HARTUNG, Levoy Dee, 1936—
BIMOLECULARITY IN DIAZONIUM ION
HYDROLYSIS.

Rice University, Ph.D., 1966
Chemistry, organic

University Microfilms, Inc., Ann Arbor, Michigan
RICE UNIVERSITY

Bimolecularity in Diazonium Ion Hydrolysis

by

Levoy Dee Hartung

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
Doctor of Philosophy

Thesis Director's signature:  

Houston, Texas

June 1966
ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. E.S. Lewis for conceiving and guiding this study. The author is also grateful to Rice University and the Robert A. Welch Foundation for financial support.
"The highest that we can attain to is not Knowledge, but Sympathy with Intelligence."

--Thoreau
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INTRODUCTION

The thermal solvolysis mechanism of the aromatic diazonium salts has been a perplexing issue ever since the first investigations around 1900. Not only does the mode of nitrogen loss apparently change with hydrogen ion concentration (1), but certain catalysts, such as copper and cuprous salts, accelerate and alter the decomposition process (2). Both radical and ionic C-N bond cleavage are required to explain the various observations.

In polar solvents, diazonium salts normally behave as strong electrolytes (3), giving a diazonium cation relatively free from its anion. This cation decomposes under the influence of heat or light, involving loss of the diazonio group as nitrogen and replacement of it by a nucleophile. Such a nucleophile may be a dissolved anion or derived from the solvent molecule.

Thermal hydrolysis of diazonium salts at pH below 7 has been studied in detail, and phenol is known to be the major product. Nearly all the evidence supports a first-order rate of decomposition, obeying the two-step mechanism written by Waters (4). Waters' mechanism postulates nitrogen loss in a slow, rate-determining first step to give an aryl cation which is rapidly attacked by a water molecule (or other nucleophile) in a second fast step, neither step being reversible:

\[
\text{ArN}^+_2 \xrightarrow{\text{slow}} \text{Ar}^+ + \text{N}_2 \xrightarrow{\text{fast}} \text{ArOH} + \text{H}^+ \quad (1)
\]
The evidence overwhelmingly seems to support this mechanism and historically, nearly all the arguments until the 1950's favored an aryl cation intermediate. The minor deviations from first-order kinetics were usually rationalized as insignificant, and other kinetic schemes which would give apparent first-order kinetics were not considered to explain these deviations. Some of the strong evidence for the kinetically first-order, two-step mechanism will now be discussed.

Moelwyn-Hughes and Johnson (5) measured first-order rate constants for the benzenediazonium ion decomposition over a wide range of temperatures and were able to prepare an accurate Arrhenius plot. DeTar and Ballentine (6) made precise rate measurements showing that acidity and the nature of the anion have no significant effect at small concentrations. Other evidence showing that acidity and anions have little effect on the rate was found by Cain (7) and Euler (8). Pray (9) showed that the rate is nearly insensitive to the presence of a wide variety of added metal salts.

Furthermore, diazonium ions demonstrate low selectivities in various solvent mixtures, as shown by Pray (10) and confirmed by Godfrey (11). Godfrey found that in equimolar water-methanol mixtures nearly equivalent amounts of phenol and anisole are formed.

Low selectivities for dissolved anions are also observed. Pfeil (12) showed that in concentrated aqueous sodium chloride solution, the yield of p-nitrophenol from p-nitrobenzenediazonium salt is always proportional to the molar ratio of water to chloride ion. In a more precise study, Lewis (13) measured competition factors between chloride ion and water for the unsubstituted benzenediazonium
ion in its decomposition in aqueous sodium chloride or hydrochloric acid. The competition factor, $k_{Cl} / k_{Br}$, found by Lewis ranged from 2.0 to 3.5. Such small ratios are consistent with an unselective intermediate such as the phenyl cation. Cooper (14) found this intermediate to be nearly equally reactive with both ends of the thiocyanate ion, also consistent with a very unselective species.

Another reaction strongly implies the aryl cation as an intermediate. For instance, Sandin and Hay (15) were able to prepare diphenyleneiodonium iodide from diazotized 2-amino-2'-iodobiphenyl as shown in reaction 2.

\[
\begin{align*}
\text{[Image: Reaction 2]} \quad &
\end{align*}
\]

The intermediacy of the shown aryl cation was not demonstrated, but they prepared similar halonium salts for the corresponding chloride and bromide. Then Nesmeyanov, Makarova and Tolstaya (16) succeeded in making oxonium salts and non-cyclic halonium salts such as $\text{Ar}_3\text{O}^+\text{BF}_4^-$ and $\text{Ar}_2\text{Cl}^+\text{BF}_4^-$ by decomposing aryl diazonium salts in the presence of the aryl ether or aryl chloride. An example of the salts they prepared is diphenylbromonium fluoborate.

Only slight changes in the decomposition rates are observed when the alkyl substituents at various positions on the aromatic ring are altered so as to change their electron-donating ability. For instance, Lewis and Miller (17) found only a maximum variation of 1.8 in the
ratio of the rates for a series of para alkyl-substituted diazonium salts having from zero to three alpha hydrogens. An aryl cation intermediate could not be stabilized by hyperconjugated resonance structures as shown below because of the orthogonality of the vacant orbital with the $\pi$ orbitals. Stabilization can occur only through an inductive effect, thus explaining the small variations.

The evidence supporting the aryl cation mechanism is therefore extensive. Inherent in this two-step decomposition is the supposition that the rate-determining and product-determining steps in the reaction are different. The first step is merely the rate-limiting production of aryl cations. Once formed, the aryl cation immediately reacts with a nucleophile to give the observed products. Two distinct steps are implied and the product distribution should not depend on the rate at which diazonium ions decompose. In other words, reaction of a nucleophile with the aryl cation depends only on the nature of this intermediate and not on its source or how rapidly it appears.

For such a reactive species as the aryl cation, combination with a nucleophile would be expected to occur with almost no activation energy and the product distribution would then be independent of the reaction temperature, in close agreement with observed facts (13). The product ratio should also be linearly related to the solution
composition for various mixtures, but this is not in strict agreement
with observation for potassium thiocyanate solutions (18) for example,
although salt effects offer a possible explanation for the deviation.

However, Field and Franklin (19) questioned the formation of an
aryl cation intermediate because no rearrangements are ever observed
as would be expected by analogy with their gas phase studies of aryl
cations in the mass spectrometer. Of course the analogy to solution
is weak, but the benzyl cation and the tolyl cation appear to be
identical when formed in the mass spectrometer and rearranged products
would then be expected from decomposition of the p-toluenediazonium
ion in solution if it produces a tolyl cation.

A pathway involving a reversibly-formed intermediate which reverts
to diazonium ion much faster than it reacts bimolecularly with the
nucleophiles present would also obey the observed first-order kinetics.
Such a mechanism was proposed by Lewis and Cooper (20) to explain the
rate accelerations of benzenediazonium ion hydrolysis in the presence
of thiocyanate ion. In this study, five molar potassium thiocyanate
increased the rate by about twenty percent at 40°C. over the value
with no salt present. The structure of the intermediate could only
by speculated on, but the proposed mechanism is shown below, where
X⁻ represents some anion:

\[
\begin{align*}
\text{ArN}_2^+ & \overset{k_1}{\rightleftharpoons} [\text{ArN}_2^+]^* \\
[\text{ArN}_2^+]^* + \text{H}_2\text{O} & \overset{k_2}{\rightarrow} \text{ArOH} + \text{N}_2 + \text{H}^+ \\
[\text{ArN}_2^+]^* + \text{X}^- & \overset{k_3}{\rightarrow} \text{ArX} + \text{N}_2
\end{align*}
\]

(3) (4) (5)
The existence of a reversible step in the mechanism is supported by Lewis and Insole's observation (21) that isotopic rearrangement of the nitrogens accompanies the hydrolysis of a labelled diazonium salt. A nitrogen-15 label in the alpha position shifts to the beta position at 1.4% of the hydrolysis rate for the benzenediazonium ion, as shown in the following reaction:

$$\text{(C}_6\text{H}_5\text{N}^{15}\text{N})^+ \rightarrow \text{(C}_6\text{H}_5\text{N}^{15}\equiv\text{N})^+$$  \hspace{1cm} (6)

Lewis and Insole later found that the isotopic shift is greater for p-toluenediazonium ion (18); in this case the isomerization rate is 2.9% of the hydrolysis rate. Such observations suggest that the carbon-nitrogen bond is broken, or nearly so, in the reversibly-formed intermediate previously proposed, but an intermediate with indistinguishable nitrogen atoms was excluded.

Both the nitrogen turnaround and the acceleration of the hydrolysis by thiocyanate ion were later reconciled by Lewis and Insole (22) by postulation of two intermediates. One could be an unselective species resembling the oft-advanced aryl cation and the other could have the spirocyclic nitrogen structure as given for the p-toluenediazonium ion:

![](image)

The observed kinetics with thiocyanate ion fit a scheme involving two such intermediates.
Further investigation of the nature of the nitrogen turnaround has been done. In a recent study, Holliday (23) found the percent turnaround for p-toluenediazonium ion to be unchanged by the presence of 3M potassium bromide. Although the hydrolysis rate increases with low concentrations of added potassium bromide, further addition of this salt causes the rate to fall off so that at 3M the rate is identical to that in water. However, the turnaround's insensitivity to the presence of bromide is not consistent with a scheme involving both a selective and an unselective intermediate.

