>1032</td>
</tr>
<tr>
<td>2,3 dinitro-1,1'-dibromobenzene</td>
<td>12.22</td>
<td>818</td>
</tr>
<tr>
<td>2,5 dinitro-1,1'-dibromobenzene</td>
<td>11.90</td>
<td>840</td>
</tr>
<tr>
<td>2,6 dinitro-1,1'-dibromobenzene</td>
<td>13.95</td>
<td>718</td>
</tr>
</tbody>
</table>

Table VIII shows the accuracy with which several synthetic mixtures were analyzed using the absorption bands indicated above. The greatest deviation was approximately three percent.

The analytical accuracy for the dibromo compounds was not as reliable as that for the dichloro compounds. This was due for the most part to the fact that most of the dibromo nitration runs still contained unreacted starting material in the reaction product analyzed. This introduced another source of error since the starting material and the 2,3-dinitro isomer had the same absorption band. The amount of starting material had to
Table VIII

Analysis of Synthetic Mixtures of Dinitro-Isomers of 1,4 dichlorobenzene

<table>
<thead>
<tr>
<th>Mixture No.</th>
<th>Compound</th>
<th>Actual %</th>
<th>Calculated %</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2,3 dinitro</td>
<td>48.3</td>
<td>46.6</td>
<td>-1.7</td>
</tr>
<tr>
<td></td>
<td>2,5 dinitro</td>
<td>16.7</td>
<td>16.9</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>2,6 dinitro</td>
<td>34.9</td>
<td>36.5</td>
<td>1.6</td>
</tr>
<tr>
<td>2.</td>
<td>2,3 dinitro</td>
<td>49.8</td>
<td>47.4</td>
<td>-2.4</td>
</tr>
<tr>
<td></td>
<td>2,5 dinitro</td>
<td>21.8</td>
<td>21.2</td>
<td>-0.6</td>
</tr>
<tr>
<td></td>
<td>2,6 dinitro</td>
<td>28.4</td>
<td>31.3</td>
<td>2.9</td>
</tr>
<tr>
<td>3.</td>
<td>2,3 dinitro</td>
<td>26.9</td>
<td>26.7</td>
<td>-0.2</td>
</tr>
<tr>
<td></td>
<td>2,5 dinitro</td>
<td>21.7</td>
<td>21.8</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>2,6 dinitro</td>
<td>51.4</td>
<td>51.5</td>
<td>0.1</td>
</tr>
</tbody>
</table>

be determined and taken into account in calculating the intensity of the characteristic 2,3-dinitro absorption band. Also, in the high temperature runs, the presence of another product made the analysis more uncertain. The precision, however, between two identical runs was good, the deviation being of the order of two percent.
Fig. 4 Infra-red spectra of 2,6-Dinitro bromobenzene, Typical Synthetic Mixture of Isomers, and Nitration Run No. 12.
Fig. 5 Infra-red spectra of Nitration Run No. A-12, Nitration Run No. A-14-z, and 2,3,5 Trinitro-1,4-dibromobenzene.
DISCUSSION

In order to analyze the mixtures obtained in the nitration of 2,5-dibromonitrobenzene and 2,5-dichloronitrobenzene and thus study the isomer ratios obtained, it was necessary to prepare the pure compounds. Having these pure compounds, it was deemed of interest to study their ultraviolet absorption spectra with the hope of being better able to elucidate the species present in solution under nitration conditions. The spectra measured was confined in all cases to wave lengths from 4000 Å to approximately 2200 Å, the effective range of the spectrophotometer used in this study.

The ultraviolet absorption spectral data is summarized in the following tables. In general, all of the nitro halobenzenes exhibited the same type of spectra having three absorption maxima in the ultraviolet range as shown in Figure 6. As can be seen from Table IX, the first absorption maximum at approximately 2250 Å is essentially unaffected by changes in solvent. This intense band has the same approximate wave length as the band which the para dihalobenzenes themselves exhibit. In water, p-dichlorobenzene has a maximum at 2240 Å and p-dibromobenzene, one at 2265 Å. It is generally assumed that the intense absorption of light
Fig. 6 The Ultraviolet Absorption Spectra of 2,5-Dinitro-1,4-dibromobenzene.
<table>
<thead>
<tr>
<th></th>
<th>95% Ethanol</th>
<th></th>
<th>Water</th>
<th></th>
<th>conc. H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ max.</td>
<td>ε</td>
<td>λ max.</td>
<td>ε</td>
<td>λ max.</td>
</tr>
<tr>
<td>Cl⁻CN₂NO₂⁻</td>
<td>2235</td>
<td>17,400</td>
<td>2265</td>
<td>14,900</td>
<td>2265</td>
</tr>
<tr>
<td>Br⁻CN₂NO₂⁻</td>
<td>2225</td>
<td>18,200</td>
<td>2225</td>
<td>15,750</td>
<td>2238</td>
</tr>
<tr>
<td>Cl⁻NO₂⁻</td>
<td>2235</td>
<td>19,300</td>
<td>2250</td>
<td>17,550</td>
<td>2245</td>
</tr>
<tr>
<td>Br⁻NO₂⁻Cl⁻</td>
<td>2200</td>
<td>16,500</td>
<td>2190</td>
<td>19,100</td>
<td>2225</td>
</tr>
<tr>
<td>Br⁻NO₂⁻NO₂⁻</td>
<td>2250</td>
<td>18,100</td>
<td>2225</td>
<td>18,550</td>
<td>2260</td>
</tr>
<tr>
<td>Cl⁻CN₂NO₂⁻</td>
<td>2200</td>
<td>25,800</td>
<td>2210</td>
<td>23,900</td>
<td>2240</td>
</tr>
<tr>
<td>Cl⁻NO₂⁻Cl⁻</td>
<td>2272</td>
<td>23,100</td>
<td>2290</td>
<td>22,800</td>
<td>2330</td>
</tr>
<tr>
<td>O₂N⁻Cl⁻NO₂⁻</td>
<td>2200</td>
<td>19,300</td>
<td>2150</td>
<td>19,800</td>
<td>2210</td>
</tr>
</tbody>
</table>

