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REACTIONS OF BENZENEDIAZONIUM ION WITH
SODIUM BROMIDE AND SODIUM IODIDE

by

Bruce M. McKay

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Thesis Director's signature:

Houston, Texas
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To L.L.M., I.L.Y.A.T.P.
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INTRODUCTION

The solution chemistry of diazonium ions has been under investigation for over one hundred years. Reactions in polar and non-polar solvents with both radical and ionic mechanisms are known (1). The summary below will be limited, in general, to reactions in polar solvents, particularly water.

Aromatic diazonium salts can be prepared and isolated as stable solids, in contrast to the aliphatic analogs (2). Many of the aromatic diazonium salts have appreciable lifetimes in solution, the exact reaction time being very temperature dependent. In polar solvents the salts behave as strong electrolytes, the diazonium cation reacting independently of the nature of the counter ion (2). Of the several reactions of the diazonium ion one of the most perplexing from a mechanistic point of view has been the replacement of the diazonio nitrogen by nucleophiles, reacting either as ions (X⁻) or as solvent molecules (SH). The formulation of this reaction mechanism has

\[ \text{ArN}_2^+ + X^- \xrightarrow{\text{SH}} \text{ArX} + \text{ArS} + H^+ + N_2 \]  \hspace{1cm} (1)

progressed through two, broad, stages which will now be reviewed.

Thermally induced diazonium ion decompositions have long been known to yield phenols, when the reaction is carried out in aqueous solutions at a pH of less than seven. Kinetic studies showed the reaction to be first-order, with only minor deviations being observed. The results presented below were fitted into a mechanistic scheme by
Waters (3). The solvolysis was believed to be a two-step process involving an aryl cation intermediate.

\[
\text{ArN}_2^+ \xrightarrow{\text{slow}} \text{Ar}^+ + \text{N}_2 \tag{2}
\]

\[
\text{Ar}^+ + \text{X}^- \xrightarrow{\text{fast}} \text{ArX} \tag{3}
\]

\[
\text{Ar}^+ + \text{SH} \xrightarrow{\text{fast}} \text{ArS} + \text{H}^+ \tag{4}
\]

Euler, in 1902, reported the rate of hydrolysis of benzenediazonium chloride to be nearly independent of both acid concentration and the nature of the acid anion (4). These results have been confirmed by DeTar and Ballantine (5). They found no significant deviations from first-order kinetics for diazonium ion hydrolyses in solutions containing chloride, bisulfate or fluoborate anions.

Hydrolysis rates were found to be variable under certain conditions. Pray observed rate retardations in aqueous solutions with high salt concentrations (6). The reaction kinetics, however, were still of the first-order in these solutions.

Pray, among others, examined the diazonium ion decomposition in different solvent systems. In each of a wide variety of organic acids and alcohols first-order kinetics were observed. The overall rate of decomposition was nearly the same in each of the solvents studied (7).

The character of the decomposition intermediate has been investigated by several methods. Pray's studies suggested that the intermediate could react with each of the components of a mixed solvent system, if they are not completely dissimilar. Godfrey has in fact found that the anisole-
phenol ratio is nearly unity from reaction of benzenediazonium ion in equimolar methanol-water (8).

These, and many other, results are consistent with the high activation energy of the hydrolysis reaction. A value of 27 kcal/mole for the activation energy was found by Moelwyn-Hughes and Johnson (9). They observed only first-order kinetics over the temperature range 15-60°. This activation energy, for reaction of benzenediazonium ion, is several times that estimated for decomposition of ethyldiazenium ion (5-10 kcal/mole) (10).

The low selectivity of the intermediate, the aryl cation, has received additional support from product studies. Nesmayonov decomposed diazonium salts, as suspensions, in halobenzene solvents. One of the isolated products was the corresponding diarylhalonium salt, \( \text{Ar}_2X^+\text{BF}_4^- \). In diarylethers diazonium salt decompositions gave oxonium salts, \( \text{Ar}_3\text{O}^+\text{BF}_4^- \) (11). Sandin and Hey were able to prepare cyclic halonium salts by decomposition of diazonium salts (12). The cationic

\[
\begin{align*}
\text{I}^+ & \quad \text{N}_2^+ \quad \text{O} \quad \text{O} \\
& \quad \Delta \\
& \quad \text{KI} \\
\end{align*}
\]

\[ (5) \]

intermediate postulated above was never observed directly.
Other product studies have been directed toward investigations of the properties of the postulated aryl cation. Specifically, the reactions of diazonium ions with fairly strong nucleophiles have been examined. The low selectivity of the intermediate was found to be operative, although this is not necessarily predicted by kinetic studies. The work of Godfrey with mixed solvent systems, which has been cited above, is one example of such a study.

The chlorobenzene-phenol ratios from hydrolysis of benzenediazonium ion in sodium chloride and hydrochloric acid solutions have been investigated by Lewis (13). These experiments enabled competition factors (rate ratios), $k_{Cl}/k_{W}$, to be obtained. Lewis found that in the solutions he studied the competition factors fell in the range 2.0-3.5. The low values confirm the expected low selectivity of the reaction intermediate; especially when compared to reactions of aliphatic cations, which involve factors of several hundred to several thousand (14).

Pfeil studied the hydrolysis of p-nitrobenzenediazonium ion in solutions containing chloride ion (15). He suggested that the product ratios, $(p$-nitrochlorobenzene)/(p-nitrophenol), were proportional to the molar chloride ion-water ratios.

The results of the above experiments are consistent with the first-order, two-step mechanism. Other mechanisms of higher order were not excluded, although they were felt to be unimportant. Further work, however, led to a reevaluation of the mechanistic details of the reaction.
The existence of aryl cations in solution was questioned, perhaps fortuitously, by Field and Franklin (16). Their results from gas phase electron impact experiments suggested rearrangements of aryl cations, in the gas phase, to be an important reaction; rearrangements are not observed, however, in diazonium ion solution reactions.

Reexamination of the reaction was made more compelling due to solution chemistry results appearing at this time. Cooper observed significant rate increases, compared to the rate in water, for the hydrolysis of benzenediazonium ion in solutions containing thiocyanate ion (17). Reaction in five molar thiocyanate solution occurred twenty percent faster than in water alone. It might be noted that products with either nitrogen or sulfur attached to the aromatic ring are obtained. However, the sulfur end of the anion reacts faster, \( k_S/k_N = 1.4 \), than does the nitrogen end. The mechanism postulated to account for the rate increases and first-order kinetics is shown below. A rapidly reversible step was included, which involved some diazonium ion intermediate. The structure of the intermediate could not be deduced from the data.

\[
\begin{align*}
\text{ArN}_2^+ & \overset{\leftrightarrow}{\longrightarrow} [\text{ArN}_2^+]^* \\
[\text{ArN}_2^+]^* + H_2O & \longrightarrow \text{ArOH} + H^+ + N_2 \\
[\text{ArN}_2^+]^* + X^- & \longrightarrow \text{ArX} + N_2
\end{align*}
\] (6) (7) (8)

Lewis and Hinds observed a factor of two rate increase when \( p \)-nitrobenzenediazonium ion was hydrolyzed in eight molar sodium bromide (18). The apparent first-order rate constants were consistent
with unimolecular loss of nitrogen accompanied by bimolecular reaction involving bromide ion. The rate law for reaction of this type is:

$$\frac{d(N_2)}{dt} = k(ArN_2^+) + k'(ArN_2^+)(Br^-)$$

Eq. 1

Complete second-order reaction was observed by Lewis and Johnson for displacement of one of the diazonio groups of $p$-benzenetetrazonium ion, by chloride, bromide or thiocyanate ion (19).

The results of experiments in this, historical, category suggested the possibility that all diazonium hydrolysis reactions could be bimolecular, at least in part. An alternative explanation was that only diazonium ions having powerful electron withdrawing groups appropriately substituted were capable of bimolecular reaction. The initial resolution of this question has recently been completed and will be reviewed now.

One of the simplest tests, in principle, of bimolecularity is that the reacting nucleophile is present in both the rate and product determining steps of the reaction. This test has been applied to the hydrolysis of benzenediazonium ion in solutions containing chloride ion. A question to be raised is why a reinvestigation of the kinetics and products of this reaction would be expected to lead to new conclusions. One, not necessarily trivial, answer is knowing what to look for. Secondly, the ability to obtain very precise kinetics, as well as product data, allows the application of fairly sensitive quantitative tests to the results.
The work of Hartung was directed toward a compilation of both kinetic and product data for the reaction of benzenediazonium ion in aqueous chloride salt solutions (20). The equations presented below would then be applied to the data as a test for bimolecular reaction.

The basic idea involved was to predict the apparent rates using product yields (chlorobenzene/phenol). The necessary equations were derived by assuming initially that the mechanism was second-order, both for phenol and for chlorobenzene formation. Assuming bimolecular reaction to form phenol the rates in water and salt solutions are related by the rate ratios given as eq 2:

\[
\frac{k}{k_0} = \frac{k_{W}(H_2O)}{k_{W}(H_2O)_0} \frac{\text{eff}}{k_{Cl}^{'}} + \frac{k_{Cl}^{'}}{k_{Cl}^{'}} \frac{(Cl^-)}{k_{Cl}^{'}} \frac{(Cl^-)}{k_{Cl}^{'}} \frac{k_{Cl}'}{k_{Cl}'}
\]

All \(k\)'s are rate constants; \(k\) is the apparent, first-order rate constant for disappearance of diazonium ion, in salt solutions; \(k_0\) is the apparent, first-order rate constant in pure water; \(k_{Cl}^{'\text{Cl}}\) is the rate constant for bimolecular reaction of chloride and diazonium ions and \(k_{W}\) is the rate constant for reaction of diazonium ion and water. The rate constant \(k_{Cl}^{'\text{Cl}}\) represents the rate of reaction of diazonium ion with water in the primary solvation shell of chloride ion, to form phenol. Water of solvation, of the anion, was expected to be slightly more nucleophilic toward diazonium ion than the bulk of the solvent. This term was expected to be small and is immeasurable; it will be neglected in further derivations.
Rates and product yields of chloride ion reactions are related by eq 3:

\[
\frac{k_{\text{Cl}}}{k_W} = \frac{Y_{\text{ArCl (H}_2\text{O)}}}{Y_{\text{ArOH (Cl}^-)}},
\]

Eq. 3

Rearrangement, and substitution into eq 1 produces the relationship between rate ratios and yield ratios:

\[
k/k_0 = \frac{(\text{H}_2\text{O})_{\text{eff}}}{(\text{H}_2\text{O})_0} + \frac{Y_{\text{ArCl (H}_2\text{O)}}}{Y_{\text{ArOH (H}_2\text{O})}}
\]

Eq. 4

The water concentrations used in these equations take into account solvation of the salt cation. The concentration \((\text{H}_2\text{O})_0\) is just the concentration without salts present. The second concentration, \((\text{H}_2\text{O})_{\text{eff}}\), is a reduced water concentration introduced to account for rate depressions in inert salt solutions. It is assumed that water solvating the salt cation is unavailable for nucleophilic reaction; therefore, the overall water concentration is effectively lowered by addition of salts.

Each of the quantities in eq 4 is measurable. Water concentration ratios were determined by comparison of the hydrolysis rate in pure water with the rates in solutions containing inert electrolytes, which had the same cations as the chloride salts. The quantitative data used in eq 4 were obtained using sodium bisulfate and sodium chloride (other salt studies are reviewed in the Discussion section of the present work).
Addition of water concentration ratio values to the yield ratios, also corrected for salt effects, results in a set of calculated rate ratios. If the bimolecular hypothesis were correct the calculated and measured rate ratios ought to agree. The results were, in fact, in very good agreement (see fig 1 below).

Hartung could then conclude that chloride ion was present in both the rate and product determining steps of the reaction. A distinction could not be made between the existence of a bimolecular transition state only, or the presence also of a discrete intermediate (Meisenheimer type complex).

A general conclusion for aqueous diazonium ion reactions was that an aryl cation is so unstable that bonding to some extent with a nucleophile is necessary before the diazonio nitrogen completely departs. Bonding to the nucleophile in the case of benzenediazonium ion is apparently weak and the carbon-nitrogen bond greatly stretched in the transition state. Ions such as the p-tetrazonio, however, may well have a high degree of bond formation between carbon and the nucleophile before nitrogen is lost. Between these two extremes may exist, Hartung suggested, a broad spectrum of bond development between carbon and the displacing nucleophile.

The structure given below is meant only to be a visual aid for understanding the transition state; no stereochemistry is meant to be implied.
Figure 1. Calculated and Measured Relative First-order Hydrolysis Rates for the Benzenediazonium Ion in Sodium Chloride Solution.
The conclusion from Hartung's work was that the aromatic $S_{N1}$ mechanism in solution must be very rare, since diazonium ion solvolyses were, previously, the only well established examples (1,21).

The purpose of the present study was twofold: first, to demonstrate bimolecularity in the hydrolysis of benzenediazonium ion when bromide ion is the added nucleophile; second, a basis of comparison was desired with which the reactions in iodide ion solutions would be compared. It was expected that benzenediazonium-iodide ion reactions would be more complex than reactions involving chloride and bromide ions.