Other cases have been reported where added electrolytes cause rate accelerations or reductions. A striking example was uncovered by Lewis and Hinds (24) in their study of the reaction of bromide ion with p-nitrobenzenediazonium ion. Eight molar sodium bromide accelerates the rate by a factor of two, and the rate data fit a scheme involving unimolecular loss of nitrogen accompanied by bimolecular displacement by bromide ion. The apparent first-order rate constant is given by Eq. 1:

\[ k_{\text{apparent}} = k_1 + k_2(\text{Br}^-) \]  

Eq. 1

Here is an example of probable bimolecular kinetics in the diazonium ion decomposition. In fact, a scheme proposing bimolecular reaction of p-nitrobenzenediazonium ion with both water and bromide ion will fit the observed kinetics and product distribution in this case.

As another example, p-benzenetetrazonium ion reacts with chloride, bromide, or thiocyanate ion with almost pure second-order kinetics, yielding the corresponding p-substituted benzenediazonium ion, as
found by Lewis and Johnson (25). These reactions are so fast that room temperature or below is required to limit the rate for measurement by the spectrophotometric method used. The question that arises is whether this represents a change of mechanism for the substituted diazonium ions or is merely an exaggeration of an effect present in all diazonium ion decompositions.

Replacement of the diazonio group by a nucleophile is a reaction within the class of nucleophilic substitutions at aromatic carbon (26). Such nucleophilic substitutions are promoted by the influence of strong electron-withdrawing groups in the ortho and para ring positions (27), among which are the nitro and diazonio groups. The three possible mechanisms of nucleophilic aromatic substitution given by Bunnett (26) in his review include the $S_{N}^{1}$, or carbonium ion pathway, the $S_{N}^{2}$ (bimolecular) mechanism, and the elimination-addition (benzyne) mechanism. Bunnett states: "The great majority of aromatic nucleophilic substitutions occur by a bimolecular mechanism." He further says that the carbonium ion mechanism is rare for these aromatic substitutions, and, "It is well-established only for the thermal decomposition of diazonium cations in aqueous solution."

The bimolecular nucleophilic substitution, or $S_{N}^{2}$Ar reaction, is best understood in terms of an intermediate formed by addition of the nucleophile to the aromatic ring, or Meisenheimer complex. Such a complex was proposed by Ainscough and Caldin (28) for the displacement of methoxide by ethoxide in 2,4,6-trinitroanisole:
This type of intermediate, although not isolable, could also be written for the reactions with the p-nitrobenzenediazonium and p-benzenetetrazonium ions and would explain the observed bimolecular kinetics.

The kinetics for diazonium ions not containing these activating substituents appear to be bimolecular only in part, a first-order term comprising the major portion of the rate. Perhaps this is because the tendency to form a Meisenheimer-type complex is so greatly reduced, and nitrogen must be displaced before a nucleophile can attach itself to the aromatic ring.

Blumberger (29), suspecting a dependence of the rate on water concentration, measured rates of decomposition of the unsubstituted
benzenediazonium ion at 40°C. in the presence of various inorganic electrolytes. He used very concentrated solutions so the water concentration would decrease to a significant extent. But only in the case of potassium chloride did his observed rates closely match those predicted from the reduced water concentration. His data can perhaps best be presented as a plot of observed first-order rate constant with electrolyte present, \( k \), relative to the first-order rate constant in water, \( k_0 \), as shown in Fig. 1.

![Graph](image)

**Fig. 1**

Relative First-order Decomposition Rates for the Benzenediazonium Ion in Aqueous Potassium Chloride Found by Blumberger (29)
Poor agreement was found for other electrolytes, with the observed rates for hydrochloric acid above the theoretical and those for sulfuric acid, sodium sulfate, sodium chloride, and potassium nitrate below the theoretical water concentrations. In nitric acid, no simple pattern was observed as seen in Fig. 2.

![Graph](image)

Fig. 2

Relative First-order Decomposition Rates for the Benzenediazonium Ion in Nitric Acid Found by Blumberger (29)
The effects are small, but Blumberger's results still show no close correspondence with the water concentration. Nevertheless, the deviations are large enough to be real and they indicate that the rate of diazonium ion decomposition is dependent on added electrolytes to some extent. The problem is clouded by salt effects and the presence of more than one nucleophile.

Blumberger's results are not readily understood in terms of the two-step, aryl cation mechanism. Added electrolytes should affect the rate of diazonium ion decomposition only if they are in some way involved in the rate-determining step of the reaction. One possible explanation is that the rate-determining step is really bimolecular and therefore the rates are responsive to changes in the composition of the medium.

However, bimolecularity in the rate-controlling step should be reflected in the product distribution as well as in the rate changes. The purpose of this study was to obtain new data on the decomposition rates and chlorobenzene yields in various aqueous chloride salt solutions, and to correlate these data to see if the product ratio changes are concurrent with the rate changes. Are the product-determining and rate-determining steps in the reaction indeed the same? In other words, is the attacking nucleophile present in the rate-controlling transition state?

Products arising from the photochemical decomposition are of the same nature as those from the thermal process, suggesting a similar intermediate in both cases. Lee, Calvert and Malmberg (30) found p-nitrophenol and p-nitrochlorobenzene as the products from the
photolysis of \( p \)-nitrobenzenediazonium salt in aqueous sodium chloride solutions, which apparently arise only from a heterolytic loss of nitrogen. However, Boudreaux and Boulet (31) felt that free radicals were involved in the photolytic decomposition of \( p \)-dimethylamino-benzenediazonium salt, as supported by their magnetic susceptibility measurements. Questioning this result, Zandstra and Evleth (32) investigated the same system and obtained an electron spin resonance spectrum corresponding to the \( p \)-dimethylamino phenoxy radical, suggesting that this was the paramagnetic species responsible for the measured magnetic susceptibilities. The implication is that aryl radicals are not necessarily involved in the mechanism of nitrogen loss, since a paramagnetic species could be formed from the \( p \)-dimethylaminophenol product.

For any discrete intermediate, the product distribution should be independent of the origin of this intermediate. Therefore, it was of further interest to find how closely the photochemical decomposition resembled the thermal process, as indicated by the relative yields of chlorobenzene and phenol in sodium chloride solutions.
RESULTS

Results obtained in this study are the yields of chlorobenzene and first-order rate constants for the benzenediazonium ion decomposition in acidic (pH=2) aqueous solutions of chloride salts. First-order rate constants were also measured for the hydrolysis of benzenediazonium ion and the three isomeric toluenediazonium ions in aqueous bisulfate salt solutions.

Table I presents the chlorobenzene yields, as percent, for the hydrolysis of the benzenediazonium ion. In aqueous sodium chloride, yields are tabulated for photochemical decomposition at 5°C and for thermal decomposition at 3, 40, and 50°C. Chlorobenzene yields are also given for thermal hydrolysis in lithium chloride and tetra-n-butylammonium chloride at 40°C. Standard unbiased deviations for the thermal yields at 3°C in 0.258, 1.76, and 3.51 M sodium chloride are, respectively, 1.1, 4.2, and 2.1% of the mean.

Competition factors given in Table I were calculated from the yields by Eq. 2, using the water concentration determined from standard densities. The phenol yield was calculated as 100 minus the chlorobenzene yield in percent, an operation considered valid (13) on the basis of previous results for the thermal decompositions. The same assumption of quantitative conversion of the diazonium ion to only chlorobenzene and phenol was considered reasonable for the photochemical runs on the basis of the nitrogen yields close to 100% found in this study (see Experimental).
Table I

Chlorobenzene Yields and Competition Factors for Benzenediazonium Fluoborate in Aqueous Chloride Salt Solutions  
\((H_2SO_4 = 0.01 \text{ M})\)

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<th>Temperature</th>
<th>Chloride Salt, MCl</th>
<th>MCl Conc., m/1</th>
<th>Chlorobenzene Yield, %</th>
<th>Competition Factor, (k_{Cl}/k_{W})</th>
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<td><strong>Photochemical runs</strong></td>
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<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>.582</td>
<td>4.24</td>
<td>4.16</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>.61</td>
<td>3.7 (13)</td>
<td>3.5 (13) (d)</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>.864</td>
<td>5.83</td>
<td>3.87</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>.864</td>
<td>5.96</td>
<td>4.01</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>1.22</td>
<td>7.68</td>
<td>3.70</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>2.08</td>
<td>11.5</td>
<td>3.30</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>2.08</td>
<td>10.5</td>
<td>3.00</td>
<td></td>
</tr>
</tbody>
</table>

(a) Calculated from Eq. 2.
(b) These runs were done in an ice bath, and the temperature varied between 2 and 8°C.
(c) This temperature varied ± 2°C.
(d) 55.5 M was used for the water concentration.
Chlorobenzene Yields for Benzenediazonium Fluoborate Decomposition in Aqueous Sodium Chloride

Fig. 3

(Original Data in Table I)
Fig. 4

Competition Factors for Benzenediazonium Fluoborate Decomposition in Aqueous Sodium Chloride

(Original Data in Table I)
\[
\frac{k_{\text{Cl}}}{k_{\text{W}}} = \frac{Y_{\text{ArCl}(H_2O)}}{Y_{\text{ArOH}(Cl^-)}}
\]  
(13) Eq. 2

Figure 3 is a plot of chlorobenzene yield as a function of chloride ion concentration for the 40° runs in sodium chloride and is typical of the yields for the other chloride solutions. Figure 4 shows the thermal and photochemical competition factors obtained at temperatures close to 5° plotted together. The competition factor varies only slightly with temperature, so all the values are reasonably valid for 5°.

