Reactions of the 2,4-dinitrobenzenediazonium Ion

by

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I wish to thank Dr. E. S. Lewis for his advice and encouragement in the course of this work.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>II. Results</td>
<td>5</td>
</tr>
<tr>
<td>III. Discussion</td>
<td>14</td>
</tr>
<tr>
<td>IV. Experimental</td>
<td>25</td>
</tr>
<tr>
<td>V. Bibliography</td>
<td>30</td>
</tr>
<tr>
<td>VI. Summary</td>
<td>32</td>
</tr>
</tbody>
</table>
Reactions of the 2,4-dinitrobenzenediazonium Ion

A wide variety of work has been done in studying the reactions of diazonium salts. Work of particular interest is that done with diazonium salts containing electron-withdrawing substituents. Lewis and Johnson studied the reaction of the p-phenylene-bis-diazonium ion with water and observed that one of the diazonium groups was easily displaced by a hydroxyl ion to give the p-hydroxybenzene-diazonium salt. They postulated a mechanism involving the formation of the oxy-diazohydroxide which decomposed to give the phenol (Sn reaction) in a reaction analogous to a nucleophilic substitution reaction activated by the p-diazonium group. Lewis and Johnson also studied the reactions of the p-phenylene-bis-diazonium ion with bromide, chloride, and oxide ions. These also displaced one diazonium group leaving the other intact. In the case of iodide ion, p-diiodobenzene or p-iodobenzenediazonium ion were rapidly obtained, the product dependent on iodide concentration, and at concentrations of iodide low enough to measure rates, p-hydroxybenzenediazonium ion was produced. Hinds observed a similar result with iodide ion using the p-nitrobenzenediazonium salt; the diazonium group was replaced by hydroxyl, the reaction being activated by the p-nitro group. Lewis and Suhr studied the reactions of the p-nitrobenzenediazonium ion with acids and base, and they suggested that at intermediate pH, a diazo-oxide may be produced or that nucleophilic substitution on the aromatic ring has occurred.
Nucleophilic substitution of an aromatic ring activated by the diazonium group has been studied previously. In 1896, Hantsch and Hirsch reported the substitution of chloride by thiocyanate in the positions ortho and para to the diazonium group. In 1903, Orton studied the interchange of halide and hydroxyl groups in the 2,4-trichloro- and 2,4-dibromobenzodiazonium salts of weak acids. He found that a halogen ortho to the diazonium group was easily replaced by hydroxide ion. The replacement of halide by hydroxyl occurred even more readily in the naphthalene series of diazonium salts. More recently, Lewis and Suhr investigated the substitution of halogen by thiocyanate in the p-halobenzodiazonium salts. They concluded that the reaction was a nucleophilic substitution on the aromatic ring strongly activated by the diazonium group.

Bolto, Riveris, and Miller studied the replacement of fluoride by methoxide ion to determine the order of activation of different electron-withdrawing groups in this nucleophilic substitution reaction. They studied the following series: fluorobenzene, p-nitrofluorobenzene, p-fluorobenzodiazonium ion, p-fluorotrimethylaminium ion. They suggested the following order of activation:

\[ -\text{N}^+ > > -\text{NO}_2 > > -\text{N}(\text{CH}_3)_3 \]

Lewis and Johnson measured the substitution constants of the diazonium group and found it to be the most electron-withdrawing substituent and, therefore, the most activating in aromatic nucleophilic substitution. Bunnett and Zahler, in their review of aromatic nucleophilic substitution reactions, state that the diazonium
The group is powerfully activating. They postulate the following sequence for the p-nitro group as a substituent activating the aromatic ring towards nucleophilic substitution:

![Chemical Structure](image)

The ortho or para diazonium group would be analogous.