Table IX The Ultraviolet Absorption Maxima for Various Nitrohalobenzenes.
which characterizes certain organic compounds is associated with some form of resonance in the molecule.\textsuperscript{56} Since the resonance structures usually written for the halobenzenes involve separation of charge, these structures, if they were major contributors to the observed electronic transitions would be affected by changes in solvent. The ionic forms should become greater contributors in the more polar solvents with a corresponding shift in the observed absorption to longer wave lengths.\textsuperscript{57} Very small shifts in this first absorption maximum have been found for these compounds in solvents ranging from 95 percent ethanol to concentrated sulfuric acid. These solvents represent a very great change in dielectric constant of the medium.

\textsuperscript{57} G. N. Lewis and M. Calvin, Chem. Revs., 25, 273 (1939).
Thus, it would appear that the halobenzenes do not interact very strongly with the solvent. The small shifts observed are probably due to the greater polarization of the molecules in the more polar solvents. This first maximum probably corresponds to the 1800 Å band in benzene shifted to longer wave length by some perturbation due to the polarization of the halogen atom. The near ultraviolet spectra of the phenyl halides has been recently interpreted on the basis of molecular orbital theory by Matsen. 58 He calculated the position and intensity of the low intensity bands at approximately 2500 Å in good agreement by making allowances for the inductive effect of the substituents. This was necessary for the phenyl halides since the resonance and inductive effects oppose each other. He took account of the inductive effect by assuming that the high electron affinity of the substituent polarizes the C-X bond in such a way as to raise the electron affinity on carbon atom one.

The second absorption band, shown in Table X, is due to the aromatic nitro function in the molecule.

<table>
<thead>
<tr>
<th>Nitrohalobenzenes</th>
<th>95% Ethanol λ&lt;sub&gt;max&lt;/sub&gt;</th>
<th>E</th>
<th>Water λ&lt;sub&gt;max&lt;/sub&gt;</th>
<th>E</th>
<th>conc. H&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;O&lt;sub&gt;4&lt;/sub&gt;&lt;/sub&gt; λ&lt;sub&gt;max&lt;/sub&gt;</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;Br</td>
<td>2500</td>
<td>4000</td>
<td>2580</td>
<td>2870</td>
<td>2725</td>
<td>3140</td>
</tr>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;Br</td>
<td>2400</td>
<td>5970</td>
<td>2550</td>
<td>2780</td>
<td>2780</td>
<td>2300</td>
</tr>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;Cl</td>
<td>2415</td>
<td>7420</td>
<td>2525</td>
<td>6250</td>
<td>2575</td>
<td>5080</td>
</tr>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;Cl</td>
<td>2465</td>
<td>9070</td>
<td>2615</td>
<td>4970</td>
<td>2625</td>
<td>3720</td>
</tr>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;Cl</td>
<td>2360</td>
<td>9100</td>
<td>2365</td>
<td>8600</td>
<td>2440</td>
<td>7550</td>
</tr>
</tbody>
</table>

* Shoulders not true max.

Table X The Ultraviolet Absorption Maxima for Various Nitrohalobenzenes.
It corresponds to the 2600 Å absorption band which is found in nitrobenzene. This band is modified by the other substituents on the molecule, for example; a second nitro group causes this band to shift to shorter wave lengths. This is probably due to cross conjugation of the two nitro groups in the molecule as shown below.