Examples of such reactions have appeared in the literature; the first example due, as in many other cases, to Hantzsch(22,23). In 1895 Hantzsch reported the reaction of 2,4-diodobenzenediazonium chloride with aqueous potassium iodide produced an adduct which he characterized as the "diazio-iodide" (22). A similar product was also found when mesitylenediazonium chloride and potassium iodide reacted (23). Treatment of the adduct from this reaction with iodine was said to result in the formation of the corresponding diazonium triiodide salt.

Interest in diazonium-iodide ion reactions was then centered in the area of synthetic organic chemistry for many years. It has been known for many years that the preparation of aromatic iodides is readily accomplished by reaction in aqueous solution of the corresponding diazonium ion and potassium iodide (24).
This reaction accomplishes the same type transformation as does the well known Sandmeyer reaction. There is, however, an important difference between the two reactions. The Sandmeyer procedure utilizes copper salt catalysts for introduction of bromide or chloride, whereas the iodide procedure requires no catalyst.

The diazonium-iodide ion reaction is known to yield iodine as a product in at least some cases (25,26,27). In many cases the iodine does not, apparently, appear by air oxidation of iodide ion.

The reaction observed by Hantzsch (see above) was extended in the work of Carey, Millar and Jones (26,27). They isolated fifteen-twenty percent yields of diazonium triiodide salts by addition of potassium iodide to cold, concentrated, aqueous diazonium ion solutions. The yields of salts were raised to sixty percent if a solution of triiodide ion was added in place of the iodide ion solution. High yields (~70%) of the corresponding aryl iodides could be obtained by warming the reaction mixtures (from either procedure).

The triiodide salts were readily decomposed either by heating the salt as an aqueous suspension or as the solid. Several of the salts, for example the benzenediazonium triiodide, decomposed explosively when completely dry.

The reaction products were examined in hopes of finding a reduced diazonium ion species, in order to account for the formation of iodine. It was reported that no products of this nature, for example biaryls and hydrazines, could be found.
At least one "diazo-iodide" was prepared by these workers. Using very concentrated solutions they were able to isolate a mono-iodo adduct from reaction of iodide ion and o-toluenediazonium ion. The product was assumed to have retained the diazonio nitrogen since it couples, in basic solution, with β-naphthol to give the expected azo dye.

Warming the adduct in water produced a high yield, based on isolated products, of o-cresol. It was reported that hydrogen iodide was evolved during the heating period.

It was also reported that aniline, presumably after diazotization, yielded a mono-iodo adduct. No data are given about the reactions of this adduct.

Kinetic studies have been made in the reaction of p-nitrobenzene-diazonium ion with iodide ion in aqueous solutions, by Hinds (28). The rate of reaction, followed by nitrogen evolution, was much more rapid in iodide ion solutions than in water alone. The initial rate of reaction increased as the iodide ion concentration was raised. In several instances, however, the overall rate of reaction was less than the starting rate.

Hinds also observed rate changes as the solution pH was varied. The rate changes were not a simple function of hydrogen ion concentration. It was also reported that addition of iodine caused rate changes. The interpretation was not clear, since the rate variations were not a linear function of the added iodine concentrations. Hinds did note, though, that iodine, when it did affect the rate, caused a
decrease in the rate of reaction. The data obtained were best fitted by a reaction first-order in both diazonium ion and iodide ion.

The reaction products were examined for the presence of p-nitrophenylhydrazine, a possible reduction product. Although the compound was reported to be stable under the reaction conditions it could not be found. One route leading to the hydrazine is given below.

$$\text{ArN}_2^+ + 3\text{H}^+ + 6\text{I}^- \rightarrow \text{ArNH}_2^+ + 2\text{I}_3^-$$  (9)

Products possibly due to free radical reactions have been reported in one, special, case. The reaction of p-n-decyl oxybenzenediazonium ion with iodide ion in benzene-acetone solutions yielded iodine, p-n-decyl oxybiphenyl, biphenyl and p-n-decyl oxyiodobenzene (the major product) (29). Analogy to reactions in aqueous solutions is not necessarily convincing.

A free radical mechanism was suggested by Lewis and Johnson to account for the kinetics and products of the reaction between iodide ion and p-benzenetetrazonium ion (30).

$$\text{ArN}_2^+ + \text{I}^- \rightarrow \text{Ar}^+ + \text{N}_2 + \text{I}^-$$  (10)

$$2\text{I}^- \rightarrow \text{I}_2$$  (11)

$$\text{Ar}^+ + \text{O}_2 \rightarrow \text{ArO}_2.$$  (12)

$$2\text{ArO}_2^- \rightarrow 2\text{ArO}^- + \text{O}_2$$  (13)

$$\text{ArO}^- + \text{H}^+ + \text{I}^- \rightarrow \text{ArOH}^- + \text{I}^-$$  (14)
When oxygen was excluded from the reaction the mechanism appeared to be that of the normal bimolecular substitution, with p-iodobenzene-diazonium ion as an intermediate. Neither was iodine observed in oxygen free solutions, although the very low reactant concentrations may have been responsible for this (31). One explanation of these data is that free radical reaction, to form phenol, was limited by the oxygen concentration (30).

Arguments for and against ionic and radical mechanisms appeared, twenty years ago, in papers authored, separately, by Waters and Hodgson.

Waters favored a radical mechanism, arguing by analogy to the Sandmeyer reaction (32). Waters suggested that the oxidation potentials of copper (I) and iodide ion were close enough that iodide ion might be able to function as an electron transfer agent almost as easily as copper (I). Waters' formulation of the initial stage of the reaction is given below.

\[
\begin{align*}
\text{Ar} & \quad \text{---} \quad \text{N}_2^+ \\
& \quad \downarrow \quad (\text{I})^- \\
& \quad (\text{I})^-
\end{align*}
\]

(14)

The broken arrows were used to represent one-electron transfers. The process is pictured as concerted; Waters, however, evidently did not exclude other reaction pathways, since he discusses possible reactions of free radicals in the reaction solutions.

A directly opposite view of the mechanism was taken by Hodgson (33). He would admit only ionic reactions into his mechanistic formulation.
He further suggested that triiodide ion was the only effective species for nitrogen displacement. Hodgson's visualization of the reaction is given below.

\[
\begin{align*}
&\text{C}^+ \xrightarrow{\text{N}_2} \text{ArI} + \text{I}_2 + \text{N}_2
\end{align*}
\]

(15)

Hodgson rejected a free radical mechanism on the grounds that expected products, such as biaryls, are not observed. He argued that triiodide ion was the effective displacing species from the results of one of his own experiments. Hodgson observed that a reaction formally equivalent to the Sandmeyer reaction could be carried out using substituted nitrosophenols. The reaction required the use of a copper salt catalyst and hydroxylamine hydrochloride (34).

The reaction was used to rapidly replace the nitroso group with bromide or chloride ion. If the copper salt were excluded from the iodide ion system the reaction was very slow and gave low yields of the desired iodo compound. This, Hodgson argued, was contrary to the results expected on the basis of Waters' mechanism. Furthermore, triiodide is implicated in the mechanism, according to Hodgson, since hydroxylamine destroys the iodine as it is produced; thus, no triiodide is formed and the reaction is necessarily slow.

A rather brief outline of the arguments of Hodgson and Waters has been given, and critical discussion has been excluded here. The relative merits of ionic and radical mechanisms are to be found in the Discussion section of this study.
It is felt that the only sound conclusion to be made on the basis of the available data is that diazonium-iodide ion reactions are not simple. It was hoped that the study of this reaction would clarify at least some of the mechanistic details.
RESULTS

Apparent first-order rate constants for disappearance of benzene-diazonium ion have been measured in solutions containing the following (reaction temperature in parentheses): sodium bromide (40.1°), sodium iodide (40.1°, 32.9°), sodium iodide-iodine (40.1°), iodine (32.8°).

The following series lists products whose yields were determined, for the stated conditions: bromobenzene (sodium bromide, 40.1°), iodo-benzene (sodium iodide, 40.1°, 32.8°), phenol (sodium iodide, 40.1°, 32.8°), phenol (iodine, 32.8°), iodine (sodium iodide, 40.1°, 32.8°).

Competition factors have been calculated using eq 5. Yields of phenol from diazonium ion hydrolyses in bromide ion solutions were assumed to be one hundred minus percent bromobenzene; an approximation known to be valid (35). Measured phenol yields were used for calculations using iodide ion reaction data, since other products are formed in this system.

\[
\frac{k_X}{k_W} = \frac{Y_{ArX (H_2O)}}{Y_{ArOH (X^-)}}
\]

Eq. 5

Water concentration corrections for sodium bromide were assumed to be the same as for sodium chloride. No correction was applied for sodium iodide solutions.

All data were obtained for an initial benzenediazonium ion concentration of 5 x 10^{-3} M, and for deoxygenated solutions, unless otherwise noted.
TABLE I

First-order Rate Constants for Hydrolysis of Benzenediazonium Ion in Sodium Bromide Solutions

\( T = 40.14 \pm 0.02^\circ, \ H_2\text{SO}_4 = 0.01 \ M \)

<table>
<thead>
<tr>
<th>[NaBr] m/l</th>
<th>( k \text{ sec}^{-1} \times 10^5 )</th>
<th>( k/k_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>41.50</td>
<td>1.000</td>
</tr>
<tr>
<td>0.10</td>
<td>41.33</td>
<td>0.996</td>
</tr>
<tr>
<td>0.20</td>
<td>41.58</td>
<td>1.002</td>
</tr>
<tr>
<td>0.20</td>
<td>41.62</td>
<td>1.003</td>
</tr>
<tr>
<td>0.30</td>
<td>41.87</td>
<td>1.009</td>
</tr>
<tr>
<td>0.40</td>
<td>41.67</td>
<td>1.004</td>
</tr>
<tr>
<td>0.60</td>
<td>41.33</td>
<td>0.996</td>
</tr>
<tr>
<td>0.60</td>
<td>41.50</td>
<td>1.000</td>
</tr>
<tr>
<td>1.00</td>
<td>40.92</td>
<td>0.986</td>
</tr>
</tbody>
</table>
Figure 2. Relative First-order Hydrolysis Rates for the Benzenediazonium Ion in Sodium Bromide Solutions.
TABLE II

Bromobenzene Yields and Competition Factors for Benzenediazonium
Ion Hydrolysis in Sodium Bromide Solutions

\( (T = 40.14 \pm 0.02^\circ, \text{H}_2\text{SO}_4 = 0.01 \text{ M}) \)

<table>
<thead>
<tr>
<th>[NaBr] m/l</th>
<th>Bromobenzene Yield, %</th>
<th>Competition Factor, (k_{Br}/k_W) (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>3.12</td>
<td>17.91</td>
</tr>
<tr>
<td>0.20</td>
<td>5.19</td>
<td>15.22</td>
</tr>
<tr>
<td>0.40</td>
<td>5.11</td>
<td>7.48</td>
</tr>
<tr>
<td>0.60</td>
<td>6.00</td>
<td>5.92</td>
</tr>
<tr>
<td>1.00</td>
<td>8.61</td>
<td>5.24</td>
</tr>
</tbody>
</table>

(a) Calculated from eq 5.
Figure 3. Bromobenzene Yields for Decomposition of Benzenediazonium Ion in Sodium Bromide Solutions.
### TABLE III
First-order Rate Constants for Hydrolysis of Benzenediazonium Ion in Aqueous Sodium Iodide

\( (H_2SO_4 = 0.01 \text{ M}) \)

<table>
<thead>
<tr>
<th>[NaI] m/1</th>
<th>( k \text{ sec}^{-1} \times 10^5 ) (^{(a)})</th>
<th>( k/k_0 )</th>
<th>T°C (^{(d)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>41.50</td>
<td>1.000</td>
<td>40.14</td>
</tr>
<tr>
<td>0.01</td>
<td>44.67</td>
<td>1.076</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.05</td>
<td>45.17</td>
<td>1.088</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.075</td>
<td>45.00</td>
<td>1.084</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.10</td>
<td>46.00</td>
<td>1.108</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.15</td>
<td>48.00</td>
<td>1.157</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.20</td>
<td>50.83</td>
<td>1.225</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.25</td>
<td>52.83</td>
<td>1.273</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.30</td>
<td>57.33</td>
<td>1.382</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.35</td>
<td>56.50 (^{(b)})</td>
<td>1.361</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.40</td>
<td>58.83</td>
<td>1.418</td>
<td>&quot;</td>
</tr>
<tr>
<td>0</td>
<td>15.20</td>
<td>1.000</td>
<td>32.93</td>
</tr>
<tr>
<td>0.01</td>
<td>18-20 (^{(c)})</td>
<td>1.2-1.3</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.05</td>
<td>16.62</td>
<td>1.093</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.10</td>
<td>19.42</td>
<td>1.277</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.20</td>
<td>24.42</td>
<td>1.606</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.30</td>
<td>29.17</td>
<td>1.919</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.40</td>
<td>33.33</td>
<td>2.193</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Data from reactions in deoxygenated solutions.

\(^{(b)}\) Based on one run.

\(^{(c)}\) This value was reproduced with very low precision; plots of \([ArN_2^+]\) versus time were not linear.