Table II tabulates the observed first-order rate constants for the hydrolysis of benzenediazonium fluoborate in solutions of the chlorides and bisulfates of sodium, lithium, and tetra-n-butylammonium ions. All the data are for a temperature of 40.14 ± 0.02°, determined by a National Bureau of Standards thermometer. Relative rate constants, or \( k/k_o \), are calculated for each observed \( k \), using the first-order rate constant with no added electrolyte as \( k_o \) (41.51 x 10^{-5} \text{sec}^{-1}). Each value of \( k \) is for one run, but \( k_o \) was determined precisely, where the standard unbiased deviation for seven runs is 0.51%.

Figure 5, a plot of the calculated values of \( k/k_o \) in the chloride solutions, shows how the relative rate constant varies with added chloride salt concentration.

Observed first-order rate constants for the decomposition of o-, m-, and p-toluenediazonium fluoborate in aqueous solution at 40.14 ± 0.02° are given in Table III. These data are somewhat less
Table II

First-order Rate Constants for Benzenediazonium Ion Hydrolysis
in Electrolyte Solutions
\( (T = 40.14 \pm 0.02 ^\circ, H_2SO_4 = 0.01 \, M) \)

<table>
<thead>
<tr>
<th>Added Electrolyte</th>
<th>Electrolyte Conc., m/l</th>
<th>( k \times 10^5 ) (sec(^{-1}))</th>
<th>( k/k_o )</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0</td>
<td>41.51 ± 0.21</td>
<td>1.000</td>
</tr>
<tr>
<td>&quot;</td>
<td>0</td>
<td>41.36 (a)</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>0</td>
<td>41.4 (b)</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>0.10</td>
<td>41.37</td>
<td>0.997 (c)</td>
</tr>
<tr>
<td>&quot;</td>
<td>.25</td>
<td>41.46</td>
<td>.999</td>
</tr>
<tr>
<td>&quot;</td>
<td>.25</td>
<td>41.48</td>
<td>.999 (c)</td>
</tr>
<tr>
<td>&quot;</td>
<td>.50</td>
<td>41.17</td>
<td>.992 (c)</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.00</td>
<td>40.53</td>
<td>.976 (c)</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.01</td>
<td>41.04</td>
<td>.988</td>
</tr>
<tr>
<td>&quot;</td>
<td>2.02</td>
<td>39.7 (d)</td>
<td>.955</td>
</tr>
<tr>
<td>&quot;</td>
<td>2.02</td>
<td>39.8 (d)</td>
<td>.959</td>
</tr>
<tr>
<td>LiCl</td>
<td>0.34</td>
<td>41.20</td>
<td>0.992</td>
</tr>
<tr>
<td>&quot;</td>
<td>.69</td>
<td>40.87</td>
<td>.984</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.00</td>
<td>40.73</td>
<td>.981</td>
</tr>
<tr>
<td>&quot;</td>
<td>2.00</td>
<td>39.63</td>
<td>.955</td>
</tr>
<tr>
<td>&quot;</td>
<td>3.00</td>
<td>38.38</td>
<td>.925</td>
</tr>
<tr>
<td>(n-Bu)(_4)NC1</td>
<td>0.20</td>
<td>41.63</td>
<td>1.003</td>
</tr>
<tr>
<td>&quot;</td>
<td>.31</td>
<td>42.23</td>
<td>1.017</td>
</tr>
<tr>
<td>&quot;</td>
<td>.40</td>
<td>44.47</td>
<td>1.071</td>
</tr>
<tr>
<td>&quot;</td>
<td>.50</td>
<td>42.48</td>
<td>1.023</td>
</tr>
<tr>
<td>&quot;</td>
<td>.80</td>
<td>42.48</td>
<td>1.023</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.01</td>
<td>42.07</td>
<td>1.013</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.38</td>
<td>42.72</td>
<td>1.029</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.70</td>
<td>43.98</td>
<td>1.059</td>
</tr>
</tbody>
</table>
Table II (con't.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Value 1</th>
<th>Value 2</th>
<th>Value 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaHSO₄</td>
<td>0.25</td>
<td>40.13</td>
<td>0.967</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.50</td>
<td>38.63</td>
<td>0.931</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.00</td>
<td>36.38</td>
<td>0.876</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.50</td>
<td>33.43</td>
<td>0.806</td>
</tr>
<tr>
<td>LiHSO₄</td>
<td>0.25</td>
<td>39.18</td>
<td>0.944</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.50</td>
<td>37.51</td>
<td>0.903</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.75</td>
<td>36.28</td>
<td>0.874</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.00</td>
<td>35.33</td>
<td>0.851</td>
</tr>
<tr>
<td>(n-Bu)₄NHSO₄</td>
<td>0.10</td>
<td>40.30</td>
<td>0.971</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.20</td>
<td>39.65</td>
<td>0.955</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.31</td>
<td>38.49</td>
<td>0.927</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.39</td>
<td>37.87</td>
<td>0.911</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>0.25</td>
<td>39.50</td>
<td>0.951</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.25</td>
<td>39.62</td>
<td>0.954</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.50</td>
<td>38.74</td>
<td>0.933</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.75</td>
<td>37.68</td>
<td>0.908</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.00</td>
<td>36.69</td>
<td>0.884</td>
</tr>
</tbody>
</table>

(a) Calculated from the Arrhenius parameters given by DeTar and Ballentine (6).

(b) Observed value by Pray at 40.0°C. (9).

(c) Unpublished results by E.M. McKay.

(d) Data by Blumberger (29).
Fig. 5

Relative First-order Hydrolysis Rates for the Benzenediazonium Ion in Chloride Salt Solutions

(Original Data in Table II)
Table III

First-order Rate Constants for Selected Diazonium Ion Hydrolyses
(T = 40.14±0.02°)

<table>
<thead>
<tr>
<th>Diazonium Ion</th>
<th>Water at pH2 $k_0 \times 10^5$ (sec$^{-1}$)</th>
<th>1/2M NaHSO$_4$ $k \times 10^5$ (sec$^{-1}$)</th>
<th>$k/k_0$</th>
<th>1M NaHSO$_4$ $k \times 10^5$ (sec$^{-1}$)</th>
<th>$k/k_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene-</td>
<td>41.51±0.21 (a)</td>
<td>38.63</td>
<td>0.931</td>
<td>36.38</td>
<td>0.876</td>
</tr>
<tr>
<td>o-Toluene-</td>
<td>185.2±1.7 (b)</td>
<td>173.9</td>
<td>0.939</td>
<td>162.1</td>
<td>0.875</td>
</tr>
<tr>
<td></td>
<td></td>
<td>174.2</td>
<td>.941</td>
<td>169.5</td>
<td>.915</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>160.3</td>
<td>.866</td>
</tr>
<tr>
<td>m-Toluene-</td>
<td>159.2±2.0 (c)</td>
<td>143.2</td>
<td>0.899</td>
<td>134.7</td>
<td>0.846</td>
</tr>
<tr>
<td></td>
<td></td>
<td>143.5</td>
<td>.901</td>
<td>133.3</td>
<td>.838</td>
</tr>
<tr>
<td></td>
<td></td>
<td>143.4</td>
<td>.901</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>143.6</td>
<td>.902</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Toluene</td>
<td>4.223±0.013 (d)</td>
<td>3.841</td>
<td>0.910</td>
<td>35.68</td>
<td>0.845</td>
</tr>
<tr>
<td></td>
<td>4.19 (e)</td>
<td>3.813</td>
<td>.903</td>
<td>35.68</td>
<td>.845</td>
</tr>
<tr>
<td></td>
<td>4.27 (f)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Seven runs.
(b) Three runs.
(c) Four runs.
(d) Four runs.
(e) Calculated from the Arrhenius parameters of DeTar and Ballentine (6), where the rate was followed by nitrogen evolution. These are probably the most precise data published for this compound.
(f) Estimated from an Arrhenius plot of the data of Lewis, Kinsey, and Johnson (33), where the coupling method used in this study was originally employed to follow the rate.
precise than those in Table II, but they are accurate enough to follow the general variation of \( k/k_0 \) at 1/2 and 1 M sodium bisulfate, as the plot of the relative rate constants shows (Fig. 6).