The second nitro group will decrease the mobility of the electrons required for the conjugation of the first nitro group with the benzene nucleus. Therefore, the energy required for this transition will be greater and thus the absorption will be shifted to shorter wave lengths. Thus, \textit{m}-dinitrobenzene has an absorption maximum at 2425 Å in water as compared to a maximum at 2670 Å for nitrobenzene. The sensitivity of this band to solvent can be explained on the basis of the interaction of the molecule with the solvent especially by
means of hydrogen bonding. In ethanol solution, the hydrogen bonds between the nitro compounds and the solvent are very weak as has been previously reported by Gordy\textsuperscript{59} on the basis of his spectroscopic work using O-deutero methanol and nitrobenzene. However, it seems very reasonable that the shift observed in going to more polar solvents is actually due to hydrogen bonding since a study of the ultraviolet spectra of nitrobenzene in sulfuric acid solutions of varying concentrations show a definite correlation between the wave length and acid strength. Table XI presents the data for nitrobenzene in sulfuric acid solutions.

The nitro group has a relatively large dipole moment which is attributed to the formal charges on the nitrogen and oxygen. The formal negative charge on the oxygen atom should make this group a good hydrogen bonding species. It has been shown by Gillespie\textsuperscript{2} that in 100 percent sulfuric acid, a compound such as nitrobenzene is actually 41 percent ionized, that is, present in solution as the conjugate acid. Thus, the shift to longer wave lengths shown by the

\textsuperscript{59} W. Gordy, \textit{J. Chem. Phys.}, I, 93 (1939).
second absorption maximum for the nitrohalobenzenes can be easily be rationalized as due to the greater contribution of the hydrogen bonded complexes as the solvent gets more polar.

Table XI

Ultraviolet Absorption Maxima of Nitrobenzene in Changing Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Maxima</th>
<th>Maxima</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isooctane</td>
<td>2520 Å</td>
<td>8900</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>2520 Å</td>
<td>10000</td>
</tr>
<tr>
<td>Water</td>
<td>2670 Å</td>
<td>8950</td>
</tr>
<tr>
<td>69.6% H₂SO₄</td>
<td>2760 Å</td>
<td></td>
</tr>
<tr>
<td>84.4% H₂SO₄</td>
<td>2840 Å</td>
<td></td>
</tr>
<tr>
<td>87.9% H₂SO₄</td>
<td>2865 Å</td>
<td></td>
</tr>
<tr>
<td>93.6% H₂SO₄</td>
<td>2890 Å</td>
<td></td>
</tr>
<tr>
<td>96.8% H₂SO₄</td>
<td>2885 Å</td>
<td></td>
</tr>
<tr>
<td>98.4% H₂SO₄</td>
<td>2885 Å</td>
<td></td>
</tr>
</tbody>
</table>


Since resonance between the nitro group and the benzene nucleus requires coplanarity of the resonating system, it would be expected that steric effects which would interfere with this coplanarity could be observed. As can be seen from Table X, this fact has been observed. The compound, 2,3-dinitro-1,4-dibromobenzene, does not exhibit an absorption maximum in the region of 2500 Å. The bulk of the bromine groups next to the two nitro groups exerts enough steric hindrance to prevent the nitro groups from lying in the plane of the benzene ring. As would be expected, the greater size of the bromine group exerts a noticeably larger steric effect upon the nitro groups than the chlorine group. This same steric effect is observed in the spectrum of o-dinitrobenzene. No definite absorption maximum can be found in the spectra though shoulders are observed at 2480 Å and 2140 Å in 95 percent ethanol.

The third absorption band found in these systems is presented in Table XII. This band is of low intensity and is probably most easily correlated with the low intensity absorption maximum of nitromethane at 2700 Å in hexane. It corresponds to the 3300 Å band found in nitrobenzene and has an intensity of approximately one-hundredth that of the 2600 Å band. The
<table>
<thead>
<tr>
<th></th>
<th>95% Ethanol</th>
<th>Water</th>
<th>conc. H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λₘₐₓ. E</td>
<td>λₘₐₓ. E</td>
<td>λₘₐₓ. E</td>
</tr>
<tr>
<td>Br-ClNO₂</td>
<td>3090 1520</td>
<td>3150 1520</td>
<td>3400 1500</td>
</tr>
<tr>
<td>Br-ClNO₂</td>
<td>3100 1610</td>
<td>3130 1530</td>
<td>3375 1535</td>
</tr>
<tr>
<td>Cl-ClNO₂</td>
<td>3050 1680</td>
<td>3150 1530</td>
<td>3300 1680</td>
</tr>
<tr>
<td>Cl-ClNO₂</td>
<td>3100 1570</td>
<td>3165 1900</td>
<td>3290 1900</td>
</tr>
<tr>
<td>Cl-ClNO₂</td>
<td>3125 1430</td>
<td>3210 2280</td>
<td>3450 1300</td>
</tr>
<tr>
<td>Cl-ClNO₂</td>
<td>3125 2660</td>
<td>3225 2780</td>
<td>3545 1990</td>
</tr>
<tr>
<td>Cl-ClNO₂</td>
<td>3175 2510</td>
<td>3265 2780</td>
<td>3525 1960</td>
</tr>
<tr>
<td>Cl-ClNO₂</td>
<td>3050 1520</td>
<td>3125 1750</td>
<td>3375 1460</td>
</tr>
</tbody>
</table>

Table XII The Ultraviolet Absorption Maxima for Various Nitrohalobenzenes.
shift to longer wave lengths of this absorption band in aromatic nitro compounds may be due to rehybridization of the bond orbitals about nitrogen in the aromatic compounds. This band is observed in all of the compounds examined in this study. It shows about the same solvent effects as the 2600 Å band, however, it does not seem to reflect any steric effects.