\(^{(d)}\) There was no significant temperature differential between the water bath and the solution in the reactor vessel when sampling was begun.
Figure 4. First-order Decomposition Rates for the Benzenediazonium Ion in Aqueous Sodium Iodide.
Figure 5. First-order Decomposition Rates for the Benzenediazonium Ion in Aqueous Sodium Iodide.
### TABLE IV

Yields of Iodobenzene for Benzenediazonium Decomposition in Aqueous Sodium Iodide

\((H_2SO_4 = 0.01 \, M)\)

<table>
<thead>
<tr>
<th>[NaI] m/l</th>
<th>Iodobenzene Yield, %</th>
<th>Competition Factor (k_I/k_W) (a)</th>
<th>T°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.85</td>
<td>49.5</td>
<td>40.14</td>
</tr>
<tr>
<td>0.05</td>
<td>2.61</td>
<td>32.6</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.10</td>
<td>3.77</td>
<td>26.2</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.20</td>
<td>6.84</td>
<td>27.1</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.30</td>
<td>10.25</td>
<td>33.9</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.40</td>
<td>12.40</td>
<td>36.3</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.20</td>
<td>8.90</td>
<td>39.9</td>
<td>32.93</td>
</tr>
<tr>
<td>0.30</td>
<td>14.30</td>
<td>47.2</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.40</td>
<td>16.40</td>
<td>58.3</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.10</td>
<td>18.6(^{(b)})</td>
<td>----</td>
<td>40.14</td>
</tr>
<tr>
<td>0.20</td>
<td>23.5(^{(b)})</td>
<td>----</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.40</td>
<td>27.3(^{(b)})</td>
<td>----</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

\(a\) Calculated from eq 5, using measured phenol yields.

\(b\) From reaction in air-saturated solution.
Figure 6. Iodobenzene Yields for Decomposition of Benzenediazonium Ion in Aqueous Sodium Iodide.
TABLE V

Yields of Phenol for Decomposition of Benzenediazonium Ion in Aqueous Sodium Iodide

\( (\text{H}_2\text{SO}_4 = 0.01 \text{ M}) \)

<table>
<thead>
<tr>
<th>[NaI] m/l</th>
<th>Phenol Yield, (%^{(c)})</th>
<th>T°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>89.8</td>
<td>40.14</td>
</tr>
<tr>
<td>0.20</td>
<td>69.7(^{(e)})</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.30</td>
<td>57.2</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.40</td>
<td>57.0</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.40</td>
<td>47.6</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.01</td>
<td>68.6</td>
<td>32.80</td>
</tr>
<tr>
<td>0.20</td>
<td>63.0</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.30</td>
<td>50.0</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.40</td>
<td>44.3</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.0</td>
<td>106(^{(a)})(d)</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.0</td>
<td>99(^{(b)})</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

(a) Iodine added \((1.3 \times 10^{-3} \text{ M})\).
(b) Iodine added \((7 \times 10^{-4} \text{ M})\).
(c) Calculated from \(\lambda_{\text{max}} = 287 \text{ m}_{\text{u}}\) and \(\varepsilon_{\text{max}} = 2600 \text{ l/mole-cm}\), for phenol in basic solution, except for (d).
(d) Calculated from \(\lambda_{\text{max}} = 270 \text{ m}_{\text{u}}\) and \(\varepsilon_{\text{max}} = 1450 \text{ l/mole-cm}\).
(e) This value is not changed if the absorbance is measured after extraction of the basic solution with methylene chloride.
TABLE VI

Yields of Iodine for Decomposition of Benzenediazonium Ion in Aqueous Sodium Iodide

\( (H_2SO_4 = 0.01 \text{ M}) \)

<table>
<thead>
<tr>
<th>[NaI] m/1</th>
<th>Iodine Yield, %(^{(a)})</th>
<th>T°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.7</td>
<td>40.14</td>
</tr>
<tr>
<td>0.20</td>
<td>5.1</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.30</td>
<td>9.2</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.40</td>
<td>6.7</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.01</td>
<td>1.2</td>
<td>32.80</td>
</tr>
<tr>
<td>0.20</td>
<td>9.7</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.30</td>
<td>7.8</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.40</td>
<td>18.9</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

(a) Measured as triiodide ion, \( \lambda_{max} = 350 \text{ m} \mu \), \( \epsilon_{max} = 2.64 \times 10^4 \) l/mole-cm. These data are for \([\text{ArN}_2^+]_o = 5 \times 10^{-3} \) M, and assume one mole of diazonium ion gives one mole of molecular iodine.
Other rate and product data have been obtained for reactions of benzenediazonium ion, but for various reasons they are not entirely reliable. They may, however, be of some value and will be briefly presented, with accompanying qualifications.

A nearly complete set of rate constants has been obtained for hydrolysis of benzenediazonium ion in sodium iodide solutions; however, the solutions were degassed with w-p grade nitrogen. Oxygen was, therefore, not excluded. The initial rates in these solutions were different from the final rates. The rate constants listed below were obtained after about one half life of the reaction.

\[(T = 40.14^\circ, \text{H}_2\text{SO}_4 = 0.01 \text{ M})\]

<table>
<thead>
<tr>
<th>[NaI] m/l</th>
<th>(k \text{ sec}^{-1} \times 10^5)</th>
<th>(k/k_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>46.00</td>
<td>1.108</td>
</tr>
<tr>
<td>0.05</td>
<td>48.33</td>
<td>1.165</td>
</tr>
<tr>
<td>0.10</td>
<td>48.33</td>
<td>1.165</td>
</tr>
<tr>
<td>0.20</td>
<td>51.83</td>
<td>1.249</td>
</tr>
<tr>
<td>0.30</td>
<td>61.50</td>
<td>1.482</td>
</tr>
</tbody>
</table>

Several iodobenzene yields were measured for the above conditions. They are unreliable because of the presence of oxygen in the reaction solutions. The procedure used to obtain these data was the same as when bromobenzene yields were measured (see Experimental).
\( T = 40.14^\circ, \text{H}_2\text{SO}_4 = 0.01 \text{ M} \)

<table>
<thead>
<tr>
<th>[NaI] m/1</th>
<th>Iodobenzene Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>23.6, 22.2</td>
</tr>
<tr>
<td>0.15</td>
<td>20.8, 19.1</td>
</tr>
<tr>
<td>0.20</td>
<td>17.7, 16.2</td>
</tr>
<tr>
<td>0.30</td>
<td>33.9, 33.7</td>
</tr>
</tbody>
</table>

Reaction rates were examined for an initial benzenediazonium ion concentration of \(2.5 \times 10^{-2} \text{ M} \). These rate constants were not reproducible, but were apparently much higher than rate constants for the lower diazonium ion concentration.

The effect of added iodine was checked \( (\text{oxygen present and } \text{ArN}_2\text{BF}_4 = 5 \times 10^{-3} \text{ M}) \). The kinetic data were not reproducible, but rate accelerations were found. At an iodide ion concentration of 0.05 M and an iodine concentration of about \(2 \times 10^{-2} \text{ M} \) the rate was too fast to be measured. Lower iodine concentrations produced measurable rate effects, \( k/k_0 \approx 1.4-1.5 \), for added \( \text{I}_2 = 1-5 \times 10^{-3} \text{ M} \).

Rate constants for benzenediazonium hydrolysis in solutions containing sodium perchlorate were not reproducible, but were very much higher than the rate constants for hydrolysis in water alone. The apparent rates were similar to those listed above for reaction in iodide ion solutions containing oxygen \( (\text{see Experimental for products}) \).

Yields of phenol have been measured after reactions in iodide ion solutions different from those cited earlier in this section. The yields
of phenol from reaction of the diazonium ion in 0.4 M iodide ion solution when oxygen was not excluded was found to be 48% \((\text{ArN}_2\text{BF}_4 = 5 \times 10^{-3} \text{ M}, \text{H}_2\text{SO}_4 = 0.01 \text{ M}, T = 40.14^\circ)\).

Phenol yields from reactions at higher acid concentrations have been investigated. Both yields are for deoxygenated 0.4 M iodide ion solutions at 40.14°, and \(\text{ArN}_2\text{BF}_4 = 5 \times 10^{-3} \text{ M}\). At \(\text{H}_2\text{SO}_4 = 0.10 \text{ M}\), the yield of phenol was measured as 64%; at \(\text{H}_2\text{SO}_4 = 1.0 \text{ M}\), the yield was 62%. The yield of iodine from the reaction in 1.0 M sulfuric acid was 8.6-11.3%.

The rate constants for reaction at these two acid concentrations were measured, but not checked for reproducibility. The rate was unchanged in 0.10 M \(\text{H}_2\text{SO}_4\) and \(\text{I}^- = 0.4 \text{ M}\) \((k = 58.83 \times 10^{-5} \text{ sec}^{-1})\); \(k = 51.67 \times 10^{-5} \text{ sec}^{-1}\) for \(\text{H}_2\text{SO}_4 = 1.0 \text{ M}\) and \(\text{I}^- = 0.4 \text{ M}\).

The rate of iodine formation has been qualitatively determined at 18°. The solutions used were not thoroughly deoxygenated (see Experimental). Diazonium ion concentrations were 5 \(\times 10^{-3}\) to 1 \(\times 10^{-2}\) M, and iodide ion concentrations were 1 \(\times 10^{-3}\) to 1 \(\times 10^{-1}\) M. Solutions having the highest concentrations of reactants gave the maximum absorbance value in ten-twenty minutes. The maximum absorbance for solutions of the lowest concentrations was not achieved in less than one hundred minutes. In all cases the absorbance had reached one-half the final value less than thirty seconds after the diazonium ion and iodide ion solutions were mixed together.
DISCUSSION

The hydrolysis of benzenediazonium ion has recently been shown to be consistent with a bimolecular mechanism (20). Hydrolyses of diazonium ions had previously been postulated as the only established examples of aromatic $S_N^1$ reaction (1,2,21).

The available data suggest that there exists a broad spectrum of bonding between the substrate and displacing nucleophile, for differently substituted diazonium ions, in the reaction transition state (17,18,19,20). The degree of bond formation is also dependent, by inference, on the nature of the nucleophile, although relative nucleophilicities are very much compressed in this reaction.

The present study was undertaken to add further support to the bimolecular postulate. The results would also be expected to further define the nature of the reactive intermediate apparently involved in the reaction. Since only sodium bromide and sodium iodide were used in this study a brief presentation of results from the more complete studies of Hartung will preface the discussion of the present work.

Hartung has measured hydrolysis rate constants in solutions containing bisulfate and chloride salts, using several different salt cations (20). The aim of Hartung's work was to correlate rates and product yields obtained under varying conditions. It was necessary, therefore, to determine whether or not the rate constant of the major reaction, phenol formation, would be affected in salt solutions.
The apparent rate of phenol formation in salt solutions can be related to the rate in pure water by eq 6, derived by Bronsted and Bjerrum (36).

$$k_W = \left( k_W \right)_o \frac{\gamma_{\text{ArN}_2^+} \gamma_{\text{H}_2\text{O}}}{\gamma_{\text{ArN}_2^+ \text{OH}_2^-}^{\frac{1}{2}}}$$

Eq. 6

The rate in salt solutions is $k_W$; the rate in water alone is $(k_W)_o$. The activities of the reactants and the transition state are given as $\gamma_i$. Assuming the activity of water is unchanged (remains unity) in salt solutions and assuming the activities of benzenediazonium ion and the activated complex are the same, it is then seen that $k_W = (k_W)_o$.

The rate constant for phenol formation was then assumed to be the same in each of the solutions studied.

The validity of the final results was dependent on the ability to separate rate effects due to solvation of the salts from rate effects due to nucleophilic participations. Salt solvation causes a rate retardation since water in the primary solvation shell of the salt cation will be much less nucleophilic than the bulk of the solvent; the overall water concentration is thus effectively reduced in salt solutions. Hydrolysis rates were measured in solutions of sodium, lithium and tetra-n-butylammonium bisulfate. Chloride salts to be studied would use the same cations. The results obtained were themselves partial justification of the bimolecular hypothesis. Rates in the salt solutions were different from the rate in pure water. Since bisulfate
ion is not nucleophilic toward benzenediazonium ion the rate changes were attributed to changes in the effective water concentrations.

Hartung was able to duplicate the observed rates in bisulfate salt solutions by calculations using reported solvation data for the salt cations. As expected the rate was decreased most by lithium bisulfate, since lithium is the most strongly solvated cation among those studied (37).

The rate depressions observed in sodium bisulfate solutions were shown to be general for different diazonium ions. Hydrolysis rates in sodium bisulfate solutions relative to the rates in water alone were measured for o-, m- and p-toluenediazonium ion. The relative rates for these three diazonium ions and for the unsubstituted compound were essentially the same at each concentration of sodium bisulfate examined.

The reasonable conclusion, then, is that salt cations effect rate retardations through a decrease of effective water concentration. Rate changes for other salts with the same cations as studied above could then be separated into cation solvation and nucleophilic anion effects.

Hydrolysis of benzenediazonium ion in chloride ion solutions was examined by Hartung. The data from reactions in sodium chloride solutions were used for quantitative tests, since they were expected to suffer least from complications such as ion aggregation. Results from reactions in lithium chloride were to be used as qualitative confirmation of the sodium chloride results.
A set of relative rate ratios was calculated and compared with measured rate ratios. Calculated rate ratios were obtained by use of eq 4 (see Introduction for derivation):

\[
\frac{k}{k_0} = \frac{(H_2O)_{eff}}{(H_2O)_0} + \frac{Y_{ArCl} (H_2O)_{eff}'}{Y_{ArOH} (H_2)_0}
\]

\[\text{Eq. 4}\]

\(k\) = apparent rate in sodium chloride

\(k_0\) = rate in pure water

\[(H_2O)_{eff}/(H_2O)_0\] = rate in sodium bisulfate/rate in water

\(Y\) = yield, of chlorobenzene or phenol

\[(H_2O)_{eff}'/(H_2O)_0\] = correction for water concentration differences between sodium (lithium) chloride and bisulfate salt solutions

In practice \(k/k_0\) is calculated merely by adding values of relative rates (bisulfate/water) to yield ratios. The very good agreement between calculated and measured rate ratios has been shown in Figure 1. The results from lithium chloride solutions were not as good, quantitatively, but were in qualitative agreement with the sodium chloride results.