The solubilities of benzenediazonium hexafluorophosphate at melting ice temperature in various concentrations of sodium chloride are given in Table IV. At a given molarity of sodium chloride, the relative solubility is calculated as the measured solubility divided by the solubility in water. Mean ionic activity coefficients for benzenediazonium hexafluorophosphate in aqueous sodium chloride are then the reciprocals of the relative solubilities.
Fig. 6

Relative First-order Decomposition Rates for Diazonium Ions in Aqueous Sodium Bisulfate

(Original Date in Table III)
Table IV

Mean Ionic Activity Coefficients for Benzenediazonium
Hexafluorophosphate in Aqueous Sodium Chloride
(T = melting ice temperature)

<table>
<thead>
<tr>
<th>NaCl Conc., m/1</th>
<th>Solubility of C₆H₅N₂⁺PF₆⁻ m/1 x 10²</th>
<th>Relative Solubility of C₆H₅N₂⁺PF₆⁻</th>
<th>Mean Ionic Activity Coefficient, γ⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.81</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>0.103</td>
<td>2.98</td>
<td>1.06</td>
<td>0.944</td>
</tr>
<tr>
<td>.311</td>
<td>3.00</td>
<td>1.07</td>
<td>.935</td>
</tr>
<tr>
<td>.516</td>
<td>3.29</td>
<td>1.17</td>
<td>.855</td>
</tr>
<tr>
<td>.820</td>
<td>3.34</td>
<td>1.19</td>
<td>.841</td>
</tr>
<tr>
<td>1.27</td>
<td>3.34</td>
<td>1.19</td>
<td>.841</td>
</tr>
<tr>
<td>1.56</td>
<td>3.29</td>
<td>1.17</td>
<td>.855</td>
</tr>
<tr>
<td>2.65</td>
<td>2.84</td>
<td>1.01</td>
<td>.990</td>
</tr>
<tr>
<td>3.33</td>
<td>2.78</td>
<td>0.99</td>
<td>1.01</td>
</tr>
<tr>
<td>4.14</td>
<td>2.47</td>
<td>.88</td>
<td>1.14</td>
</tr>
</tbody>
</table>
DISCUSSION

Decomposition of the benzenediazonium ion requires high activation energy ($E_a = 27$ kcal/mole (5)), demonstrates low selectivity for dissolved anions (13)(14), and no intermediate has been detected by physical methods. A reactive intermediate is apparently involved in this reaction.

An intermediate is normally thought of as corresponding to an energy minimum along the reaction coordinate and some stability is associated with it (34). That is, the species is discrete and independent of outside influences for some instant of time. Whether the diazonium ion hydrolysis proceeds through such an intermediate or just a transition state is open to question, but for the purpose of discussion, we may refer to the transitory structure as an intermediate.

The problem of characterizing a reactive intermediate can be difficult because of its short-lived, elusive nature. Nevertheless, scavengers may be added to trap the reactive species as a stable compound whose formation is accounted for in terms of a postulated structure for the intermediate. Unless the scavenger exclusively captures every reactive intermediate as it forms, then it competes with the solvent and other species present.

This is the situation when chloride ion is added to aqueous solutions containing the diazonium ion. Chloride ion is a much stronger nucleophile than water, but it does not trap all the reacting diazonium ions and prevent their reacting with water. It merely competes with water and the relative rates reveal some of the character of the diazonium ion intermediate.
The chloride ion competition factors tabulated in Table I indicate that the benzenediazonium ion in its decomposition reacts only 3-8 times faster with chloride ion than with water. Nearly the same values of $k_{Cl}/k_\text{w}$ are obtained for all the chloride salts and they are very close to competition factors reported by Lewis (13), although the values in Table I are probably more precise. Such competition factors less than 10 are consistent with an unselective, or reactive intermediate, since cations such as tertiary butyl and triphenylmethyl demonstrate selectivities of 180 and 3100, respectively, for chloride ion over water in their hydrolyses (35).

The decrease in $k_{Cl}/k_\text{w}$ with chloride ion concentration is definite, as Fig. 4 shows. This decrease is rationalized in terms of a salt effect and the relative $k_{Cl}/k_\text{w}$ follows reported values for sodium chloride activities at 25°C. to a first approximation. If the thermal values of Fig. 4 are extrapolated to zero chloride ion concentration, an approximate value for the competition factor at infinite dilution is obtained. This value of $k_{Cl}/k_\text{w}$, or 8.7, may then be used to calculate mean ionic activity coefficients for benzenediazonium chloride by assuming the decrease in $k_{Cl}/k_\text{w}$ with sodium chloride concentration is due to the reduced activity of benzenediazonium chloride.

The reduced activity of benzenediazonium chloride may be quantitatively accounted for in terms of its effect on the rate constant for the chlorobenzene-forming reaction. Bronsted and Bjerrum independently derived an algebraic expression for the dependence of the apparent rate constant on activities (Eq. 3 (36)) which follows from transition state
theory, although that theory was not used as such by Bronsted and Bjerrum.

\[ k = \frac{k_o \gamma_A \gamma_B}{\gamma_{AB}^+} \]  

Eq. 3

In Eq. 3, \( k_o \) is the rate constant at the standard state for the dissolved particles (infinite dilution in this case), and the \( \gamma \)'s are activity coefficients for the reacting ions and for the activated complex.

Applying Eq. 3 to the reaction of chloride ion with benzene-diazonium ion we obtain:

\[ k_{Cl} = (k_{Cl})_o \frac{\gamma_{ArN_2} + \gamma_{Cl^-}}{\gamma_{ArN_2Cl}^+} \]  

Eq. 4

Changing activity coefficients are considered to exert no important effect on the apparent rate constant for the phenol-forming reaction. It is assumed that the activity coefficient of water remains near unity and that those of the diazonium ion and the activated complex for this reaction are nearly the same, so that they cancel. Eq. 5 shows that the rate constant for phenol formation is independent of sodium chloride concentration on the basis of these assumptions.

\[ k_{W} = \frac{(k_{W})_o \gamma_{ArN_2} + \gamma_{H_2O}}{\gamma_{ArN_2OH_2}^+} = (k_{W})_o \]  

Eq. 5

The expressions for \( k_{Cl} \) and \( k_{W} \) given by Eqs. 4 and 5 are now substituted into Eq. 2 (Results). A further simplifying assumption
is that the activity of the activated complex for the chlorobenzene-forming reaction is unity. When the mean ionic activity coefficient of benzenediazonium chloride is used instead of the individual activity coefficients, Eq. 6 results:

\[
\frac{(k_{Cl})_o}{(k_w)_o} = \frac{Y_{ArCl}(H_2O)}{Y_{ArOH}(Cl^-)(Y_{ArN_2Cl}^\pm)^2}
\]

Eq. 6

Eq. 6 is a version of Eq. 2 with the activity term included. If \((k_{Cl})_o/(k_w)_o\) is assumed to be 8.7 and the values of yields and concentrations are those used in calculating the uncorrected competition factors from Eq. 2, then activity coefficients may be calculated from Eq. 6 at various sodium chloride concentrations. These values are shown in Fig. 7 along with sodium chloride activities from the literature (37) and the mean ionic activities of benzenediazonium hexafluorophosphate from Table IV. Activities calculated from Eq. 6 are not precise because the value of 8.7 is not based on extensive data at low concentrations and no correction is included for variation of the water concentration due to solvation effects. Mean ionic activity coefficients calculated from Eq. 6 with the water concentration corrected for solvation effects in terms of the effective water concentration as calculated later are also shown in the figure.

Inspection of Fig. 7 suggests that mean ionic activities obtained from the solubilities of benzenediazonium hexafluorophosphate are not valid for benzenediazonium chloride, although close correspondence is not necessarily expected because of the large difference in the ionic diameters of the anions. However, the activity coefficients calculated
Mean Ionic Activity Coefficients for Salts in Aqueous Sodium Chloride

- From Solubility of C₆H₅N⁺PF₆⁻ at melting ice temp.
- Calculated from Competition Factors at 3°.
- Calculated from Competition Factors with correction for solvation effects on water concentration.
- Standard NaCl Activities at 25° (37).

Fig. 7
with and without the water concentration corrected for solvation
effects fall between those for other salts containing either the same
cation or anion, as measured in aqueous sodium chloride solutions.
The variation in $k_{CI}/k_W$ is therefore understandable in terms of salt
effects even if it is not readily calculable, and the curvature of
the product plots for diazonium ion decomposition in the presence of
potassium thiocyanate previously interpreted by Lewis and Insole (18)
in terms of the selective intermediate now is explained in terms of
salt effects on the product-determining step.

In the investigations of the rate accelerations of diazonium ion
decomposition by thiocyanate ion (20), it is noticed that the plot of
the rate constants exhibits similar curvature to that of the product
plots, suggesting a salt effect on the rate-determining step as well.
This returns us to the essential question posed in this study. Are
the rate-controlling and product-determining steps in the reaction
identical? This question may be answered affirmatively by showing
that the product data may be correlated with the rate data while
considering the salt effects.

A one-step reaction is considered, involving one transition
state. If the nucleophile attacking the diazonium ion is present in
this transition state, then it will appear in the true kinetic
expression for the reaction rate. The reaction is then bimolecular
and will follow second-order kinetics, although all nucleophiles may
attack at similar rates. This is consistent with the low selectivity
of the process.
It is postulated that the reaction is bimolecular to explain the deviations in the first-order rate constants in the presence of added electrolytes. Because the solvent and added anions are present in great excess over the diazonium ions, first-order kinetics are always observed experimentally. The algebraic expression for these pseudo first-order rate constants will now be derived.

For decomposition in water, the rate would be

\[ \frac{-d(ArN_2^+)}{dt} = k_w(H_2O)_o(ArN_2^+) \]

Eq. 7

where Ar represents the aryl group and the subscript on the water concentration indicates that it is free of added salts. The pseudo first-order rate constant for reaction with water is:

\[ k_o = k_w(H_2O)_o \]

Eq. 8

At any water concentration,

\[ k = k_w(H_2O) \]

Eq. 9

as when the water concentration is altered by density changes.