The study of the ultraviolet spectra of nitrobenzene in varying concentrations of sulfuric acid was undertaken to be better able to understand the variation in the rate of nitration with acid concentration. The kinetics of nitration in a particular solvent depend not only upon the nature and concentration of the nitrating agent, but also upon the state of the aromatic substance being attacked. Nitrobenzene has been assumed to exist in sulfuric acid - water solutions either as the conjugate acid or as a hydrogen bonded complex. The data presented in Table XI and plotted in Figure 7 confirms the view that nitrobenzene is present in solution as a hydrogen bonded complex. The shift of the absorption maximum to longer wave lengths as the concentration of sulfuric acid increases conforms very closely with the solubility work of Hammett on nitrobenzene in sulfuric acid - water mixtures. That
Ultraviolet Absorption
Spectrum of Nitrobenzene
in Sulfuric Acid Solutions

Fig. 7 The Ultraviolet Absorption Spectrum of Nitrobenzene in Sulfuric Acid Solutions.
the absorption maximum remains constant above 90 percent sulfuric acid is very significant. Thus, it would appear that all of the nitrobenzene has been converted into a hydrogen bonded complex with sulfuric acid at acid concentrations above 90 percent. This fact would seem to indicate that the viewpoint expressed by Gillespie in explaining the falling off of the nitration rate in solutions of sulfuric acid above 90 percent is not necessarily correct. He suggested that the concentration of the hydrogen bonded complex of nitrobenzene was changing in these high acid concentrations.

The extent to which the conjugate acid was formed was determined by the basicity of the compound. He correlated the decrease in nitration rate with the increase in concentration of this species in solution. If the conjugate acid became an important species in solutions above 90 percent sulfuric acid, it would be expected that large bathochromic shifts would be observed in the absorption spectra. Essentially the nitrobenzene molecule would be converted into an ion and large shifts in wave length have been shown to occur for such systems by Brooker in his work on indicators.

and dyes. No such shift has been observed in this investigation. It would be extremely fortuitous if the conjugate acid and the hydrogen bonded complex had the same absorption maximum. It has also been noted that in carrying out nitration reactions in fuming sulfuric, the addition of 2,5-dibromonitrobenzene causes the acid solution to turn red. It is probable that this was due to the formation of the conjugate acid of the nitro compound. This result would be very plausible in view of the work of Brooker cited previously.

The problem of explaining the maximum in the rate of nitration in the vicinity of 90 percent sulfuric acid has still not been satisfactorily solved. The rate determining step in the reaction involves the electrophilic attack of the nitronium ion upon the aromatic compound, essentially a neutral molecule.

![Diagram of the reaction](attachment://reaction_diagram.png)

Transition State

\[
\text{Rate} = k_1(a_{ArH})a_{NO_2}^+ - k_-1(a_{ArHNO_2}^+)\]
The rate constant $k_{-1}$ is very small and the rate constant $k_2$ is very large, thus, the overall rate is determined by $k_1$. The rate of a reaction of this type should be influenced by the ionic strength and the dielectric constant of the medium. Since the effective radius of the activated complex in the transition state is greater than that of the nitronium ion, it will be less susceptible to changes in the medium. The charge in the transition state can be spread out to a much greater extent than can the charge on the nitronium ion. Thus, as the dielectric constant of the medium is increased, the rate of the reaction should decrease since the activity coefficient of the nitronium ion will be affected to a greater degree. Thus, a possible explanation for the falling off of rate may be rationalized on the basis of the changing dielectric constant of the medium. The increase in rate upon the addition of bisulfate ion can then be considered due to a general salt effect upon the reaction producing the nitronium ion.

The compounds, 2,5-dibromonitrobenzene and 2,5-

dichloronitrobenzene, were chosen for the study of the ortho-para ratios obtained from the nitration of aromatic nitro compounds. These compounds were especially convenient in that they had only one available ortho or meta position. The other two positions were both blocked by the same substituent, thus effectively eliminating any complications due to the blocking group. As shown below,

![Diagram of dichloronitrobenzene]

the positions will be referred to with respect to the nitro group.

These nitration experiments were essentially internal competition experiments between the available positions on the halonitrobenzenes. The isomer ratios produced could be correlated directly with the differences in the free energies of activation of the corresponding transition states. This was true since the external conditions were obviously the same during any one reaction. The results of these experiments could enable us to evaluate critically the importance of the
different factors which influence the free energies of activation of the different transition states.