Hartung's procedure was followed in detail, using sodium bromide solutions. The results are presented in Table VII and Figure 7. The observed agreement, although not as good as might be hoped for, substantiates the postulate of bimolecular diazonium ion decomposition in aqueous solutions.

Not unexpectedly bromide ion acts as a stronger nucleophile in the reaction than does chloride ion, as measured by the relative competition
TABLE VII

Rate and Product Correlation for Benzenediazonium Ion Decomposition in Aqueous Sodium Bromide Solutions

(T = 40.14°, H₂SO₄ = 0.01 M)

<table>
<thead>
<tr>
<th>[NaBr] m/l</th>
<th>Bromobenzene Yield, %</th>
<th>(\frac{k}{k_0}) NaHSO₄ Sol'n.</th>
<th>(\frac{k}{k_0}) Calculated</th>
<th>(\frac{k}{k_0}) Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>3.12</td>
<td>0.985</td>
<td>1.025</td>
<td>0.996</td>
</tr>
<tr>
<td>0.20</td>
<td>3.80</td>
<td>0.974</td>
<td>1.023</td>
<td>1.002</td>
</tr>
<tr>
<td>0.30</td>
<td>4.50</td>
<td>0.962</td>
<td>1.020</td>
<td>1.009</td>
</tr>
<tr>
<td>0.40</td>
<td>5.11</td>
<td>0.948</td>
<td>1.012</td>
<td>1.004</td>
</tr>
<tr>
<td>0.60</td>
<td>6.00</td>
<td>0.923</td>
<td>0.999</td>
<td>0.998</td>
</tr>
<tr>
<td>1.00</td>
<td>8.61</td>
<td>0.873</td>
<td>0.978</td>
<td>0.986</td>
</tr>
</tbody>
</table>
Figure 7. Rate and Product Correlation for Benzenediazonium Ion Decomposition in Aqueous Sodium Bromide.
factors \( \frac{k_{Cl}}{k_{W}} \approx 8-4, \frac{k_{Br}}{k_{W}} \approx 17-5 \). The relative nucleophilicity of the bromide and chloride ion as measured by this reaction is much less, however, than for normal bimolecular reaction. Winstein has assigned the relative halide nucleophilicities as \( I^- > Br^- > Cl^- > 1 \), for direct bimolecular displacements \( 38 \).

The intermediate in the benzenediazonium ion hydrolysis reaction, if it exists, must possess a very small amount of stability relative to its immediate neighbors on the reaction pathway. That is, displacement of the diazonio nitrogen is apparently not very susceptible to agents normally thought of as aiding nucleophilic reaction.

A quantitative measure may be obtained for the nucleophilic character of the replacement reaction. Comparison of the nucleophilic reactivity of a reagent toward substitution on carbon may be approximated by its reactivity toward a standard substrate. The method of Swain and Scott is considered to be suited to the present purpose \( 39 \). They have developed eq \( 7 \),

\[
\log \left( \frac{k}{k_0} \right) = s_n + \text{const.} \\
\text{Eq. 7}
\]

where \( n \) is a measure of the nucleophilic character of the reagent and \( s \) is a reaction constant. The added constant \( (\text{const.}) \) in eq \( 7 \) may be ignored for reactions in the same solvent. Application of the Swain and Scott equation is known to be of limited value when applied to nucleophilic aromatic substitution \( 40 \).
In at least one case, however, the method was not without value when applied to a diazonium ion reaction. Replacement of one of the diazonio groups of p-phenylene-bis-diazonium ion using several nucleophiles has been studied and the Swain-Scott equation applied to the results, by Lewis and Johnson (19). The most reasonable results were obtained with rate data from reactions of bromide and chloride ion \( s = 1.5 \). Analogy to this reaction is, however, tenuous in this instance. The value of \( g \) calculated was as large as any originally mentioned by Swain and Scott, while the value of \( s \) for reactions of benzenediazonium ion ought to be very low.

The rates we have used are calculated second-order rate constants. The value of \( k_0 \) used is \( 7.48 \times 10^{-6} \) 1/mole-sec, calculated from the apparent rate constant for diazonium ion hydrolysis in 0.01 M sulfuric acid. Rates in halide ion solutions are those at infinite dilution, interpolated from a plot of halide ion concentration versus

\[
k_2 = \frac{k_X - k_{\text{HSO}_4^-}}{(X^-)} \quad \text{Eq. 8}
\]

where \( k_X \) is the apparent rate in the chloride or bromide ion solutions, \( k_{\text{HSO}_4^-} \) is the apparent rate in a solution of sodium bisulfate at the same concentration as the halide ion solution, and \( (X^-) \) is the halide ion concentration producing the apparent rate.

We have chosen to calculate and compare \( s \) values for chloride and bromide ion reactions as a test of applicability of the method. Data from benzenediazonium ion reaction in chloride ion solutions yields the
value $s = 0.29$; reaction in bromide ion solutions yields the value $s = 0.25$. The data are at least internally consistent.

The lowest $s$ value mentioned by Swain and Scott was for ethyl tosylate, with $s = 0.66$. We are hesitant to make rigorous comparison with Swain and Scott's original data or, for example, that of Lewis and Johnson (see above). It is, however, gratifying to find that the apparent nucleophilic susceptibility of the benzenediazonium ion reaction is small.

Another linear free energy relationship can be applied to our data, at least as a check on the use of the Swain-Scott method. A four parameter equation has been developed by Edwards, relating substrate constants to anion nucleophilicities, as measured by the anion oxidation potential (41).

$$\log \left( \frac{k}{k_0} \right) = \alpha E_N + \beta H$$

Eq. 9

Edwards' equation is quite useful for the prediction of rates, but is of limited theoretical value since the constants $\alpha$ and $\beta$ are calculated so as to give the best fit of eq 9 to observed rate data (42). Using the rate ratios calculated above and Edwards' values for $E_N$ and $H$ (for bromide and chloride ion) the values $\alpha = 0.620$ and $\beta = -0.034$ are calculated. The parameters listed for reaction of ethyl tosylate are $\alpha = 1.68$ and $\beta = 0.014$. The $\alpha$ value for the ethyl tosylate reaction is the smallest given by Edwards; the lowest $\beta$ value listed is for reaction of benzylchloride, $\beta = 0.128$. Although theoretical
interpretation of the constants is not possible, it does appear that once again the benzenediazonium ion is calculated to have a low susceptibility toward nucleophiles.

Results obtained from hydrolysis of benzenediazonium ion in bromide and chloride ion solutions indicate that the entire reaction is bimolecular. This substrate is, however, rather insensitive to changes in the strengths of displacing nucleophiles. The results of treatment of data for different diazonium ions by the method of Swain and Scott suggests that Hartung's postulate of a broad spectrum of carbon-nucleophile bond development is valid (20,41).

The results of iodide-benzenediazonium ion reactions have been subjected to the same analyses as were carried out with the bromide and chloride ion reaction results; however, the data obtained in this way for the iodide ion system are not amenable to simple interpretations. Collated rate data (measured and calculated) are presented in Table VIII and Figures 8 and 9. It seems apparent that this reaction is not simple.

The complexity of the reaction can be further illustrated by different treatments of the collected rate data. The measured, apparent first-order rate constants, \( k \), can be separated into the pseudo first-order rate constants for phenol formation, \( k_W(H_2O) \), and for reactions with iodide ion, \( k_1(I^-) \). The rate constant for formation of phenol is just Hartung's rate data for decomposition of benzenediazonium ion in sodium bisulfate solutions (20).
TABLE VIII

Rate and Product Correlation for Benzenediazonium Ion Decomposition in Aqueous Sodium Iodide Solutions

\((H_2SO_4 = 0.01 \text{ M})\)

<table>
<thead>
<tr>
<th>[NaI] m/l</th>
<th>(\frac{k}{k_0}^{(a)}) Calculated</th>
<th>(\frac{k}{k_0}^{(b)}) Observed</th>
<th>T°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
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<tr>
<td>0.40</td>
<td>1.220</td>
<td>2.193</td>
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(a) Based on measured phenol and iodobenzene yields.
(b) From reactions in deoxygenated solutions.
Figure 8. Rate and Product Correlation for Benzene-
diazonium Ion Decomposition in Aqueous
Sodium Iodide.
Figure 9. Rate and Product Correlation for Benzene-diazonium Ion Decomposition in Aqueous Sodium Iodide.
At 40.1° the observed rates, for I⁻ ≥ 0.075 M, are approximated by the calculations of eq 10:

\[
\frac{k_p}{k} = \frac{k_{HSO_4}}{50(I^-)} \times 10^{-5} \text{ sec}^{-1} \quad \text{Eq. 10}
\]

In order to use this equation at 32.9° it was assumed that the decreases in the rates of phenol formation had the same form as at 40.1° (that is, the slope of \( k_{HSO_4} \) vs. NaHSO₄ is the same at both temperatures). The measured data, at 32.9°, were found to follow eq 10, with the same value of \( k_{I} \) as at 40.1°. The measured rate data were rearranged and the value of \( k_{I} \) determined; these values are presented graphically in Figure 10. The rate constant for I⁻ = 0.01 M at 32.9° has been included, although this value could not be well reproduced (see Table III); the rate at I⁻ = 0.05 M for this temperature is also in some doubt, however, it was reproducible.

The data of Figure 10 suggest that minor change of the \( k_{I} \) value of eq 10 would improve the correlation somewhat. The data show that the apparent rate constant for reaction of iodide-benzenediazonium ion is little affected by temperature, \( E_a \approx 0 \); the Arrhenius preexponential factor must be very low for this reaction.

The measured data can be treated as a combination of the reactions of eq 10 plus reaction with triiodide ion, from iodine formed in the reaction. This treatment leads to eq 11:

\[
k_p = \left[ k_{HSO_4} + k_{I} (I^-) \right] \times 10^{-5} \text{ sec}^{-1} + [0.1 (I_3^-)] \text{ sec}^{-1} \quad \text{Eq. 11}
\]
Figure 10. Second-order Rate Constants for Reaction of Benzenediazonium Ion with Aqueous Sodium Iodide.
Reaction with $I_j^-$ alone, analogous to eq 10, has been ignored. The data can be approximated by an equation of this type; however, it should not represent the actual reactions being observed. The measured rate data can be approximated by eq 11 with $k_I = 40$ at $40.1^\circ$ and $k_I = 30$ at $32.9^\circ$. Since the rate effects of triiodide are much larger than those of iodide ion (found from experiments with added iodine) the triiodide rate constant has been assumed to be temperature independent. The decrease in the iodide rate constant corresponds to a reaction with an activation energy of less than 10 kcal/mole.

The actual reactions of this system need not actually correspond to those represented by eq 11; however, the available data does not allow a distinction to be made between eq 11 and eq 10, since the rate data for reactions carried out with added triiodide ion were not obtained from deoxygenated solutions and were not well reproduced.

Common to eq 10, 11 is that each fails to correctly predict the rate of reaction for $I^- = 0.01, 0.05$ M. The form of the data suggests a rate inhibition by one of the reaction products. Since added iodine increases the rate of reaction, the iodine formed in the reaction is apparently not responsible for the rate decrease at higher iodide ion concentrations. Rate retardation by added iodine has been reported in another diazonium-iodide ion reaction (28); however, the rates were determined by nitrogen evolution and are not necessarily analogous to the rates observed in the present study.

Competition factors, $k_I/k_N$ (Table IV), based on measured phenol and iodobenzene yields, also exhibit a minimum at $40.1^\circ$, presumably also at
32.9°, so that the various data appear to be consistent. A possible, but not necessary, reason for this behavior is given below.

Plots of rate and product data for reaction of diazonium ions with bromide ion (Figures 2, 3), chloride ion (20) and thiocyanate ion (43) all exhibit curvature. This curvature has been interpreted as arising from salt effects on the rate and product determining steps of diazonium ion decompositions (20). It is tentatively suggested that the form of the decomposition rates in sodium iodide solutions can also be rationalized by recourse to salt effects.

Hartung has shown that the reaction rates in salt solutions follow the activities of the reacting species, although quantitative correlations were not readily obtained (20). His calculations have not been carried out for the iodide ion system; however, it is felt that enough analogies exist between the reactions of the two studies to suggest salt effects as an explanation of the iodide ion solution reaction results.

The form of the apparent rates above 0.1-0.2 M sodium iodide may result from the predominance of other reactions. For example, the triiodide ion concentrations may become high enough that reaction of this species with diazonium ion becomes kinetically important. An alternative explanation is that reactions higher than first-order in iodide ion are important at higher sodium iodide ion concentrations.

These considerations assume that the diazonium ion disappears by chemical reaction and not by, for example, precipitation of the diazonium triiodide salt.
Returning to the data of Table VIII, it seems apparent that decomposition of benzenediazonium ion to phenol and iodobenzene does not account for the observed results. This conclusion is confirmed by addition of measured phenol and iodobenzene yields, which shows that about ten-thirty percent of the initial diazonium ion is unaccounted for, depending on the temperature and iodide ion concentration.