In the presence of electrolytes such as bisulfate salts, the effective water concentration should decrease due to solvation of the cation present, since water in the cation solvation shell might well be expected to be unreactive toward even a very unselective cationic species. The effective water concentration is designated as \((H_2O)_{\text{eff.}}\), and the pseudo first-order constant \(k\) should follow \((H_2O)_{\text{eff.}}\) since
this represents the concentration of water available to attack the diazonium ions. Bisulfate ion, a very weak nucleophile, is assumed to have no important effect on the rates.

The data of Table II show that the first-order rate constant does fall off in bisulfate solutions. The magnitude of the depression in sodium, lithium, and tetra-n-butylammonium bisulfates would be expected to follow the order of the solvation numbers of these cations, with the solvation number inversely proportional to the ionic diameter. Tetra-n-butylammonium ion is expected to require the least solvation because of its large ionic diameter and lithium ion should be solvated most strongly because, of the three, it more nearly approximates a point charge. Such an order is observed for sodium and lithium, with lithium causing greater rate depression, but the tetra-n-butylammonium ion falls out of order because of its large effect in reducing the water concentration by the density effect.

The effective water concentration in sodium bisulfate may be expressed by Eq. 10.

$$\left( H_2O \right)_{\text{eff.}} = \left( H_2O \right) - n(\text{Na}^+)$$

Eq. 10

where $\left( H_2O \right)$ is calculated from the density and $n$ is the hydration number of the sodium ion. Then the relative rate constants in sodium bisulfate solution from Eqs. 8 and 10 are:

$$\frac{k}{k_0} = \frac{\left( H_2O \right) - n(\text{Na}^+)}{\left( H_2O \right)_{\text{o}}}$$

Eq. 11
Eq. 11 is followed most nearly for sodium bisulfate when \( n = 5 \), but close fit to Eq. 11 for lithium requires a change in hydration number with sodium ion concentration, as seen in Fig. 8. The depression in sulfuric acid (hydrogen bisulfate) is similar to that shown in Fig. 8 for lithium bisulfate, with best fit for an integral solvation number of 5 for the proton.

In a review on ionic solvation, Bockris (38) reported hydration numbers obtained by various investigators for the sodium ion, which ranged from one to 700! Of course, most of the variation can be attributed to the different methods, which emphasize to varying degrees the secondary and higher-order solvation. Bockris felt that the sodium ion is most probably hydrated by four water molecules in the primary shell. These are the water molecules which are bound tightly enough that they move as one entity with the sodium ion and are therefore rendered quite inactive toward other species present.

Bockris' solvation numbers are for solutions at infinite dilution. At common electrolyte concentrations of 0.1M or above, the amount of solvation may be reduced by the presence of ion aggregates. Thus, no integer can be applied for the amount of cationic solvation in terms of the concentration of cations in the solution. It is more realistic to think of the solvation as an effect which reduces the concentration of water molecules in terms of their reaction with other species.

The rate depression in tetra-n-butylammonium bisulfate solution is perhaps a more clear-cut example. Since the tetra-n-butylammonium ion is so large, it can be considered to be hydrated to a very small
Relative First-order Decomposition Rates for the Benzenediazonium Ion in Aqueous Lithium Bisulfate

(Original Data in Table II)
extent. This electrolyte is essentially inert, and the rate depression is due only to a density effect. Fig. 9 shows that the first-order rate constants in this solution very closely follow the water concentration calculated from the density. Here is dramatic evidence for bimolecularity in the benzenediazonium ion hydrolysis.

The slight departure above the relative-water concentration at electrolyte concentrations above 0.2M might be explained as some contribution to the rate by bisulfate ion. Bisulfate ion could increase the observed rate by direct bimolecular reaction with diazonium ions or by accelerating the phenol-forming reaction by increasing the nucleophilicity of water, as is discussed below for chloride ion. If it is assumed that bisulfate contributes only by the bimolecular effect, then Eq. 17 (derived later) with \( k_{\text{HSO}_4^-} \) in place of \( k_{\text{Cl}^-} \) may be used to calculate \( k_{\text{HSO}_4^-}/k_w \) at 0.39M tetra-n-butylammonium bisulfate. The value of 3 obtained, however, is not reliable because it is based on a small difference between the measured \( k/k_0 \) and the relative water concentration calculated from the measured solution density, and both the solution density and the relative rate constants for this electrolyte are not determined with high precision. The competition factor of 3 for bisulfate is certainly larger than expected for this weak nucleophile.

The following reactions are considered for the decomposition in aqueous sodium chloride:

\[
\begin{align*}
\text{ArN}_2^+ + \text{H}_2\text{O} & \overset{k_w}{\longrightarrow} \text{ArOH} + \text{H}^+ + \text{N}_2 \\
\text{ArN}_2^+ + \text{Cl}^- & \overset{k_{\text{Cl}^-}}{\longrightarrow} \text{ArCl} + \text{N}_2 \\
\text{ArN}_2^+ + \text{Cl}^- \cdot \text{nH}_2\text{O} & \overset{k'_{\text{Cl}^-}}{\longrightarrow} \text{ArOH} + \text{HCl} + \text{N}_2
\end{align*}
\]
Fig. 9
Relative First-order Decomposition Rates for the
Benzenediazonium Ion in Aqueous
Tetra-n-butylammonium Bisulfate

(Original Data in Table II)
Reactions 7 and 8 are the direct reaction of the nucleophiles water and chloride ion with the diazonium ion. Reaction 9 is the chloride ion catalyzed formation of phenol, considered because of the presence of solvated chloride ions in the solution. For reaction of an unselective species such as the benzenediazonium ion, we expect this reaction to be significant because the intermediate can't distinguish between water molecules and chloride ions that are even weakly bonded together but reacts with the nucleophile which happens to be nearest. For a solvated chloride-ion this would many times be one of the water molecules residing next to the ion, and some rate increase would occur because these water molecules appear somewhat more nucleophilic than free water molecules.

Bockris (38) reported solvation numbers of two, three, and four for chloride ion at infinite dilution, but the degree of solvation at significant concentrations is certainly uncertain. However, these solvation numbers may be used as a guide in estimating the magnitude of reaction 9 for the solution concentrations of less than 1M used in this study. If three water molecules are hydrogen-bonded to a chloride ion, we may expect these to shield about half the surface of the chloride ion. About half the surface is left free for direct reaction with a diazonium ion, but the contribution to the rate from the attached water molecules should be about the same order of magnitude. Therefore, this reaction may make an important contribution to the rates observed.
The second-order rate expression based on reactions 7, 8, and 9 is,

\[- \frac{d(ArN_2^+)}{dt} = (k_w(H_2O) + k_{Cl}^-(Cl^-) + k_{Cl}^-(Cl^-))(ArN_2^+) \quad \text{Eq. 12}\]

and the pseudo first-order rate constant is:

\[k = k_w(H_2O) + k_{Cl}^-(Cl^-) + k_{Cl}^-(Cl^-) \quad \text{Eq. 13}\]

Dividing Eq. 13 by Eq. 8 and using the effective water concentration for the reactions with sodium ions present, we obtain:

\[\frac{k}{k_0} = \frac{(H_2O)^{\text{eff.}}}{(H_2O)_0} + \frac{k_{Cl}^-(Cl^-)}{k_w(H_2O)_0} + \frac{k_{Cl}^-(Cl^-)}{k_w(H_2O)_0} \quad \text{Eq. 14}\]

Eq. 14 expresses the pseudo first-order rate constant for reaction in sodium chloride solution (as well as other aqueous chloride salts) relative to that in water. It is noted that \(k_{Cl}\) and \(k_{Cl}^-'\) are dependent on salt effects, so Eq. 14 is not exact for this reason.

Inspection of Eq. 14 reveals that the competition factor appears in the second term as it also does in the expression for the ratio of the yields:

\[\frac{Y_{ArCl}}{Y_{ArOH}} = \frac{k_{Cl}^-(Cl^-)}{k_w(H_2O)} \quad \text{Eq. 15}\]

In fact, noting that the yield ratio automatically accounts for the activity of chloride ion and solvation effects, then a more exact
expression would result by using this ratio. Solving Eq. 15 for
\( k_{Cl} / k_W \) and substituting in Eq. 14, we obtain:

\[
\frac{k}{k_0} = \frac{(H_2O)_{\text{eff.}}}{(H_2O)_0} + \frac{Y_{ArCl}(H_2O)_{\text{eff.}}}{Y_{ArOH}(H_2O)_0} + \frac{k'_{Cl}(Cl^-)}{k_W(H_2O)} \tag{Eq. 16}
\]

The effective water concentration is used for \((H_2O)\) in Eq. 16 because \((H_2O)_{\text{eff.}}\) most accurately represents the water concentration demonstrated by the yield ratio.

Now we have one expression, based on the postulated bimolecular process, which consolidates the rates, solvation effects, and yields. The rate constant ratio, \( k/k_0 \), is equivalent to the sum of three terms, the first term arising from the considered reaction of diazonium ions with water, the second from reaction with chloride ions, and the third from reaction with solvated chloride ions. If the rate-determining and product-determining steps in the reaction are identical—that is, the reaction is bimolecular—then this equation should hold up when the experimental quantities are used in it. It is the basis of the rate and product correlation.