Since the attack of the nitronium ion upon the benzene nucleus is the rate controlling step during the process of nitration, the rate of formation of the ortho-isomer will be given by the following equation.

\[ \frac{d}{dt} [\text{ortho-isomer}] = k_0 (\text{ArH})(\text{NO}_2^+) \]

Similarly, the rate of formation of the para isomer will be

\[ \frac{d}{dt} [\text{para-isomer}] = k_p (\text{ArH})(\text{NO}_2^+) \]

The ratio of the relative amounts of the two isomers will be independent of time and a function only of the relative specific reaction rates.

\[ \frac{[\text{ortho-isomer}]}{[\text{para-isomer}]} = \frac{k_0}{k_p} \]

The problem of the effect of structure upon the rate of reaction and upon its temperature coefficient reduces to the consideration of the sum of two terms, one, dependent only upon potential energies and the
Other, dependent upon the kinetic energies of vibration and rotation.

\[ \Delta F^* - \Delta F_p^* = (\Delta E_{p0}^* - \Delta E_{pp}^*) + (\Delta E_{k0}^* - \Delta E_{kp}^*) \]

\[ -RT \ln \frac{f_{p0}^* f_p}{f_{p0}^*} \]

The orientation of substituents in the benzene ring may be considered a case where only the potential energy terms are involved. This has been shown to be true for a number of different substitution reactions.\(^\text{64}\) If the relative rate of reaction in the different positions is just a purely potential energy problem, it is possible to calculate the entropy differences which exist in the corresponding transition states. In terms of the collision theory, this implies that the product \(P_0Z_0\) will have the same value as \(P_pZ_p\) where \(P\) is the probability factor and \(Z\) the frequency factor.

\[ k_0 = P_0Z_0e^{-E_0/RT} \]

Since the frequency factor is not likely to differ

---

\(^{64}\) L. P. Hammett, \textit{op. cit.}, p. 126.
greatly, this is equivalent to the condition that the probability factor has the same value for both isomers.

Therefore, it is necessary only to determine the isomer ratios at several different temperatures to be able to calculate the entropy differences.

\[
\Delta S^+ - \Delta S^+_p = \frac{d}{dT} \left[ RT \ln \frac{k_0}{k_p} \right]
\]

Using this relationship, the following values have been calculated for the nitration of 2,5-dichloronitrobenzene and 2,5-dibromonitrobenzene. For 2,5-dichloronitrobenzene in concentrated sulfuric acid:

\[
\Delta S^+ - \Delta S^+_p = +2.7 \text{ e.u.}
\]
\[
\Delta S^+ - \Delta S^+_m = +5.8 \text{ e.u.}
\]

For 2,5 dibromonitrobenzene in concentrated sulfuric acid:

\[
\Delta S^+ - \Delta S^+_p = +24.0 \text{ e.u.}
\]
\[
\Delta S^+ - \Delta S^+_m = +12.0 \text{ e.u.}
\]

The differences shown above for the two compounds are probably due to the greater steric effects found in 2,5-dibromonitrobenzene.

As a comparison for the above compounds, several
other literature values will be cited. For the nitration of toluene: 65

\[ \Delta S^+ - \Delta S^+ = +0.5 \text{ e.u.} \]
\[ \Delta S^+ - \Delta S^+ = +3.1 \text{ e.u.} \]

For the nitration of benzoic acid: 65

\[ \Delta S^+ - \Delta S^+ = +2.0 \text{ e.u.} \]

An interesting result is found in the determination of the temperature dependence of the isomer ratio of the nitration of 2,5-dichloronitrobenzene in fuming sulfuric acid. The ortho-para ratio decreases with increase in temperature. In this case, the calculation of the entropy differences of the corresponding transition states presents a new problem. If it is assumed that all of the 2,5-dichloronitrobenzene is present in fuming sulfuric acid as the conjugate acid, then the entropy calculation can be made in a straightforward manner.

\[ \frac{d \left[ \text{ortho-isomer} \right]}{d \left[ \text{para-isomer} \right]} = \frac{k_o (ArNO_2^+)(NO_2)}{k_p (ArNO_2^+)(NO_2)} \]

65. L. P. Hammett, op. cit., p. 126.
Therefore

\[
\begin{align*}
\frac{[\text{ortho-isomer}]}{[\text{para-isomer}]} &= \frac{k_o}{k_p} \\
\Delta S^\ddagger_o - \Delta S^\ddagger_p &= -7.8 \text{ e.u.} \\
\Delta S^\ddagger_o - \Delta S^\ddagger_m &= -7.4 \text{ e.u.}
\end{align*}
\]

If, however, the 2,5-dichloronitrobenzene is present as both the conjugate acid and the hydrogen bonded complex, then the entropy calculation becomes too involved.

\[
\frac{d[\text{ortho-isomer}]}{dt} = k_o(ArNO_2)(NO_2^+) + k_o'(ArNO_2H)(NO_2^+) \\
\frac{d[\text{para-isomer}]}{dt} = k_p(ArNO_2)(NO_2^+) + k_p'(ArNO_2H)(NO_2^+) \\
ArNO_2 + H^+ \rightleftharpoons ArNO_2H \\
K = \frac{(ArNO_2H)}{(ArNO_2)(H^+)}
\]