It was hoped that this system would show a rather high degree of bonding between the nucleophile, iodide ion, and aromatic carbon, providing more evidence for bimolecular diazonium ion reactions. It is felt that owing to the side reactions observed in this system the evidence obtained in this study cannot be used as conclusive proof of bimolecular reaction, although it is believed to be occurring.

The occurrence of bimolecular reaction can be rationalized by recourse to the expected products, phenol and iodobenzene. Since iodobenzene is not necessarily formed in one reaction only, it is perhaps unreliable for quantitative calculations.

It is possible to estimate, very approximately, the extent of bimolecular reaction expected by a comparison of observed half-lives and calculated half-lives (for bimolecular reaction). The assumption is that the ratio of the half-life of the observed reaction and the calculated half-life for, in this case, phenol formation is related to the actual product ratios, through eq 12:

\[
\% \text{ArOH} = \left( \frac{t_{1/2}^\circ}{t_{1/2}^\circ} \right) \left( \frac{1}{2} + \frac{1}{4} + \frac{1}{8} + \ldots \right) \times 100
\]

\[
= \left( \frac{t_{1/2}}{t_{1/2}^\circ} \right) (1) \times 100 \quad \text{Eq. 12}
\]
where \( t_{1/2} \) is the half-life of the observed reaction, \( t_0 \) is the half-life of the phenol forming reaction (from Hartung's rate data in sodium bisulfate solutions (20)), and the numbers in parentheses are extents of reaction. This equation reduces to the form shown for complete (100%) reaction of starting material. What is assumed by this treatment for example is that if the half-life ratio is one half, then the yield of phenol will be fifty percent, since the observed reaction (phenol formation + other reactions) is proceeding twice as rapidly as the formation of phenol alone.

When sodium bromide is the added salt, at a concentration of 0.2 M, the half-life ratio is 0.965; the bromobenzene yield is about four percent and the remainder (~96%) is phenol. This treatment may then be satisfactory for the desired purpose.

At 40.1° the yields of phenol are calculated to be 93-65% for reaction at 0.01-0.4 M iodide ion; the measured phenol yields (from 0.05-0.4 M iodide ion reaction solutions) are 90-48% or 90-57%, depending on the value used for 0.4 M iodide ion reaction. At 32.8° the yields of phenol are calculated to be 90-39% for reaction at 0.05-0.4 M iodide ion; the measured phenol yields (0.2-0.4 M iodide ion) are 63-44%. Not unexpectedly the agreement between the measured and calculated phenol yields is not perfect; however, it is believed that they are close enough to justify the method. At 32.8° and 0.01 M iodide ion the phenol yield is calculated as 75% and measured at 69%, confirming the very rapid reaction observed at this iodide ion concentration.
The temptation to assume iodobenzene arises from simple displacement of diazonio nitrogen by iodide ion, and thus use calculated rate ratios, has not been (and perhaps should not be) entirely overcome. Even if a set of rate ratios are calculated using lower iodobenzene yields and higher phenol yields the result is still a prediction of a rate increase for this set of reactions. It is felt that a substantial rate increase due to iodide ion nucleophilicity is occurring; however, until more data are obtained this suggestion must remain unconfirmed.

The question now is whether or not it is possible to distinguish between radical and ionic mechanisms for other reactions, iodine formation, etc., observed in this study. Arguments in favor of either type of reaction have appeared in the literature (see Introduction).

An ionic reaction has been postulated by Hodgson, with triiodide ion being specific for displacement of diazonio nitrogen (33,34). Before examining this argument it should be noted that Hodgson, and Waters below, based a mechanistic scheme, apparently, on the results of synthetic procedures, which are designed to give high yields of iodobenzenes (24,25). This result is different from those of the reactions investigated in the present study. However, even with this qualification, Hodgson's mechanism appears to explain the data inadequately.

Hodgson's mechanism requires triiodide ion to be orders of magnitude better as a nucleophile than iodide ion. As far as the author is aware the relative nucleophilicities of these two ions is not well established, but it appears that triiodide ion is little, if any, better
a nucleophile than iodide ion. It is true that triiodide ion does
catalyze the formation of iodobenzene, but it is felt that Hodgson's
explanation for this is incorrect.

A more serious fault is Hodgson's failure to account for the forma-
tion of iodine. He has attempted to show that free diazonium ion is
responsible for oxidation of iodide ion (33); however, the consequences
of this possible redox reaction were ignored in subsequent explanations
of the reaction. Finally, the ionic mechanism would appear to be inade-
quate for explaining the appearance of products other than iodobenzene
(and phenol).

A radical mechanism has been advanced by Waters (32). This postu-
late is based on analogy to the Sandmeyer reaction, with iodide ion
acting as its own catalyst. Waters originally suggested that the oxi-
dation potentials of copper (I) and iodide ion were enough similar that
both could transfer an electron to a diazonium ion. It seems more
reasonable now to use the oxidation potentials of iodide ion and cuprous
chloride as the basis of an analogy. The oxidation potentials (versus
the NHE) of the iodide-iodine couple and the cuprous chloride-cupric
chloride couple are -0.53 and -0.57 volts, respectively (44).

A free radical scheme is able to account for the appearance of
iodine and iodobenzene, as well as some side products. However, the
benzenediazonium-iodide ion reaction gives products which, although not
identified, are apparently more complex than expected from reactions of
"simple" free radicals.
It is believed that the Waters scheme will come closest to fitting the observed results, although the mechanism as proposed originally by Waters will apparently require modification. A mechanism must account for the following facts: the decomposition of benzenediazonium ion in iodide ion solutions is more rapid than expected by analogy to reaction in solutions of bromide or chloride ion; the decomposition is very much more rapid when iodine is added to the iodide ion solutions (iodine itself has a negligible rate effect); iodine (acting as tri-iodide ion) catalyzes the formation of iodobenzene; reaction in air saturated iodide ion solution gives no more phenol than reactions in deoxygenated solutions; iodine is rapidly formed, the ultimate yield depending on the initial iodide ion concentration, and apparently on the initial diazonium ion concentration; as far as can be observed no products appear after the diazonium ion has completely disappeared; the activation energy of the diazonium-iodide ion reaction is apparently less than 10 kcal/mole; the activation energy calculated from the apparent rates at each iodide ion concentration, at two temperatures, decrease as the iodide ion concentration increases (for \( I^- \leq 0.01 \text{ M} \) the apparent \( E_a \) is close to 27 kcal/mole, the activation energy for simple hydrolysis); solid sodium iodide and benzenediazonium fluoborate react, open to the atmosphere, rapidly, giving iodine and iodobenzene as well as solid organic products; reaction of benzenediazonium ion in solutions of sodium perchlorate gives at least one product apparently identical to one product, aside from phenol, of the iodide ion solution reactions; iodide ion solution reactions give at least two products which do not
correspond to iodobenzene, phenol, or expected coupling products of simple free radicals.

It should be remembered that the "side reactions," while they are very important, do not comprise the major reactions, under the conditions used in this study. A large fraction of the diazonium ion is apparently reacting "normally." That is, much of the diazonium ion decomposition yields phenol and iodobenzene, the expected products. The overall reaction should be kept in perspective.

The very interesting formation of iodine can be explained either by a radical or an ionic mechanism. Hinds has suggested reaction (9) as a possible ionic mechanism:

\[
\text{ArN}_2^+ + 3\text{H}^+ + 6\text{I}^- \leftrightarrow \text{ArNHNH}_2^- + 2\text{I}_3^-
\]  \hspace{1cm} (9)

However, he was unable to isolate a hydrazine (p-nitrophenyl-) from his reaction solutions, although the hydrazine was reported to be stable under the conditions he used (9). Hinds did find rate variations in solutions of different acid concentrations, consistent with the proposed scheme. However, this does not necessarily confirm the existence of an equilibrium, since rate depressions due to varying acidity are expected because of solvation of the proton. Rate increases observed by Hinds in strong acid solutions (> 1 M) may be due to a change in the equilibrium, although this was not definitely established.

Other reactions of this type with variable stoichiometry may be written, for example reaction (16):
\[
\text{ArN}_2^+ + 2\text{H}^+ + 4\text{I}^- \rightleftharpoons \text{ArNHNHI} + \text{I}_3^-
\]  (16)

Equilibria somewhat similar to (9) and (16) have been found for anions other than iodide (see below).

Formation of iodine by a free radical scheme has been suggested by Waters (see Introduction):

\[
\text{ArN}_2^+ + 2\text{I}^- \rightarrow \text{Ar} \cdot + \text{N}_2 + \text{I}_2
\]  (14)

There is, however, apparently no reason why reaction (14) could not be first-order in both diazonium ion and iodide ion, with subsequent combination of two iodine atoms to form iodine.

The rate of decomposition, under varying conditions, of benzene-diazonium ion in 0.4 M iodide ion solutions at 40.1° has been examined in the course of this study. When the medium is changed from 0.01 M in sulfuric acid to 1.0 M the rate decreases slightly, consistent with solvation effects; the yield of iodine at the higher acid concentration is 8.6-11.3% and at the lower acid concentration the yield is 6.9-6.6%. Since the data have not been checked for reproducibility the results are not conclusive. There is, however, no drastic change in the final iodine concentration, although nothing is known about intermediate concentrations.

It is proposed that other results, specifically the rate of iodine formation (Experimental), appear to exclude radical reactions such as (14). The initial formation of iodine is in most cases too rapid to measure by ordinary methods; at least one half of the final iodine
concentration is found less than one minute after diazonium ion and iodide ion solutions are mixed. An equilibrium reaction is apparently involved, since the diazonium ion half-life would be on the order of two-three minutes, at most, if iodine formation were irreversible. The equilibrium is apparently a function of diazonium ion also because of the substantial phenol yields, which ought to come from reaction of free benzenediazonium ion and water.

Lewis and Suhr have investigated equilibria reactions in diazonium ion solutions containing sulfite, cyanide and hydroxide ion (45,46,47). Both sulfite and cyanide ion can react to form a reduced diazonium ion containing two moles of the anion, as shown below for sulfite ion:

\[
\text{ArN}_2^+ + \text{SO}_3^- \rightleftharpoons \text{Ar-N=N-SO}_3^- \quad (17)
\]

\[
\text{Ar-N=N-SO}_3^- \xrightarrow{\text{SO}_3^-} \text{Ar-N-NH-SO}_3^- + \text{OH}^- \quad (18)
\]

The equilibrium (17), with any of the anions, is correlated by the Hammett relationship, the reactions having large, positive rho values. Co-valent diazo compounds are, however, not known with iodide ion as the nucleophile. The formation of iodine will be set aside for the present, while other reactions are examined.

Lewis and Cooper while studying the reaction of benzenediazonium ion with thiocyanate ion found that rate increases of twenty percent (at 5 M thiocyanate) relative to the hydrolysis rate in water alone, could be observed (17). The rates of reaction were very much larger
than expected by analogy to reactions of diazonium ion with bromide or chloride ion. In addition, some anomalous products could be isolated, thiophenol possibly and other, colored, material. The rate of reaction was affected by light and air in an erratic manner, suggesting the possibility of free radical reactions.

Cooper considered reactions of the type (17), shown above; however, as with iodide ion there is no evidence for formation of a covalent diazo species with thiocyanate ion. Cooper's data, nevertheless, indicated the presence of free radical reactions, the mechanistic details not being apparent.

It is felt that the various data can be correlated by analogy to studies carried out by Lewis and Johnson with p-benzenetetrazonium ion (30). The reactions of this ion with chloride, bromide, azide, hydroxide, thiocyanate and iodide ion were investigated, and the data analyzed by the method of Swain and Scott (39).

The plot of log $k_2$ (second-order rate constant) versus the anion constant $n$ showed a large variation in the measured rate. The data for chloride and bromide ion were chosen as representing points on the line of best slope ($s = 1.5$). The rates of reaction of the remaining four anions deviated from the line very widely; the points for N$_3$$^-$ were too large by a factor of $2 \times 10^9$, that for SCN$^-$ by $40$, OH$^-$ by $3 \times 10^{10}$ and I$^-$ by a factor of $5 \times 10^3$.

Since both N$_3$$^-$ and OH$^-$ were known to bond to diazonio nitrogen it was suggested that the reaction transition state involves bonding between the attacking nucleophile, carbon and the terminal diazo nitrogen.
It was further suggested that the mechanism for attack by SCN\(^-\) and I\(^-\) was similar, even though these ions do not form stable covalent diazo compounds.

It is the suggestion of the present author that the mechanism advanced by Lewis and Johnson is operative to some degree in reactions of diazonium ions other than the \(p\)-benzenetetrazonium ion. It is further suggested that there is a spectrum of interactions between anions and diazonio nitrogen which, even though unexplained, accounts for the different reactions observed with the different anions.

Following Waters, an analogy is perhaps indicated between the effectiveness of metal ions as catalysts for the Sandmeyer reactions and the effectiveness of anions in assisting the decomposition of benzene-diazonium ion (32). Waters postulated the unique, or nearly so, ability of copper to catalyze the Sandmeyer reactions was due to its oxidation potential. Other metal ions were thought to be ineffective because their oxidizing power was too strong or too weak. The explanation for anion reactions cannot be this simple, although examination of anion oxidation potentials may be useful.