Experimental values may be substituted for all the terms in Eq. 16 except that for the chloride ion catalyzed formation of phenol. There is no immediate way to quantitatively account for this reaction's effect on the rate although it was decided that a significant contribution may be expected. However, the correlation may be made in terms of the known values, momentarily neglecting this reaction, and then determine if the deviation is reasonable in terms of the neglected reaction.
When reaction 9 is neglected in the derivation, a simpler form of Eq. 14 results, Eq. 17:

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

Eq. 17

When the yield substitution is made in terms of Eq. 15, Eq. 18 results. Eq. 18 will be used for the rate and product correlation.

\[
\frac{k}{k_0} = \frac{(H_2O)_{\text{eff.}}}{(H_2O)_o} + \frac{Y_{ArCl}(H_2O)_{\text{eff.}}}{Y_{ArOH}(H_2O)_o}
\]  

Eq. 18

Table V is the rate and product correlation for hydrolysis of benzenediazonium fluoborate in the presence of sodium, lithium, and tetra-n-butylammonium chloride. The chlorobenzene yields at selected chloride ion concentrations are taken from Fig. 3 and similar yield plots for lithium and tetra-n-butylammonium chloride from the data of Table I. \(k/k_0\) in bisulfate solution is from Figs. 8 and 9 and a similar plot for sodium bisulfate from the data of Table II. The calculated \(k/k_0\) is determined from Eq. 18, where \((H_2O)_{\text{eff.}}\) is corrected for the water concentration difference between chloride and bisulfate solutions. This correction, calculated from the solution densities, increases the calculated rate in the chloride salt solutions. The observed \(k/k_0\) is from accurate plots of the data of Table II for the chloride solutions.

Figure 10 is a plot of these results for the sodium bisulfate-sodium chloride system, including the individual observed relative rates in sodium chloride solution. In this plot the solid upper curve
Table V

Rate and Product Correlation for Benzenediazonium Ion Decomposition in Aqueous Chloride Salt Solutions  
(T = 40.14°)

<table>
<thead>
<tr>
<th>Cation, M⁺</th>
<th>MCl Conc., m/l</th>
<th>Chlorobenzene Yield, %</th>
<th>k/k₀ MHSO₄ Sol'n.</th>
<th>k/k₀ Calculated</th>
<th>k/k₀ Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>0.2</td>
<td>2.2</td>
<td>0.974</td>
<td>1.002</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>.5</td>
<td>4.3</td>
<td>0.937</td>
<td>0.991</td>
<td>.993</td>
</tr>
<tr>
<td></td>
<td>.8</td>
<td>6.1</td>
<td>0.898</td>
<td>0.973</td>
<td>.987</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>7.2</td>
<td>0.873</td>
<td>0.961</td>
<td>.983</td>
</tr>
<tr>
<td>Li⁺</td>
<td>0.2</td>
<td>1.9</td>
<td>0.952</td>
<td>0.970</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>.5</td>
<td>4.0</td>
<td>0.904</td>
<td>0.947</td>
<td>.990</td>
</tr>
<tr>
<td></td>
<td>.8</td>
<td>5.8</td>
<td>0.869</td>
<td>0.931</td>
<td>.984</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>6.9</td>
<td>0.851</td>
<td>0.926</td>
<td>.980</td>
</tr>
<tr>
<td>(n-Bu)₄N⁺</td>
<td>0.1</td>
<td>1.2</td>
<td>0.975</td>
<td>1.017</td>
<td>1.006</td>
</tr>
<tr>
<td></td>
<td>.2</td>
<td>2.0</td>
<td>0.952</td>
<td>0.998</td>
<td>1.011</td>
</tr>
<tr>
<td></td>
<td>.3</td>
<td>2.7</td>
<td>0.928</td>
<td>0.980</td>
<td>1.016</td>
</tr>
<tr>
<td></td>
<td>.4</td>
<td>3.4</td>
<td>0.904</td>
<td>0.966</td>
<td>1.020</td>
</tr>
</tbody>
</table>
Fig. 10
Rate and Product Correlation for Benzenediazonium Ion Decomposition in Aqueous Sodium Chloride

(Original Data in Table II)
is obtained merely by adding the yield term to the lower curve, or the relative rate in sodium bisulfate. This is equivalent to adding the rates for reaction of benzenediazonium ion with chloride ion to that for reaction with water.

The correlation is good for the sodium bisulfate-sodium chloride system, as Fig. 10 shows, but less distinct for the other two-salt systems. The calculated and observed $k/k_0$ for the lithium and tetra-n-butylammonium systems diverge significantly as the concentration of added salt increases. However, the calculated $k/k_0$ always accounts for more than half of the difference between the relative rates in bisulfate and chloride solutions.

One uncertainty in the correlation is due to assuming that solvation of the sodium ion is the same in both bisulfate and chloride solutions. It is observed that the solvation number of sodium and lithium changes with ionic strength in bisulfate solution, but there is no reason to expect the change to follow the same pattern in chloride solution, because of the different ionic diameters of the anions.

In the above interpretation the reduction in rate in sodium bisulfate solution is attributed solely to a property of this solution, namely the effective water concentration. The possibility that the nature of the diazonium ion is in some way responsible for the rate depressions in sodium bisulfate solution is ruled out by the rate depressions for the toluenediazonium ion decompositions in this solution. First-order rates for benzenediazonium ion and $\mathcal{O}^-$, $\mathcal{M}^-$, and $p$-toluenediazonium ions are all depressed to essentially the same
extent, as Fig. 6 shows. This appears to be good evidence that the rate depression is due specifically to reduction of the effective water concentration by the presence of sodium bisulfate. That the rates consistently fall off when the effective water concentration is reduced is a further hint of bimolecularity in the reaction's rate-controlling step.

The value of \( k_o \) for the benzenediazonium ion given in Table II is in good agreement with that calculated from the Arrhenius parameters reported by DeTar and Ballentine (6) and with the value reported by Pray (9) in an older study. This is a good check on the precision of the procedure used in this study for determining all the rate constants, except in the tetra-n-butylammonium chloride solutions where there was some experimental difficulty obtaining reproducible values, possibly because of the presence of an impurity. Therefore, the rate constant ratios, \( k/k_o \), in the sodium and lithium salt solutions may be considered reliable enough to use as the basis for the rate and product correlation, and those for tetra-n-butylammonium chloride may be used with some reservation.

Another error is contained in the yield of phenol (\( Y_{ArOH} \)) as used in Eq. 16 (or the simpler form—Eq. 18). This yield, as calculated from the chlorobenzene yield, includes phenol formed by the chloride ion-catalyzed reaction whereas it refers only to the direct reaction with water. However, the phenol yield by chloride ion catalysis would be close to the chlorobenzene yield and this amounts to at most eight percent of the total phenol yield. The second term of Eq. 18 would not
be far different if the phenol yield could be corrected for this error, but any correction would improve the correlation.

Of course the largest error contained in the calculated rate and product correlation is due to neglecting the reaction with solvated chloride ions. To make the correlation perfect for the sodium chloride solutions, the contribution from reaction 9 would have to be approximately one-third that due to direct reaction with chloride ions. For the lithium and tetra-n-butylammonium chloride solutions the contribution from reaction 9 would have to be nearly equal to that for the direct reaction. For all three systems, it is therefore of the same order of magnitude as was predicted on the basis of solvation expected for the chloride ion.

Evidence for the existence of reaction 9 may be gleaned from the data in a different way by calculating competition factors from the observed rates and comparing them with $k_{C1}/k_{W}$ calculated from the chlorobenzene yields. Competition factors calculated from Eq. 17 for sodium and lithium chloride are shown in Figs. 11 and 12 along with the factors from Table I.

These rate competition factors inherently include the rate constant for reaction 9, since $k_{C1}$ includes $k_{C1}'$, as shown more clearly by again inspecting Eq. 14. Figs. 11 and 12 suggest that reaction 9 is significant at all concentrations, since $k_{C1}/k_{W}$ is always higher when calculated from the rates.

Thus, the relative rate constants in chloride salt solutions are experimentally consistent with the three-term expression (Eq. 16) for these ratios, and the deviations in the first-order rate constants in
Fig. 11

Competition Factors Calculated from Rates and Yields in Aqueous Sodium Chloride
Fig. 12

Competition Factors Calculated from Rates and Yields in Aqueous Lithium Chloride

- From Rates
- From Yields
- $T = 40^\circ$
these electrolyte solutions are explained in terms of the three considered bimolecular reactions. This result is consistent with identity of the rate-determining and product-determining steps in the thermal hydrolysis of the benzenediazonium ion, within the limits of experimental error.

Before drawing any conclusions about the actual structure of the transition state involved, however, the results of the photochemical studies should be reviewed. It is first noted that the photochemical competition factors at 5° closely follow those obtained thermally, as seen in Fig. 4. This similarity is more striking because of the observed salt effects on the thermal values.