Therefore

\[
\begin{align*}
\frac{d[\text{ortho-isomer}]}{dt} &= k_o(ArNO_2)(NO_2^+) + k_o'K(ArNO_2)(H^+)(NO_2^+) \\
\frac{d[\text{para-isomer}]}{dt} &= k_p(ArNO_2)(NO_2^+) + k_p'K(ArNO_2)(H^+)(NO_2^+)
\end{align*}
\]
\[
\frac{d \left[ \text{ortho-isomer} \right]}{d \left[ \text{para-isomer} \right]} = \frac{k_0 + k'_0 K(H^+)}{k_p + k'_p K(H^+)}
\]

This above equation cannot be integrated very simply, therefore, the entropy calculation would be an oversimplification for this case.

The nitrations were carried out under a variety of conditions. The variables investigated were temperature, solvent, and salt effects. The data for the nitration of 2,5-dichloronitrobenzene is presented in Table XIII.

In general, the results obtained can be satisfactorily rationalized on the basis of two effects, the polarizability of the nitro group and the effect of the dielectric constant of the medium. As has been shown previously, the nature of the aromatic nitro compound changes with solvent. Thus, in concentrated sulfuric acid, solutions of above 90 percent acid, the compound exists as a tightly bound hydrogen bonded complex. At lower concentrations of sulfuric acid, the nitro compound is still bonded to solvent, but now an appreciable number of molecules are bonded to water, which is a much weaker acid, towards the aromatic nitro compound. At the other extreme, in fuming
Table XIII

Nitration of 2,5 Dichloronitrobenzene

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp.</th>
<th>% Acid</th>
<th>Ortho</th>
<th>Para</th>
<th>Meta</th>
<th>M</th>
<th>O</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>3*</td>
<td>100°</td>
<td>Fuming</td>
<td>14.5</td>
<td>32.5</td>
<td>53.0</td>
<td>3.7</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>10*</td>
<td>100</td>
<td>96.2</td>
<td>21.4</td>
<td>27.7</td>
<td>50.8</td>
<td>2.4</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>11*</td>
<td>100</td>
<td>95</td>
<td>24.5</td>
<td>25.8</td>
<td>49.6</td>
<td>2.0</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>12*</td>
<td>100</td>
<td>89</td>
<td>29.0</td>
<td>24.1</td>
<td>46.8</td>
<td>1.6</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>14*</td>
<td>140</td>
<td>96.2</td>
<td>25.0</td>
<td>27.5</td>
<td>47.5</td>
<td>1.7</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>15*</td>
<td>140</td>
<td>Fuming</td>
<td>11.4</td>
<td>34.8</td>
<td>53.8</td>
<td>4.7</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>Fuming HNO₃</td>
<td>33.1</td>
<td>21.1</td>
<td>45.7</td>
<td>1.4</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>4*</td>
<td>100</td>
<td>96.2 KHSO₄</td>
<td>24.2</td>
<td>27.3</td>
<td>48.4</td>
<td>2.0</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>6*</td>
<td>100</td>
<td>96.2 KClO₄</td>
<td>25.8</td>
<td>26.4</td>
<td>47.8</td>
<td>1.9</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>120</td>
<td>96.2</td>
<td>23.5</td>
<td>28.0</td>
<td>48.5</td>
<td>2.1</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>140</td>
<td>96.2</td>
<td>26.2</td>
<td>29.8</td>
<td>44.0</td>
<td>1.7</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>96.2</td>
<td>35.0</td>
<td>19.3</td>
<td>45.7</td>
<td>1.3</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>Fuming HNO₃</td>
<td>No Reaction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>Fuming HNO₃</td>
<td>No Reaction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* These runs were made under identical ionic strength conditions.
sulfuric acid, the aromatic compound probably exists as the conjugate acid to a large extent. Thus, the polarizability of the nitro group caused by the approach of the nitronium ion, \( \text{NO}_2^+ \), which can be thought of as a point charge, will be decreased if the nitro group is tightly bound to solvent. In the case of fuming sulfuric acid, the conjugate acid actually repels the approaching nitronium ion, thus, the ortho-para ratio decreases since the activation energy for

\[ \text{Ortho Transition State} \quad \text{Para Transition State} \]

ortho substitution increases while that for para substitution increases relatively much less. Thus, the most favorable case for ortho substitution would be the nitration of the unsolvated compound itself since the polarizability of the nitro group would be unhindered. The nitronium ion would be attracted to the
ortho position by the negative charge on the oxygen of the nitro group.

Of course, the main product obtained under all of the conditions investigated was still the meta isomer. This is to be expected due to the contributing resonance forms for the aromatic nitro group. This would be true for all electrometric substituents, E.