Edwards has collected these data for use in his linear free energy relationship (42). The oxidation potentials of azide and hydroxide are lower (less positive) than those of iodide and thiocyanate, which are in turn lower than those of sulfite and cyanide. It is interesting to note that both sulfite and cyanide form a double adduct with diazonium ions, while azide and hydroxide apparently form only mono-adducts.
The nucleophilicity constants of Swain and Scott follow the order of the oxidation potentials. Since azide and hydroxide ion have lower oxidation potentials than thiocyanate and iodide ion and have lower nucleophilicity constants, but still form covalent diazo compounds, while iodide and thiocyanate do not, the explanation for this phenomenon must be rather more complex than suggested above. This is not surprising since the Swain-Scott constants are considered to result from a combination of several factors (basicity, polarizability, solvation, etc.), while Edwards' relationship is empirically fitted to measured data.

The very large rate effects due to triiodide ion ought to be explicable on the above basis, although a priori considerations might not have done this. Lacking relevant data for triiodide ion it can only be suggested that bonding between carbon and terminal diazonio nitrogen ought to be sterically more favorable than for iodide ion, especially if, as Lewis and Johnson suggested, the "diazo" compounds decompose as the syn-isomer.

In line with the suggestions presented above it is postulated that formation of iodine in reactions of diazonium ion and iodide ion is a result of the attraction of iodide ion to the diazonio nitrogen. It may happen that iodide ion cannot form a covalent diazo compound, but though lacking this ability it is still able to "bond" to nitrogen in some type of complex. Of course, the converse is not excluded; because it is able to form a complex (presumably for, or by, electron transfer) iodide ion does not, or cannot, form a covalent compound. Cooper's
investigation of the thiocyanate ion reaction does not rule out a similar process, since he did not exclude thiocyanogen as a possible product:

\[
\text{SCN}^- + \text{SCN}^- \rightarrow (\text{SCN})_2^-. \tag{19}
\]

\[
\text{ArN}_2^+ + (\text{SCN})_2^- \rightarrow \text{Ar}^+ + (\text{SCN})_2 + \text{N}_2 \tag{20}
\]

In the iodide ion systems it is felt that there is an equilibrium involving triiodide ion and benzenediazonium ion, which controls the amount of iodine produced. An equilibrium reaction is consistent with the fact that increases in either iodide or diazonium ion concentrations increases the iodine level. The form of the dependence on diazonium ion is, however, not established. The nature of the diazonio species on the triiodide ion side of the equilibrium (if operative) is not known.

This question as well as the final resolution of the mechanism awaits the identification of the unknown products of the iodide-diazenium ion reactions. A correlation of the properties of these products with those of known compounds has not been, as yet, possible. One of these products (Experimental, compound B, \(\lambda_{\text{max}} = 280 \text{ m} \mu\)) is apparently an oxygen containing species ("O-band", 1255 cm\(^{-1}\)) and may contain nitrogen (2300 cm\(^{-1}\), 2100 cm\(^{-1}\)). The simplicity of the infrared spectrum of this material is puzzling; the only similar spectrum we have encountered is that of \(p\)-diiodobenzene, which does not have the physical properties of compound B.
The long wavelength substitution pattern suggests the presence of an aromatic ring having two or three adjacent hydrogen atoms. The spectrum shows absorbance due to non-aromatic carbon-hydrogen bonds, although this absorbance is usually very weak (as is aromatic C-H absorbance). Only aromatic hydrogen has been found by nmr studies.

The second unknown (Experimental, compound A, $\lambda_{\text{max}} = 254 \text{ m\^u}$) is apparently rather different from compound B. Its infrared spectrum is complex; the "0-band" is present at 1255 cm$^{-1}$ (although this may be due to the presence of some compound B) as is the characteristic compound B absorption at 1000 cm$^{-1}$ and 1100 cm$^{-1}$. However, the compound A spectrum shows these bands as sharp absorptions, instead of the rather broad, sloppy bands of the B spectrum. Non-aromatic C-H absorption is seen, as well as strong aromatic C-H absorption. The nmr spectrum shows only aromatic proton bands. No correlation has been made with the spectra of known compounds.

The reaction of benzenediazonium ion in sodium perchlorate solutions yields several products, one of which has an infrared spectrum apparently identical with that of compound B, above. We have no explanation for the appearance of this product, or for the overall reaction character, since perchlorate ion was selected for study because of its inertness as a nucleophile. Correlations with iodide ion reactions, if possible, ought to be very interesting.

Finally, it is noted that benzenediazonium fluoborate and sodium iodide have been found to undergo a relatively facile reaction in the solid state (open to the atmosphere). The reaction products are iodine,
iodobenzene and unidentified organic solids. An infrared spectrum of the unknown materials is nearly identical with that of compound B, above, except that the sharp "O-band" is absent.

The reactions of benzenediazonium ion in bromide ion solutions have been found to be exactly analogous to those in chloride ion solutions. The results of this study support the postulate that the decompositions of diazonium ions in aqueous solutions are bimolecular, with a very reactive intermediate being involved.

Reactions of benzenediazonium ion in iodide ion solutions are believed to be similar to the other halide ion solution reactions, in that bimolecular reaction is occurring to a large extent. The results are complicated by side reactions which yield iodine and unknown organic products.

It is suggested that analogies exist between the reactions of \( p \)-benzenetetrazonium ion with several reactive nucleophiles and the reactions of benzenediazonium ion with these same nucleophiles. Unidentified organic products and iodine are postulated as arising from reactions of a benzenediazonium-iodide ion complex, which may possess partial, or at least incipient, free radical character.
ADDENDUM TO DISCUSSION

The author wishes to propose suggestions for further research on the reactions of iodide and benzenediazonium ion.

It seems hardly necessary to state that identification of the products observed in this study is of great importance. A tentative suggestion is that coupled products of the form shown below may be involved.

![Chemical structure]

This product has been observed from reaction of substituted phenoxy radicals (48), and as a reversibly formed intermediate in iodination of phenols and anilines (49).

Unfortunately, complete separation of the unknown products from each other has not been possible. One suggestion for accomplishing this is the use of thin layer chromatography, which can be used for separation of 100 mg amounts of material. A second possibility is the use of sublimation techniques, although this proved to be ineffective under water aspirator pressure because of apparent decomposition of the solids.

Rate and product data ought to prove informative for reactions conducted at much lower or higher temperatures than used in this study. Presumably at very low temperature hydrolysis will be negligible and the
"side reactions" will predominate; the converse should be true at high reaction temperatures.

Rate and product data for reactions in the presence of added iodine may prove to be useful. The limited data obtained suggest that the "side reactions" still occur under these conditions, although the yields of the products may be variable.

Although inconvenient at the present time perhaps, polarographic reduction of the diazonium ion could yield useful data. Kochi has observed one-electron reductions which give tarry products containing nitrogen (50). This behavior is not the same for arylazo compound decompositions, which do not give nitrogenous organic products (51, 52). Reaction at the bulky, mercury electrode may have similarities to the iodide ion reactions, in that a complex is formed which is radical in nature but not dissociated.

Polarography might be useful as a tool for identification of the unknowns from the iodide ion reactions, especially if a chromophore such as -N=N- is present.

The perchlorate ion reactions are, at this time, very puzzling. This is the only case the author is aware of where perchlorate ion reacts with a diazonium ion. The perchlorate ion is oxidizable by bromine (ref 45), but the potential for this couple has only been noted as being "more positive than -2 volts." The diazonium perchlorate is reported to be insoluble, and may be highly associated in solution. Why, or if, this leads to the observed reactions is not known. An interesting possibility is that a metal ion impurity is responsible for
the anomalous reaction; since analogous products are found in the iodide and perchlorate ion reactions a radical like reaction in perchlorate solutions ought to imply such a reaction in iodide solutions.

It should be noted that benzenediazonium ion need not always react as substituted ions do. Johnson has observed that in dimethylsulfoxide solutions halides react with p-nitrobenzenediazonium ion to yield the aryl halides, while in this solvent with any of the halides the benzene-diazonium ion yields phenol and dimethylsulfide (53). As an aside, it is encouraging to note that in the p-nitro- ion reaction the order of halide reactivity is Cl" > Br > I", which would be predicted on the basis of halide solvation effects (38) and bimolecular diazonium ion reaction.

Finally, mention should be made of the work of Edwards and Pearson in connection with the property they have termed the alpha effect (59). This effect was invoked to account for "the enhanced nucleophilicity observed for a base possessing a pair of unshared electrons α to the nucleophilic atom." It is the present author's impression that this phenomenon is very incompletely understood and thus cannot be invoked to rationalize the results of this study.

The recent work of Bruice and co-workers has done much to clarify some of the cases where the alpha effect is operative (60,61); future results may well be applicable to diazonium ion reactions. At the present time it should only be said that the results of diazonium ion reactions with several very reactive nucleophiles are not inconsistent with the published data concerning the alpha effect.
EXPERIMENTAL

Preparation of Benzenediazonium Fluoborate. The diazonium fluoborate was prepared by diazotization of the amine hydrochloride as described in Organic Reactions (54). In a typical preparation 38.2 ml (0.3 mole) of Baker and Adamson reagent grade aniline was slowly mixed with 43.5 ml (0.4 mole) of concentrated hydrochloric acid. Aniline hydrochloride crystallized when the solution was cooled in an ice bath. The hydrochloride salt was collected by filtration, washed with cold ether and recrystallized from absolute ethanol-ether. Ten grams of the aniline hydrochloride was dissolved in 25 ml of hydrochloric acid and 50 ml of water; the solution was cooled in an ice bath. Dry Ice was added periodically for cooling and to maintain an inert atmosphere. A cold, aqueous solution of 3 g of sodium nitrite was slowly added with vigorous stirring until a potassium iodide-starch endpoint was reached. The 24 ml of Baker and Adamson reagent grade fluoboric acid was added slowly with vigorous stirring. The solution was left to stand for several minutes, in order to allow complete precipitation of the diazonium fluoborate, which was collected by filtration and washed with cold ether. The salt was purified by recrystallization from methanol-ether. The isolated salt was dried at 0° under a vacuum. Storage at 0° over a desiccant effectively inhibits decomposition of the diazonium fluoborate.

Determination of Purity. About 0.1 g of benzenediazonium fluoborate, weighed to 0.1 mg, was dissolved in 250 ml of cold, 0.01 M sulfuric acid. An aliquot was diluted fifty times with cold, dilute acid.
The extinction coefficient at 262 m\(_\mu\) was determined and compared to that of the pure compound, \(\epsilon_{\text{max}} = 1.25 \times 10^4\) 1/mole-cm. Reproducibility of 1% was routinely achieved.

**Rate Measurements for Sodium Bromide Solutions.** The method and apparatus have been described previously (20,55). Aliquots of a 1 M solution of J.T. Baker reagent grade sodium bromide were diluted to give the desired bromide ion concentration, with the final solution being 0.01 M in sulfuric acid. The solution, in the reaction vessel, was equilibrated with a thermostatted water bath. About 0.04 g benzene-diazonium fluoborate was added, giving a solution 5 \(\times\) 10\(^{-3}\) M in diazonium ion. A slow stream of nitrogen was passed through the solution to complete the mixing. After allowing time for equilibration, samples were removed through a capillary outlet under nitrogen pressure. The reaction was effectively quenched by cooling the aliquots in an ice bath.

A portion of the aliquot was transferred, using an accurate micro pipette, to a flask containing 0.5 ml of a saturated sodium bicarbonate solution of 0.1 M R-salt (2-naphthol-3,6-disulfonic acid disodium salt). The solutions were allowed to stand for at least one-half hour to ensure complete coupling, after which they were acidified with 1 ml of 1 M hydrochloric acid. The carbon dioxide evolved was removed by shaking. After diluting to 10 ml, the optical density of each solution at 490 m\(_\mu\) (\(A_{\text{max}}\) of the azo dye) was measured. The correction to the guessed rate constant is then the slope of logarithm of optical density plotted against time, measured graphically as obtained by application of eq 22.
\[-\Delta k = \frac{\sum t_i \sum \ln C_i - n \sum t_i \ln C_i}{\sum t_i^2 - n \sum t_i^2}\]  
Eq. 22

where $\Delta k$ is the rate constant correction, $\ln C$ is the natural logarithm of the optical density, $t$ is the time at which the sample was quenched and $n$ is the total number of samples.

The guessed rate constant ($k$), sample size ($\lambda$) and sampling time ($t$) are related by eq 23.

$$t_i = \frac{\ln(\lambda_i / \lambda_0)}{k}$$  
Eq. 23

Rate constants were reproduced to at least $\pm$ 0.5%.

**Rate Measurements for Sodium Iodide Solutions.** The data were obtained and the results corrected as described above. Preparation of the reaction solution was, however, different. The facile air oxidation of iodide ion in acid solutions requires prior deoxygenation of the solutions to be used. Pre-purified nitrogen passed through a Fieser's solution train was used for the deoxygenation (56). A second modification was to prepare the sodium iodide (Mallinckrodt analytical reagent grade) and benzenediazonium fluoborate solutions separately, mixing them only after complete deoxygenation and thermal equilibration.