The same intermediate is suggested even though diazonium ions receive more than three times the activation energy in the photochemical irradiation. (The average wavelength of light which is absorbed is around 320 m\(\mu\), corresponding to 89.5 kcal/mole of energy added.) With such a great excess of energy supplied to the diazonium ions, it is hard to reconcile the similar results with the thermal process unless the photochemically-excited ion rapidly cascades through deactivating collisions to an excited state of comparable energy to that obtained thermally before it loses nitrogen. This appears to be good evidence that a properly-oriented collision with a nucleophile is necessary for nitrogen loss to occur, since an intermediate formed directly from such a highly-excited diazonium ion would not be expected to have the same properties as that formed at the thermal activation energy, as demonstrated by the same selectivity and lack of rearrangements.
Although the data are not thorough enough to establish this point, there is a suggestion of very slightly greater selectivity for the photochemical process, possibly due to formation of some triplet excited state diazonium ions as Lee, Calvert and Malmberg have suggested (30).

It is concluded that the benzenediazonium ion decomposes by a bimolecular process. The transition state consistent with this conclusion may now be described in some detail. That it is similar to the oft-proposed aryl cation (13)(17)(33) is enforced by the competition factors found in this study. It must also allow for the observed nitrogen turnaround that accompanies the process.

All these facts, the high activation energy required, and the consistency between the thermal and photochemical results may be reconciled by a transition state structure with the C-N bond greatly stretched and the bond to the attacking nucleophile weakly formed. Unselectivity of the decomposing diazonium ion is a consequence of the weak new bond but primarily dependent upon the requirement that the C-N bond vibration be sufficiently energized. Thus, C-N bond stretch takes precedence over strength of the attacking nucleophile in controlling the rate of nitrogen loss. The order of nucleophilic strengths is therefore compressed since no nucleophile becomes aware of an electron vacancy at the nitrogen-bearing carbon until the C-N bond is greatly weakened in the excited state.

Nitrogen turnaround suggests that the nitrogens become equivalent for some fraction of the excited vibrations, possibly by the C-N bond lying at some angle to an axis through carbons 1 and 4 of the ring.
On the basis of the foregoing considerations, the following picture is proposed for the transition state, where the positive charge is shown mostly localized at carbon 1:

This picture of the transition state is equivalent to the unselective intermediate X proposed by Lewis and Insole (18) except that the attacking nucleophile now is included. They discussed the similarity between the two-step reaction through X and the one-step bimolecular reaction. Perhaps the bimolecular process can be thought of as bonding of a nucleophile to a nascent aryl cation.

Reaction with a nucleophile is expected to follow the lowest-energy path, and it seems reasonable that this optimum would occur when the nitrogen moiety resides at some given average distance from the aryl cation moiety. The lowest-energy route, then, is a pathway involving something less than distinct aryl cation formation. The aryl cation is so unstable that it requires stabilization by some nucleophile. Before nitrogen has completely gotten away, it requires that some other nucleophile make up the electron deficiency.

Extension of the bimolecular process to other diazonium salts would then give a spectrum of transition states in which the developing new bond becomes progressively stronger as substituents with more positive σ (more strongly electron-withdrawing) are attached. For the p-diazo group (largest positive σ known (39)), bond formation
from the nucleophile may be nearly complete before nitrogen is lost, with transition state structure resembling a Meisenheimer complex. Hence, nearly pure second-order kinetics result, as observed. This is one end of a scale involving varying degrees of carbonium ion formation analogous to that observed for aliphatic solvolyses, with the benzenediazonium ion fitting in the aromatic scheme where carbonium ion formation to some degree is perceptible.

Attack on an aromatic cation is limited to frontside, so this process is analogous to the aliphatic deaminations which apparently involve attack by a nucleophile from the same side of carbon as nitrogen departs from. Zollinger (40) summarizes the anomalous nature of some aliphatic deaminations.

A bimolecular transition state for all diazonium ion decompositions has the implication that the displacement of nitrogen from the diazonium ions which apparently lose it by a unimolecular process is an example of the rare one-step $S_N^{\text{Ar}2}$ reaction, or second-order nucleophilic substitution at aromatic carbon without the aid of activating substituents. Furthermore, the results of this study suggest that the $S_N^{\text{Ar}1}$ mechanism is rare in solution, since the diazonium ion case was the only well-established example of this reaction (26).
EXPERIMENTAL

Diazonium Salts--Benzenediazonium fluoborate and the o-, m-, and p-toluenediazonium fluoborates were prepared by diazotization of the aromatic amine or its hydrochloride salt in fluoboric acid as described in Organic Reactions (39). In a typical preparation 10 g of aniline hydrochloride (0.077 mole) were dissolved in 50 ml distilled water and 40 ml of Baker and Adamson reagent-grade 37% fluoboric acid, the solution cooled below 5° by addition of ice, and diazotization accomplished by slowly adding a solution of sodium nitrite in water to the potassium iodide-starch end point. The precipitated diazonium salt was filtered from solution, rinsed with water and ether, and dried under vacuum for several hours. Purity of the salt was determined by measuring the ultraviolet extinction coefficient at the wavelength of maximum absorption, as described below.

Purification of Amines--J.T. Baker reagent-grade aniline was recrystallized as the hydrochloride from ethanol-ether (m.p. in a sealed tube 197.5°, lit. 198° (42)). Crude o-toluidine was redistilled until water-white and then recrystallized as the hydrochloride (m.p. 216°, lit. 218-220° (43)). Eastman m-toluidine redistilled until water-white was also recrystallized as the hydrochloride (m.p. 214°, lit. 228° (43)). However, a sample of the m-toluidine hydrochloride converted to m-aceto-toluidide by the procedure of Fieser (44) gave a melting point of 65° (lit. 65.5° (45) or 66-67°, as reported by Lewis and Miller (17)). Matheson, Coleman, and Bell p-toluidine melted at 41° (lit. 42-45° (46)) after recrystallization from hot water.
Diazonium Salt Purity Determination--In a typical purity determination ca. 0.1 g benzenediazonium fluoborate, weighed to 0.1 mg, was dissolved in 250 ml distilled water and a portion immediately diluted by fifty times with distilled water. The optical density of this solution was measured on a Bausch and Lomb Spectronic 505 ultraviolet spectrophotometer at 262 m\textmu. All solutions were cooled in ice water baths to prevent decomposition and the final solution was 0.1 N in sulfuric acid to inhibit coupling. Extinction coefficients for the benzenediazonium ion and the toluenediazonium ions in 0.01 N sulfuric acid at their \( \lambda_{\text{max}} \) are given in Table VI.

**Table VI**

<table>
<thead>
<tr>
<th>Diazonium Ion</th>
<th>( \lambda_{\text{max}} ), m\textmu</th>
<th>( \epsilon, \text{l}/\text{mole}\cdot\text{cm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene-</td>
<td>262</td>
<td>( 1.25 \times 10^4 ) (a)</td>
</tr>
<tr>
<td>o-Toluene-</td>
<td>264</td>
<td>( 1.1 \times 10^4 ) (b)</td>
</tr>
<tr>
<td>m-Toluene-</td>
<td>267</td>
<td>( 1.2 \times 10^4 ) (b)</td>
</tr>
<tr>
<td>p-Toluene-</td>
<td>277</td>
<td>( 1.63 \times 10^4 ) (47) (a)</td>
</tr>
</tbody>
</table>

(a) Determined from both the fluoborate and hexafluorophosphate salts.
(b) Determined only from the fluoborate salt.

Tetra-n-butylammonium Chloride--Solutions of this quaternary ammonium salt were prepared by the procedure of McMichael and Clement (48), neglecting evaporation of all the water. In a normal preparation, 50 g (0.135 mole) of Eastman standard tetra-n-butylammonium iodide and 300 ml
distilled water were stirred vigorously with 10 percent excess (21.3 g) of freshly-prepared silver chloride until a negative iodide test was obtained with acidic aqueous sodium nitrite. Silver iodide formed by the exchange was removed by filtration and the solution saturated with hydrogen sulfide. After treatment with decolorizing charcoal and filtration, the solution was concentrated on a Büchi rotary evaporator to the maximum concentration needed. Portions were then diluted as desired for kinetic runs and the actual concentration determined by a Mohr titration for chloride ion with silver nitrate to the silver chromate end point.

Identity of the tetra-n-butylammonium chloride was verified by evaporation of a portion of the solution to dryness followed by further drying over phosphorous pentoxide at less than one mm Hg pressure. A sample of this salt in a sealed capillary, introduced into the capillary inside a dry box, gave a melting point range of 52-55°, comparing with 52-54° reported by McMichael and Clement (48).

Tetra-n-butylammonium Bisulfate--Aqueous solutions of this salt were prepared in a manner similar to that used for tetra-n-butylammonium chloride, using 25 g tetra-n-butylammonium iodide, 200 ml distilled water, and 7.8 g silver oxide. Most of the silver oxide was added initially, but then only in small portions until the iodide test just became negative. One molar equivalent of sulfuric acid added to the tetra-n-butylammonium hydroxide solution gave the bisulfate. After dilution with distilled water, the concentration of the bisulfate solution was determined by titration with 0.1 N sodium hydroxide.
Yields of Chlorobenzene and Phenol

Thermal Decompositions--The product yields were determined by the procedure of Lewis (13), except that sealed flasks were used to prevent any loss of chlorobenzene by evaporation over the extensive times required for complete reaction (six weeks for the runs at 3°).