The nitronium ion was produced in solution by means of the following equilibria:

\[
\begin{align*}
NaNO_3 + H_2SO_4 & \rightarrow HNO_3 + NaHSO_4 \\
HNO_3 + 2H_2SO_4 & \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-
\end{align*}
\]

The formation of the nitronium ion also resulted in the formation of corresponding molar quantity of water which does change the composition of the nitration medium. To keep the conditions as nearly constant as
possible, the volume of acid and the weight of sodium nitrate was fixed. Thus, the percentages of sulfuric acid reported in the table of results are only relative and should not be considered to truly represent the medium during the whole course of the reaction. This fact will explain the discrepancy between the results for run one and run ten. The weight of sodium nitrate used in run one was approximately 2-1/2 times that employed in run ten, thus the actual water content of the solvent in run one should be considerably lower than that in run ten. The most significant results are those for reactions carried out under the same conditions.

The effect of added electrolytes was studied by the addition of potassium bisulfate and potassium perchlorate to the nitration mixture. Potassium bisulfate was employed since Bennett had postulated a termolecular process for the nitration reaction in which the bisulfate ion was acting as the base involved.

\[
\text{ArH} + \text{NO}_2^+ + \text{HSO}_4^- \rightarrow \text{ArNO}_2^- + \text{H}_2\text{SO}_4
\]

Potassium perchlorate was especially suitable as a general electrolyte since it has a molecular weight which is practically identical with that of potassium bisul-
fate. Both salts gave results which were practically the same, well within the experimental error. The only effect they produced was a small change in isomer ratio undoubtedly due to the changing ionic strength of the medium. This would seem to confirm the viewpoint of Ingold and Melander concerning the mechanism of nitration.

A quantitative correlation between the isomer ratios obtained from the nitration involving fuming nitric acid plus 20 percent concentrated perchloric acid with the results for sulfuric acid solutions cannot be made very readily. The difficulty arises from the fact that dielectric constants for these media are unknown. Of course, qualitatively, it would be expected that nitric acid would be a poorer hydrogen bonding solvent than sulfuric acid on the basis of the increased electronegativity of nitrogen over sulfur. Thus, the observed results are in the direction expected. The concentrated perchloric acid necessary to produce the nitronium ion complicates the picture slightly. The ortho-para ratio would probably be somewhat higher in nitric acid itself but the overall nitration rate was found to be inconveniently slow.

The ortho-para ratio decreased as the concentration
of sulfuric acid increases. Above acid concentrations of 90 percent, the nature of the aromatic compound is probably constant. This was found to be true for nitrobenzene as previously cited. Also, above this acid range, the nitronium ion concentration remains constant. Thus, the polarizability of the nitro group is effectively constant throughout this range. However, the dielectric constant of the medium is increasing, thus resulting in a relative decrease in activation energy of the transition state for para substitution. This is true if the attack of the nitronium ion is looked upon as a function of the electrostatic energy between the dipole field of the substituent and the nitronium ion. Thus, the activities of the corresponding transition states would be affected by the change in the dielectric constant of the medium. Again this problem can be treated on the basis of the reaction of a neutral molecule with an ion, the important factor in this case being the charge separation within the different transition states. Thus, increasing the dielectric constant, $D$ will cause the ratio $\frac{a^+}{a^+P}$ to decrease.

This is to be expected since the charge separation in the transition state is much greater for para substi-
tion than it is for ortho. Thus, in all these cases, two factors are operating concurrently: the effect of dielectric constant upon the activation energies of the transition states involved, and the effect of the solvent upon the polarizability of the dipole of the nitro group.

The temperature effect exhibited by the ortho-para ratios was in the expected direction, the ortho-para ratio increasing with temperature. The ratio of the relative amounts of the two isomers will be independent of time and a function only of the relative specific reaction rates. If the assumption is made that the entropy differences for the two transition states will be negligible, then

$$\frac{RT \ln k_o}{k_p} = \text{constant}$$

Thus, the proportion of the minor product must increase with increase in temperature.

In Table XIV the results obtained in the nitration of 2,5-dibromonitrobenzene are presented. As can be seen from the data, the same general trend is followed as that presented previously for dichloronitrobenzene. However, the steric hindrance of the ortho isomer is
### Table XIV