The apparatus is shown in Figure 11. The modified 50 ml Erlenmeyer flask was stoppered with a sleeve type serum cap, through which a thin, short length of plastic tubing had been inserted. The tubing was used to hold a 1 cc glass bucket above the water level. The solutions were placed in the water bath and nitrogen passed through them for at least
Figure 11. Apparatus for Deoxygenation and Mixing of Benzenediazonium Ion and Sodium Iodide Solutions.
one-half hour. The diazonium salt was then placed in the glass bucket and sodium iodide was added to the solution in the reactor vessel. Deoxygenation was continued for another half hour. Removal of the plastic tubing dropped the bucket and allowed the diazonium salt to dissolve. Once the diazonium salt was in solution the tubing was rearranged so that the diazonium salt solution could be passed under nitrogen pressure into the reactor. Using this method contact with the air was kept to a minimum. The mixing of the solutions was completed one to two minutes after dissolution of the diazonium salt. Rate constants were reproduced to about ± 1%.

_Determination of Bromobenzene Yields._ The procedure used by Hartung was followed (20). In a typical run ca. 0.2 g, weighed to 0.1 mg, of benzenediazonium fluoborate was dissolved in 250 ml of cold, 0.01 M sulfuric acid having the required bromide ion concentration. A 100-ml aliquot was transferred to the reaction flask, which was then sealed and put into the water bath. After complete reaction (at least ten half-lives) the flask was cooled in an ice bath. The cold solution was transferred to a separatory funnel and sodium hydroxide solution added to ionize the phenol formed in the hydrolysis. A known amount of the internal standard (chlorobenzene) in petroleum ether (low boiling) was added; the solution was then extracted several times with low boiling petroleum ether and the extracts combined. The extract volume (50 ml) was reduced to 2-3 ml by distillation of the petroleum ether through a Nester-Faust spinning band column.
The relative amounts of chlorobenzene and bromobenzene were obtained by vapor phase chromatography; a 7-ft, 20% Carbowax 20 M on Chromosorb P column was used for the separation. Comparison of relative peak heights with a previously prepared graph of peak height ratios plotted against mole ratios gave the relative concentrations of the aromatic compounds. The amount of standard that had been used was known, so that the yield of bromobenzene could be readily determined. Reproducibility of ± 2% was achieved.

**Determination of Iodobenzene Yields.** The deoxygenation and mixing procedures described above were continued, with the apparatus scaled up to accommodate the large solution volumes. The reactor vessel was connected to the nitrogen stream to flush out air in the flask (see Figure 11). Following the deoxygenation procedure the iodide ion and diazonium salt solutions were mixed under nitrogen pressure; this solution was then pumped into the reactor, which was then sealed. The time required to mix the solutions, pump the final solution into the reactor and seal the vessel was less than five minutes. The reactor was wrapped in aluminum foil in order to inhibit photochemical decomposition of iodobenzene. The effectiveness of the foil wrapping was checked by carrying out a reaction in a flask wrapped with black tape; the iodobenzene yields were the same in both cases.

After complete reaction the flask was cooled in an ice bath, the solution transferred to a separatory funnel and then made basic by addition of sodium hydroxide. The iodobenzene was extracted with petroleum ether, after addition of the internal standard (bromobenzene)
to the aqueous solution in the separatory funnel. The time needed to reduce the extract volume was shortened by changing the distillation technique. The petroleum ether was distilled from a 125 ml round-bottom flask, through a small diameter (ca. 10 mm), four-inch Vigreux column. The flask containing the petroleum ether solution was heated in an oil bath kept at, or below, 70°, to prevent the distillation of bromobenzene or iodobenzene. The procedure was checked by carrying out several distillations using measured amounts of both bromobenzene and iodobenzene. The mole ratios were determined before and after distillation and found to be the same for these standards.

Comparison with a prepared graph was used to determine the iodobenzene yields. Instead of measuring peak heights the relative peak areas, as measured by a digital integrator, were used for iodobenzene yield determinations.

**Identification of Products from Reactions in Sodium Iodide Solutions.** Reactions of benzenediazonium ion in sodium iodide solutions give at least two major products, in addition to phenol and iodobenzene. The two major unknown products will be designated as compounds A and B for simplicity. There may be at least one other product, in low yields, formed in these reactions, although this has not been conclusively demonstrated.

Unless stated otherwise, it may be assumed in the following discussion that iodobenzene, iodine and phenol have been removed before carrying out the stated experiments.
The organic products are readily soluble in methylene chloride. The spectrum of the product mixture in this solvent shows relatively weak visible absorption, with a maximum at 430 ± 5 \( \mu \text{m} \). Very intense absorption occurs at 257 \( \mu \text{m} \), with a small shoulder at 250 \( \mu \text{m} \). Very poorly defined absorption is usually found at 310-320 \( \mu \text{m} \) and 330-340 \( \mu \text{m} \). Evaporation of the solvent leaves a yellow-brown residue, which has no apparent crystalline structure.

Dark brown material is removed by washing the residue with ethanol (this material is designated as compound A). The remaining solid (compound B) is pale yellow, and apparently noncrystalline. The ethanol solution shows absorption in the visible region centered at 430-435 \( \mu \text{m} \). The shoulders at 340 \( \mu \text{m} \) and 310-320 \( \mu \text{m} \) are seen. The intense absorption in the 250-260 \( \mu \text{m} \) region shows a small shift in its maximum which now occurs at 254.5 \( \mu \text{m} \). Absorption at 220-225 \( \mu \text{m} \) is present; this is not observed in methylene chloride solutions because of the end absorption of this solvent.

Concentration of the ethanol solution causes a small amount of yellow solid to precipitate (this is apparently identical with compound B). Further concentration or addition of water precipitates a brown solid. This solid has no melting point, but will decompose when heated to more than 150°.

If this solid (compound A) is allowed to stand in ethanol for one week a tar-like precipitate appears. The spectrum of the mother liquor is changed very little. Visible absorption is more broad, but the maximum is not shifted from 435 \( \mu \text{m} \). The shoulder at 220-225 \( \mu \text{m} \) has
become a true band with $\lambda_{\text{max}} = 225 \text{ m}\mu$. No change is apparent for the band at 254.5 m\mu.

The infrared spectrum of compound A has been recorded in carbon disulfide (spectral grade) using a Perkin-Elmer IR-8, double-beam spectrophotometer. The band positions are listed below as cm$^{-1}$. The symbols in parentheses have the usual meaning: w = weak, m = medium, s = strong, sp = sharp, b = broad.

3580 (m), 3550 (m), 3400 (w), 3050 (s), 3025 (s), 2920 (m), 2300 (w,b), 1940 (sp,m), 1900-1890 (w), 1870 (w), 1795 (w), 1475 (w), 1330-1280 (w), 1255 (sp,s), 1210 (w), 1170 (s), 1150 (m), 1100 (w), 1060 (m), 1015 (sp,s), 1000 (s), 940 (w), 910 (w), 820 (s), 765 (s), 740 (s), 690 (s), 645 (w), 610 (w).

This spectrum (and the others listed in this section) are interpreted in the Discussion section of this work.

Compound B (pale yellow, very slightly ethanol soluble) is soluble in methylene chloride. A spectrum of B in this solvent has only slight visible absorption, with no apparent $\lambda_{\text{max}}$. The only other absorption has $\lambda_{\text{max}} = 280 \text{ m}\mu$. The solid does not melt below 250°; above 200° some decomposition has been observed. The infrared spectrum (same conditions as for compound A spectrum) of compound B has been recorded; the band positions in cm$^{-1}$ are listed below.

3040 (w), 3010 (w), 2950 (w), 2250 (w,b), 2100 (w,b), 1260 (sp,s), 1090 (s), 1020-1000 (s), 710 (s), 690 (w). The C-H stretching bands are very weak, as are the bands at 2250 cm$^{-1}$ and 2100 cm$^{-1}$. 
A mixture of compounds A and B was washed twice with ethanol to remove most of the A compound. The remaining solid was left under ethanol overnight to take up as much compound B as possible. The ethanol solution containing B was left to stand for one week. The yellow-brown color was replaced by a pink-red color. Absorption in the ultraviolet showed some compound A to be present ($\lambda_{\text{max}} = 254 \text{ m}\mu$). A large change had occurred in the visible portion of the spectrum. A new band had appeared in the region of 400-570 m\mu, with the maximum at about 505 m\mu. The ethanol solution was treated with aqueous base and then extracted with methylene chloride. The extract was yellow-brown; the visible maximum at 505 m\mu was absent. The visible maximum was found to be at 430 m\mu. The methylene chloride solution (not dried) was left to stand for one hour. At the end of this time the red color had reappeared. The residue after evaporation of the solvent was red-brown. This phenomenon did not receive further examination.

Two sets of experiments have been carried out with the A-B mixture, bromination and tin-hydrochloric acid reduction. Treatment of the A-B mixture (from reaction in 0.4 M iodide ion solution at 32.8\degree) with aqueous tribromide ion, some ethanol added, gave a tar-like, dark brown-black product. A colorless, crystalline compound could be sublimed from the mixture (under aspirator vacuum and a temperature of 60-120\degree). The sublimed solid melted at 87-91\degree. In ethanol $\lambda_{\text{max}} = 296 \text{ m}\mu$, 288 m\mu. For comparison phenol was brominated to give 2,4,6-tribromophenol. Sublimation yielded colorless crystals melting at
88-92° (lit, 95°, 96°). The spectrum in ethanol was $\lambda_{\text{max}} = 296 \text{ m}_{\mu}$, 288 m$_{\mu}$. The two samples are apparently identical. The reaction of the A-B mixture with tribromide ion could have been due to the presence of phenol, because of an inadequate separation, or due to reaction of one of the unknown products.

Reaction of one possible product with tribromide ion was checked. The ultraviolet-visible spectra suggested the possible presence of benzeneazophenol in the product mixture, so this compound was prepared and brominated. Addition of the brominating solution to an ethanol solution of the azo dye immediately destroyed the intense color of the azo solution. The products were isolated and subjected to sublimation conditions. The sublimed product was identical with the sample of 2,4,6-tribromophenol cited above.

An A-B product mixture was subjected to reducing conditions, tin and hydrochloric acid treatment. Azo compounds are reduced to the parent amines by this procedure (58). If benzeneazophenol was present the expected products would be aniline and $p$-aminophenol. A small amount of ethanol was added to the reducing medium in order to help speed the reaction. Some reaction apparently occurred, since the dark brown color of the solution became lighter as the reaction progressed.

The isolated products had a light brown color. A brownish solution resulted from ethanol washing of the products, a colorless-pale yellow solid was not soluble in the ethanol. The ethanol solution had no apparent maximum in the visible region. In the ultraviolet a band with $\lambda_{\text{max}} = 265 \text{ m}_{\mu}$ was observed with absorption found also at 230 m$_{\mu}$ and 220 m$_{\mu}$.
The remaining material was taken up in methylene chloride. The only maximum observed was at 295 μm; other absorption was found at 278 μm and 270 μm (possibly due to phenol).

These spectra were compared with those of aniline (λ<sub>max</sub> = 294 μm) and of p-aminophenol (λ<sub>max</sub> = 300 μm). Neither of the amine spectra were identical to those of the reduction products.

If the reduction did yield amines they ought to be able to be diazotized, and the diazonium salt possibly isolated, and then hydrolyzed to the corresponding phenols.

As far as could be seen the brown reduction product did not react with concentrated hydrochloric acid (to form the amine hydrochloride). The colorless material apparently reacted with the acid, although treatment with a large excess of acid (to dissolve the amine salt) did not dissolve all of the solid present.

The hydrochloric acid washings were treated with sodium nitrite, giving a red-brown solution. Fluoboric acid was then added, in order to form the diazonium fluoborate salt, but no precipitate appeared, possibly because the solution was too dilute. The solution, presumably containing diazonium ion, was diluted with 150 ml of 0.01 M sulfuric acid and left at 33° overnight.

A methylene chloride extract of this solution absorbed in the ultraviolet, λ<sub>max</sub> = 285 μm. A change had taken place since the starting material (presumed to be a diazonium ion) had λ<sub>max</sub> = 296 μm. Isolation of the hydrolysis product(s) gave a colored solid, which was soluble in aqueous base. The basic solution was dark green. The only
maximum to be found was at 396 μ. The green color (and visible maximum) disappeared when the solution was acidified with sulfuric acid. The acid solution had \( \lambda_{\text{max}} = 300 \mu \).

This behavior was like that expected of one of the hydrolysis products, hydroquinone (from \( p \)-hydroxybenzenediazonium ion). In basic solution hydroquinone has two maxima, \( \lambda_{\text{max}} = 424 \mu, 402 \mu \). These are destroyed by addition of acid, the maximum shifting to 287 μ. The spectra of \( o \)- and \( m \)-dihydroxybenzene were recorded, but they did not resemble the spectra of the hydrolysis product. These products and the starting materials (including compound A and B) remain unidentified. Some suggestions as to the identities of A and B are to be found in the Discussion section.

**Reactions of Benzenediazonium Fluoborate and Sodium Iodide in the Solid State.** Mixing solid diazonium fluoborate and sodium iodide results in a rapid reaction. These reactions were carried out open to the atmosphere. This reaction should be performed with caution. The first time the solids were mixed (in small amounts) a vigorous evolution of iodine occurred. Subsequent experiments have not had this result, but it must not be ignored.