Typically, 0.2 g (one mmole) of benzenediazonium fluoborate was dissolved in 250 ml distilled water 0.01 M in sulfuric acid and containing a weighed amount of sodium chloride or lithium chloride, or a measured volume of tetra-n-butylammonium chloride solution of known concentration. Then 100 ml of this solution was pipetted into a 200-ml round-bottom flask and the stem sealed before placing the flask in the temperature bath. All solutions were cooled in ice baths up to this point. In the cases where larger amounts of diazonium salt were necessary for measurable yields, excessive pressure build-up by nitrogen evolved during the reaction was prevented by freezing the solution in the reaction flask and evacuating the flask before sealing.

Solution of the diazonium salt in the tetra-n-butylammonium chloride solutions was very difficult, so the diazonium ion concentration was determined by ultraviolet absorption after adding excess diazonium salt and filtering, keeping the solution cold at all times.

After a minimum of seven half lives, the reaction flask was again cooled, opened, and an amount of ethylbenzene close to the expected yield of chlorobenzene was added for internal standard. Normally, this was one ml of a solution containing 200 \( \lambda \) ethylbenzene in 100 ml 20-40° petroleum ether. More petroleum ether (50 ml) was added to the product mixture along with enough sodium hydroxide to make the aqueous
portion strongly basic. After thorough shaking, the petroleum ether portion was rapidly concentrated to about 2 ml on a 10-mm Nester-Faust spinning band column. Vapor phase chromatography of the concentrated solution on a 7-ft Carbowax 20 M on Chromosorb P column calibrated for mole ratio vs. peak height ratio gave the yield of chlorobenzene from the relative peak heights. The Aerograph Hy-Fi gas chromatograph with flame ionization detector was sensitive enough for the small samples involved.

The phenol yield was calculated from the chlorobenzene yield, assuming quantitative decomposition of the diazonium salt to give only phenol and chlorobenzene. Phenol yields determined by the standard bromination procedure have been found to be lower, but close enough to that calculated in this way that the assumption is considered valid (13).

**Photochemical Decompositions**—Solutions were irradiated with a 200-watt high-pressure mercury vapor lamp (Hanovia S654A-36) in the cylindrical reaction vessel shown in Figure 13 immersed in an ice bath. Chlorobenzene was continuously extracted from the photolyzed solution with petroleum ether and the yield determined by gas chromatography as described above.

Typically, 25 ml of a solution containing 0.2 g benzenediazonium fluoroborate in 500 ml distilled water were added to 500 ml of cold (ca. 5°C) aqueous sodium chloride solution 0.01 M in sulfuric acid already in the reactor vessel. After thorough stirring, the immersion well was inserted and the solution occupied the annular space around the immersion well. Petroleum ether was added to the recycle system
Fig. 13

Photochemical Reactor Diagram
and continuous circulation started before turning on the lamp. Three hours of irradiation were sufficient for complete decomposition.

Use of a pyrex filter inside the immersion well gave clean product solutions and prevented photolysis of the chlorobenzene by cutting out most of the light with wavelength below 300 μm. To measure the amount of chlorobenzene that would be lost by photolysis, a known amount was added slowly to the reactor in a separate run, and recovered by the continuous extraction, at the conditions of yield measurement except for no filter. Quantitative determination of the chlorobenzene was accomplished by vapor phase chromatography of the concentrated extract solution with a known volume of ethylbenzene added for internal standard. It was found that chlorobenzene loss was 5-10% during a photolytic run without the filter, but recovery was nearly quantitative when the lamp was left off.

Rate Determinations—Pseudo first-order rate constants for the thermal decompositions in water or the salt solutions were measured by the method of Lewis, Kinsey, and Johnson (33), designed to eliminate many analytical errors. Here, the rates were followed by coupling unreacted diazonium ion with R-salt (2-naphthol-3,6-disulfonic acid disodium salt). A rate constant very close to that expected was guessed and samples of increasing size were taken at times calculated to give the same total quantity of unreacted diazonium ion in each. After completion of the coupling, the relative concentration of R-salt derivative in each sample was determined by spectrophotometric absorption with a Bausch and Lomb Spectronic 505. Least squares treatment of the data gave precise rate constants.
The runs in aqueous sodium chloride were typical. To a 50-ml portion of sodium chloride solution of known molarity and 0.01 M in sulfuric acid were added ca. 0.1 g diazonium salt, giving a solution $10^{-2}$ M in diazonium ion. This solution was poured into the reactor (Fig. 14) and the reactor immersed in the constant-temperature water bath. After allowing time to achieve temperature equilibrium, samples were pressured by nitrogen through the capillary outlet and immediately quenched in an ice bath.

Selected volumes of the cold solution in accurate 50, 75, 100, 200, and 300 $\mu$micro pipettes were then coupled with 50-fold excess of R-salt solution (0.5 ml of a 50 ml solution containing 1.7 g R-salt and saturated with sodium bicarbonate). One half hour was found to be sufficient for completion of the coupling at room temperature, after which the solution was acidified with 1 ml of 1 M hydrochloric acid and the carbon dioxide removed by shaking. After diluting to 10 ml, optical densities were measured at $\lambda_{\text{max}}$ for the azo coupling product, correcting for the slight absorption due to excess R-salt. The correction to the guessed rate constant is then the slope of logarithm of optical density plotted against time.

In Table VII are the observed $\lambda_{\text{max}}$ and extinction coefficients for the various azo coupling compounds of diazonium ions and R-salt:
Fig. 14

Diagram of Reactor Used in Rate Measurements
Table VII
Extinction Coefficients of R-salt Coupling Compounds

<table>
<thead>
<tr>
<th>Diazo Substituent of R-salt Coupling Compound</th>
<th>( \lambda_{\text{max}} ) m( \mu )</th>
<th>( \epsilon ), 1/mole·cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzenediazo</td>
<td>490</td>
<td>2.1 \times 10^4</td>
</tr>
<tr>
<td>o-Toluenediazo</td>
<td>492</td>
<td>2.1 \times 10^4</td>
</tr>
<tr>
<td>m-Toluenediazo</td>
<td>492</td>
<td>2.2 \times 10^4</td>
</tr>
<tr>
<td>p-Toluenediazo</td>
<td>498</td>
<td>2.4 \times 10^4, 4 \times 10^4( \text{(33)} )</td>
</tr>
</tbody>
</table>

Activity Coefficients of Diazonium Salt—Mean ionic activity coefficients for benzenediazonium hexafluorophosphate in aqueous sodium chloride were determined by Kunetka's method (49) of measuring the solubility at various concentrations of sodium chloride. Typically, 25 ml of solution containing excess solid benzenediazonium hexafluorophosphate and 0.01 M in sulfuric acid were vigorously stirred in a test tube immersed in an ice bath. From portions of this suspension filtered at cold conditions, 200\( \lambda \) samples were coupled with R-salt solution as described above until successive samples gave the same magnitude of visible absorption. The concentration of diazonium ions was then determined from the absorption of the coupling product and the mean ionic activity coefficient was calculated from the relative solubility.

Photochemical Nitrogen Yields—Five hundred-ml aqueous solutions 10^{-4} M in benzenediazonium fluoborate were photolyzed for three hours with the 200-watt, high-pressure Hanovia mercury vapor lamp in the reactor shown
in Figure 13. Carbon dioxide purified by resolidification at high vacuum in a liquid nitrogen trap was used to flush the evolved nitrogen into a nitrometer for collection over 50% potassium hydroxide. The diazonium salt solution was preflushed in the reactor with the purified carbon dioxide to a constant rate of impurity collection in the nitrometer and flushing continued after photolysis to this same rate, so a correction could be applied for the small impurity content of the carbon dioxide.

Nitrogen yields from three representative runs were 123, 97, and 80%, with the large deviations due to difficulties in measuring the small volumes (ca. 1 ml) of gas evolved and errors caused by even a very small impurity content of the carbon dioxide used. Further refinements in this technique are necessary before the results may be relied on strongly, but to a first approximation, yields of nitrogen close to quantitative are indicated.
SUMMARY

The mechanism of the thermal hydrolysis of the benzenediazonium ion supported by previous investigation is the rate-controlling loss of nitrogen to form a phenyl cation which reacts with a nucleophile in a second fast step to form the product. First-order kinetics are observed, but the first-order rate constants are slightly depressed by most electrolytes and accelerated by some such as potassium thio-cyanate.

The purpose of this study was to see if the reaction really follows second-order kinetics by correlating the first-order rate constants in aqueous sodium, lithium, and tetra-n-butylammonium chloride solutions below 1M at 40° with the yields of chlorobenzene and phenol. Salt effects are considered along with the change in the effective water concentration due to cationic solvation, represented by the rate depression in a solution of the bisulfate of that cation. The low selectivity previously found for the benzenediazonium ion in its reaction with chloride ion and water is confirmed by the competition factors, $k_{Cl} / k_W$, of less than 10 found in this study. Competition factors measured as well for photochemical decomposition in aqueous sodium chloride agree closely with the thermal values.

Reaction of the unselective intermediate with solvated chloride ions is considered. In terms of this reaction and the combination with chloride ion and water, the correlation based on second-order kinetics is reasonable and suggests that the rate-determining and product-determining steps in the reaction are the same, or that the attacking nucleophile is present in the transition state.
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