Nitration of 2,5 Dibromonitrobenzene

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp.</th>
<th>% Acid</th>
<th>% Isomers</th>
<th>M</th>
<th>O</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ortho Para Meta</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-12#</td>
<td>100°</td>
<td>Fuming</td>
<td>2.9 43.1 53.9</td>
<td>18</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>A-3#</td>
<td>100</td>
<td>Fuming</td>
<td>2.6 41.8 55.3</td>
<td>21</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>A-11#</td>
<td>100</td>
<td>96.8</td>
<td>13.7 36.3 50.0</td>
<td>3.6</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>A-1</td>
<td>100</td>
<td>96.8</td>
<td>12.4 38.2 49.4</td>
<td>4.0</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>A-2#</td>
<td>100</td>
<td>90</td>
<td>29.2 20.8 50.0</td>
<td>1.7</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>A-4</td>
<td>100</td>
<td>Fuming HNO₃ 20% HClO₄</td>
<td>29.9 21.3 48.8</td>
<td>1.6</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>A-14#</td>
<td>120</td>
<td>96.8</td>
<td>19.6 29.4 51.0</td>
<td>2.6</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>A-7#</td>
<td>100</td>
<td>96.8</td>
<td>19.2 37.5 43.2</td>
<td>2.3</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>A-6#</td>
<td>100</td>
<td>96.8</td>
<td>Trinitro compound (?)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-8#</td>
<td>140</td>
<td>96.8</td>
<td>Trinitro compound (?)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-9#</td>
<td>120</td>
<td>96.8</td>
<td>Trinitro compound (?)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-10#</td>
<td>120</td>
<td>90</td>
<td>Trinitro compound (?)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*These runs were made under identical ionic strength conditions.*
considerably greater for the dibromo compound than for the dichloro compound. Thus, the actual amount of ortho isomer formed is considerably less with the result that the ortho-para ratios obtained are much smaller. This is especially true of the nitrations carried out in fuming sulfuric acid where the species being nitrated is probably the conjugate acid.

The rate of nitration for 2,5-dibromonitrobenzene is considerably slower than that for the corresponding dichloro compound. Consequently, activation energy required for the nitration of the dibromo compound probably is greater. In the higher temperature runs on the dibromo compound, a large amount of an unexpected product was formed. This compound was probably the trinitro derivative of 1,4-dibromobenzene. Therefore, the difference between the activation energy required for mononitration of 2,5-dibromonitrobenzene and the dinitration of this compound is considerably smaller than for the dichloronitrobenzene. The activation energy for the dinitration of 2,5-dichloronitrobenzene must be relatively higher than that of the dibromo compound since, under comparable conditions, dinitration of the dichloro compound does not occur. The same product, trinitro derivative, was obtained
from the addition of the pure 2,5-dinitro-1,4-dibromo-
benzene to the nitrating solution at 140°. It was
identified by means of its characteristic infra-red
spectra. It was possible to determine the isomer ra-
tio at 120° by stopping the reaction before all of
the starting material had reacted. In this case, a
mixture of starting materials, the normal products,
and the trinitro derivative was obtained. This would
seem to indicate that the activation energy differen-
ces were relatively small. At 100° only the normal
products were isolated.

Generalizing from this work, it could be expec-
ted that all deactivating electromeric substituents,
E, would have ortho-para ratios greater than unity if
the polarizability of the substituent was not too greatly affected by the solvent. The ortho-para ratio could
be thus correlated with the polarizability of the sub-
stituent giving results in agreement with the calcula-
tions of Dewar. For systems such as 2,5-dichloronitro-
benzene, Dewar would predict on the basis of his cal-
culations that the ortho isomer would be the major pro-
duct. The reason for this being that with a -E sub-
stituent, chlorine, next to an E substituent, nitro
group, the bond order between these two carbon atoms
would be decreased thus, in effect, increasing the bond order between the adjacent carbon atoms. The remaining \(-E\) substituent will then orient the attacking nitronium ion into the adjacent position having

\[
\begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array}
\begin{array}{c}
\text{NO}_2 \\
+ \text{NO}_2^+
\end{array}
\rightarrow
\begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array}
\begin{array}{c}
\text{NO}_2 \\
\text{NO}_2
\end{array}
\]

the changed bond order. These calculations are consistent with the experimental results in that they predict the correct trend. However, the ratios are affected to such a large degree by the medium that it would be too much to expect of simplified calculations that they give all the answers.

A general conclusion regarding electrophilic substitution that can be made on the basis of this study is that all of the deactivating electromeric substituents can be considered to be ortho directors in a limited sense. This is due to the fact that all substituents of this type can be polarized by the positive ion in such a fashion as to attract the positive ion to
the ortho position. Thus, in general, all E substitu-
ents such as -NO₂, -COOH, -CN, -COOR will be meta-ortho
directors.
SUMMARY

The ultraviolet spectra of a number of different nitrohalobenzenes in solvents of widely different polarity have been reported. The spectra has been interpreted on the basis of the interaction of the compounds with the solvents and also on the basis of steric effects.

The ultraviolet spectrum of nitrobenzene in various compositions of sulfuric acid - water solutions has been reported. Nitrobenzene is considered to be completely hydrogen bonded to sulfuric acid above concentrations of 90 percent sulfuric acid. The fall in nitration rate above 90 percent sulfuric acid is rationalized on the basis of the changing dielectric constant of the medium.

The isomer ratios obtained during the nitration of 2,5-dichloronitrobenzene and 2,5-dibromonitrobenzene have been reported on the basis of an infra-red analysis of the reaction mixtures. The results are correlated on the basis of two effects operating concurrently: the effect of the solvent upon the polarizability of the nitro group and the effect of the dielectric constant of the medium upon the activation energies of the possible transition states corresponding to the available positions for nitration.
The general conclusion is drawn that all deactivating electromeric substituents such as -NO₂, -COOH, -CN, are in a limited sense, ortho directors.