The reaction very rapidly produces iodine and iodobenzene; solid, colored, organic products can be isolated after the reaction is complete (several hours at room temperature). A methylene chloride solution of the solids has no maximum in the visible region. In the ultraviolet region there is a maximum at 250 μ and absorption at 330 μ. This, latter, band is not completely separated from shorter wavelength
absorption; however, it has very much more definition than the shoulders found in this region for aqueous reaction products (spectra in methylene chloride).

An infrared spectrum of the products was recorded in carbon disulfide; however, all of the solid was not soluble in this solvent, or in carbon tetrachloride. Band positions are given as cm\(^{-1}\).

3055 (m,w), 2910 (w,b), 2280 (w,b) 2100 (w,b), 1300-1240 (w,b), 1200 (w,b), 1060 (w), 1015 (w,sp), 1000 (m, sp), 820 (w), 745 (s,sp), 690 (s,sp).

**Determination of Iodine Yields.** Iodine concentrations were determined using spectrophotometric measurements. In solutions of iodide ion iodine is present largely as triiodide ion, which has a well defined ultraviolet absorption, \( \lambda_{\text{max}} = 350 \text{ m\(\mu\)}, \epsilon_{\text{max}} = 2.64 \times 10^4 \text{ 1/mole-cm}. \) The equilibrium constant for the reaction is 710 (57).

\[
\ce{I_2 + I^- <=> I_3^-}
\]  

(21)

The measurements were made, after complete disappearance of diazonium ion, by dilution of 1 ml of the reaction solution to either 10 ml or 25 ml, with 0.01 M sulfuric acid. The absorbance of the diluted solutions at 350 m\(\mu\) was immediately measured, with dilute acid as the reference solution. The data were corrected by adding a small amount of aqueous thiosulfate to the solutions and remeasuring the absorbance at 350 m\(\mu\).

It was assumed that for all solutions in which the iodide ion concentration was at least 0.1 M (original, not diluted concentration)
essentially all iodine was present as triiodide ion, so that the measured
ion concentration was the same as the total iodine concentration.

There is an error in this method, which has been "corrected"
empirically. The concentrations of triiodide ion in reaction solutions
was calculated by multiplying the measured absorbance values by the
square of the dilution factor (100 or 625) and then applying the tri-
iodide ion extinction coefficient, to obtain a concentration value.
These data were not internally consistent. The method was checked by
using the procedure for a solution of known iodine-iodide ion concen-
tration. The calculated values were too high; the solution which had
been diluted twenty-five times gave a calculated triiodide ion concen-
tration that was too large by a factor of seven, and the solution
dilated ten times yielded a value too large by a factor of 2.8. When
these "corrections" were applied to the data obtained for solutions of
unknown iodine concentration the results became internally consistent.

The iodine (or triiodide) concentration in solutions from reaction
at low iodide ion concentrations (0.01, 0.05 M) could be measured with-
out diluting the reaction solution. The results were those expected on
the basis of the "corrected" iodine concentrations, from reactions in
more concentrated sodium iodide solutions.

The data are not reproducible with a high degree of accuracy. It
is believed that they are, however, a reasonable representation of the
ture iodine concentrations.

Data on the concentration and rate of iodine formation at several
temperatures were obtained. The solutions used were degassed with
w-p grade nitrogen, hence oxygen was not completely excluded. In addition the diazonium ion and sodium iodide solutions were contacted with the air when mixed and when a sample of the mixed solution was transferred to the cuvette used in the analysis.

The absorbance at 350 μm was followed continuously using a Cary-Model 14 spectrometer. The sample cell compartment contained a metal block for holding the cuvette and this metal block was connected to a continuously circulating, thermostatted water supply.

The bulk of the data was obtained at 18°. Cold water was passed through a thermostatted water pump and then to the metal sample-cell block. The temperature of the block was within 1-2° of the thermostat temperature setting.

The sample cell length was generally 1 mm; a longer path generally did not allow the absorbance to come on scale (i.e., A was ≥ 2) and a shorter path length did not allow thorough mixing of the solution as the reaction progressed. The sample cell cuvette had to be shaken regularly since nitrogen bubbles tended to collect on the cell windows.

Blank determinations in the absence of diazonium ion showed that air oxidation of these iodide ion solutions (< 0.1 M) was negligible for at least one hundred minutes. After this time absorbance at 350 μm due to iodide ion air oxidation became appreciable.

The benzenediazonium concentration was varied from about 5 x 10⁻³ M to about 1 x 10⁻² M for the various determinations. The iodide ion concentrations used were from 1 x 10⁻³ M to 1 x 10⁻¹ M. At the highest diazonium and iodide ion concentrations it was necessary to use a 0.1 mm
path length sample cell in order to keep the recorded absorbance on scale.

**Rate Measurements in Iodine Solutions.** The effect of iodine on the hydrolysis rate of benzenediazonium ion was measured, in the absence of iodide ion. Reactions were carried out in air-saturated acid solutions. The required iodine concentration was obtained by diluting an aqueous, acid solution which had been saturated with iodine at room temperature \( (I_2 = 1.3 \times 10^{-3} \text{ m/l}) \).

The usual procedures for measuring rates and correcting the data obtained were used (see above).

**Products of Reaction in Iodine Solutions.** Hydrolysis of benzenediazonium ion was carried out in a deoxygenated solution saturated with iodine \( (I_2 = 1.3 \times 10^{-3} \text{ m/l}) \). The apparatus and isolation method for measurement of iodobenzene yields was used (see above). Vapor phase chromatography revealed the absence of iodobenzene. Some substance was eluted which had a retention time comparable to iodobenzene. The elution period, however, was on the order of several minutes, the chromatogram being a low, broad plateau and not a resolved peak.

The ultraviolet spectrum of a reaction solution (iodine-saturated) showed only phenol absorption, \( \lambda_{\text{max}} = 270 \ \mu \text{m} \), \( c_{\text{max}} = 1450 \text{ l/mole-cm} \). The yield of phenol was calculated using its extinction coefficient (calculated phenol = 106%).

The phenol yield was measured after diazonium ion hydrolysis in a solution \( 5 \times 10^{-4} \text{ M} \) in iodine. The ultraviolet spectrum revealed the presence of phenol only. The yield was calculated using the data for
phenol in base, $\lambda_{\text{max}} = 287 \text{ m}\mu$, $\varepsilon_{\text{max}} = 2600 \text{ l/mole-cm}$. A quantitative phenol yield was calculated.

It was observed in some of the above reactions that the iodine color disappeared, even when the reaction vessel was sealed. Since products other than phenol have not been found there is no available explanation to account for this phenomenon.

**Iodobenzene Yields from Air-Saturated Solutions.** The hydrolysis of diazonium ion in iodide ion solutions was performed in the usual manner for determination of iodobenzene yields, except that oxygen was not removed from the solutions prior to reaction. Only one run was made for each of the iodide ion concentrations.

**Determination of Phenol Yields.** Hydrolysis of the diazonium ion in iodide ion solutions was carried out using the methods for kinetic determinations, except that no samples were taken. The reaction solutions were left in the water bath for at least ten half-lives. After this time a 1-ml aliquot was diluted to either 10 ml or 25 ml with aqueous sodium hydroxide. The absorbance of the solution was measured at 287 m\(\mu\) ($\lambda_{\text{max}}$ of phenoxide ion), with water used as the reference. The only blank correction applied was the measured absorbance when both cuvettes were filled with water.

The measured absorbance was corrected for the dilution and the concentration of phenoxide ion calculated using its extinction coefficient ($\varepsilon_{\text{max}} = 2600 \text{ l/mole-cm}$). The accuracy of this method is probably no better than ± 5%. It appears reasonable to assume that the calculated yields represent an upper limit for the true phenol concentrations.
Rate Measurements in Sodium Perchlorate Solutions. The method used was identical to that employed when sodium bromide was the added salt (see above). Rate measurements were initially carried out using G. Frederick Smith Co. reagent grade salt, with no prior purification. Subsequent data were obtained using sodium perchlorate (from the above source) which had been purified by one or both of two methods.

The first purification employed was recrystallization from hot, glacial acetic acid. The anhydrous salt is obtained by drying the isolated salt under vacuum at the temperature of refluxing ethylene glycol. Rate data were obtained using this salt and with perchlorate salt purified in this way and then subjected to the treatment below.

Aqueous solutions of sodium perchlorate were extracted with benzene solutions of the heavy metal complexing agent 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione. The aqueous solution was then diluted to give the required salt concentrations.

Rate constants obtained using each of the salts, treated as described above, were uniformly non-reproducible. The measured rate constants were always higher than that for hydrolysis of benzenediazonium ion in water alone.

Products from Reactions in Sodium Perchlorate Solutions. Rate increases in perchlorate ion solutions were accompanied by the appearance of colored precipitates and reaction solutions. The development of color was fairly slow (at 40.1°C); the maximum intensity was not attained until the reaction was approximately half completed. The color intensity and amount of precipitate were variable, but the reason is not known. The reaction solutions were not deoxygenated.
The anomalous reaction was found to be independent, at least to some degree, of the source of sodium perchlorate. Reaction carried out with sodium perchlorate prepared by neutralization of perchloric acid was, qualitatively, the same as when commercial salt was used. (We would like to thank Dr. David Chalmers for generously supplying a sample of sodium perchlorate prepared by neutralization of the acid.)

Spectra of aqueous solutions after complete reaction have visible region absorption, but no maximum. The characteristic phenol band is seen at 270 m\(\mu\) and 210 m\(\mu\). There is also a maximum at 242-244 m\(\mu\).

After extracting the solution with small amounts of ether or chloroform the only absorption in the spectrum of the aqueous solution is at 242-244 m\(\mu\). This maximum did not shift as the solution was made progressively more basic (pH = 8-11). When the solution was made 1 M in hydroxide ion the maximum at 242 m\(\mu\) disappeared and was replaced by absorption at 310-324 m\(\mu\). This may have been two unresolved bands rather than a single one.

An aqueous reaction solution was extracted many times with ether in order to collect as much of the products as possible. The extracts were concentrated and the nmr spectrum recorded, in ether. The only absorption found was in the aromatic proton region, and the pattern resembled that of phenol.

An isolated product mixture was brominated and the nmr spectrum of the recovered material recorded. There was a single peak present, at \(\delta = 7.6\) ppm downfield from TMS. This spectrum was assumed to be that of 2,4,6-tribromophenol. It is not known whether the products were all
brominated in the same manner, or whether other products were not isolated after the bromination.

Infrared spectra of two products, other than phenol, were obtained. The first spectrum is for material extracted into ether from the reaction solution. The spectrum was obtained in carbon tetrachloride, using a double beam instrument. Band positions are listed in units of cm\(^{-1}\).

3630 (w), 3580 (w), 3070 (w), 3040 (w), 2970 (sp,m), 2940 (sp,s), 2860 (sp,w), 1760 (w), 1650 (w), 1460-1440 (w), 1255 (sp,s), 1070 (s), 1000 (s).

This spectrum is nearly identical to that of one of the products from reaction of benzenediazonium ion in iodide ion solutions (compound B).

The second product was isolated by chloroform extraction of the reaction solution. The solvent was evaporated and the spectrum recorded in carbon tetrachloride, using a double beam instrument.

3630 (sp,m), 3570 (w), 3400 (m), 3040 (w), 2960 (sp,s), 1705 (s), 1655 (s), 1645 (s), 1580 (s), 1485 (sp,m), 1470 (sp,m), 1460 (sp,m), 1345 (m), 1330 (sp,w), 1290 (sp,m), 1250 (s), 1205 (w), 1170 (w), 1140 (w), 1075 (s), 1015-1000 (s), 900 (w), 870 (s), 680 (w).

Unfortunately, the use of carbon tetrachloride as solvent obscures absorption in the 700-850 cm\(^{-1}\) region, so that the aromatic substitution patterns are unknown.

Similarities between reactions in perchlorate and iodide ion solutions are compared in the Discussion section of this work.
SUMMARY

The reaction of benzenediazonium ion in aqueous chloride salt solutions has been postulated to be bimolecular, both for formation of phenol and for chlorobenzene. This result is in contrast to the previously accepted first-order, two-step mechanism for diazonium ion decompositions.

The purpose of the present study was, in part, to obtain further support for the postulated bimolecular decomposition mechanism. The reaction of benzenediazonium ion in sodium bromide solutions at 40.1° has been found to be consistent with the bimolecular mechanism. Decomposition rates of the diazonium ion have been correlated with yields of products, by taking account of salt effects. It was found that bromide ion is a better nucleophile toward the diazonium ion than is chloride ion, although both halides are less effective than in aliphatic, nucleophilic substitution reactions.

Reactions of benzenediazonium ion in solutions of sodium iodide appear to be in part like those of the ion in bromide and chloride ion solutions. However, other reactions are observed, which do not correspond to simple replacement of the diazonio nitrogen. Correlation of rate and product yield results, from reactions at 40.1° and 32.8°, suggest a high degree of direct bimolecular substitution in this system; this suggestion is qualified due to the possible reaction of triiodide ion to form iodobenzene and because as much as forty percent of the diazonium ion cannot be accounted for by apparent yields of phenol and iodobenzene.
The "side reactions" have been interpreted as possibly arising from interaction of iodide ion and diazonio nitrogen, to form a complex which may have incipient radical character. Such a complex may be responsible for the unidentified, organic products observed. Formation of iodine may be due to such a process as well, or, alternatively, to an equilibrium reaction involving diazonium ion and iodide ion on one side and triiodide ion and a reduced diazonium species on the other side of the equilibrium.
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