The activation of the aromatic ring by the diazonium group towards nucleophilic substitution is somewhat analogous to the activation by the heterocyclic nitrogen toward substitution at the 2- and 4- positions of pyridine. The diazonium salt formed on diazotization of pyridyl amines is so reactive that, although a coupling product with β-naphthol may be obtained, the diazonium group is readily displaced by hydroxide or chloride ions from the solvent. The ease of replacement of the diazonium group is attributed to the electron-withdrawing power of the heterocyclic nitrogen:

![Chemical Structure](image)

Angyal and Angyal state that the diazotization and stability of pyridyl amines is analogous to that of the poly-nitro substituted anilines.

The above mentioned studies of Iavic and co-workers indicated that it would be of interest to investigate the types of reaction.
obtained with the tetraoxonium salt and the p-nitrobenzenediazonium salt to see if these reactions were applicable generally to diazonium salts containing powerful electron-withdrawing substituents. It was thought that the 2,4-dinitrobenzenediazonium ion might react in a similar fashion both with iodide ion and with acids and base.
RESULTS

I. Reaction of 2,4-dinitrobenzenediazonium fluoborate with iodide ion.

In view of work done with the tetrasodium salt and the p-nitrobenzenediazonium salt involving iodide ion, it was thought to be of interest to determine whether or not the formation of 2,4-dinitrophenol from 2,4-dinitrobenzenediazonium fluoborate in aqueous solution would be catalyzed by iodide ion. Various concentrations of diazonium salt, iodide ion, and sulfuric acid were used. The results were inconclusive. 2,4-dinitroiodobenzene was readily formed. There appeared to be little or no production of 2,4-dinitrophenol as observed spectrophotometrically. However, another product was found which was thought to be either the coupling compound between any phenol produced and the diazonium salt, or a diazo-oxide in which one of the nitro groups had been replaced by hydroxyl ion. It was felt wise to study the system in the absence of iodide ion in hopes of identifying this product and then studying the kinetics and mechanism of formation of the compound which appears dominant in this reaction.

II. Reactions of 2,4-dinitrobenzenediazonium fluoborate in aqueous solutions of varying pH.

a. Spectrum of the diazonium salt in 6M sulfuric acid.

The spectrum of 2,4-dinitrobenzenediazonium fluoborate in 6M sulfuric acid was determined in the ultra-violet and visible regions. There appeared to be little or no decomposition of the diazonium ion at this concentration of acid since no change in spec-
trum was noted over a time interval of fifteen minutes. One may conclude that only the 2,4-dinitrobenzene diazonium ion was present (and of course, sulfate and fluoroborate anions).

b. Spectra of the diazonium salt in various buffers.

The spectrum of the 2,4-dinitrobenzene diazonium ion in various phosphate buffers of pH 5.2, 6.2, 7.0, 8.0, was next observed in the ultra-violet and visible regions. In pH 6.2, 7.0, 8.0, the same spectrum was obtained (same maxima and minima). The spectrum remained constant over fifteen minutes. On acidification to pH 1, the spectrum of 2,4-dinitrobenzene diazonium ion was obtained. On the basis of this, and by analogy with other diazonium salts, the compound present at pH 6.2, 7.0, 8.0, is assumed to be the diazonium salt (see discussion section).

The spectrum at pH 5.3 (the same is observed in acetate buffer, pH 4.6), was very different from either the diazonium salt or the diazotate. It was not 2,4-dinitrophenol (as determined by a comparison of the spectra of an authentic sample of 2,4-dinitrophenol with that obtained). On making the solution basic, the spectrum of the diazotate was not observed, nor on acidification of the pH 5.3 solution, was that for the diazonium salt obtained. On the basis of this and from literature on similar diazonium salts, the compound present at these pH was tentatively assigned the structure of a diazo-hydrate in which one of the nitro groups had been replaced by hydroxyl yielding nitrite ion.

III. Structure of the decomposition product of 2,4-dinitrobenzene diazonium ion at intermediate pH.

a. Nitrite determination.
As evidence for the diazo-oxide structure postulated above, solutions of 2,4-dinitrobenzenediazonium fluoroborate in the buffers used above were tested for the presence of nitrite using a modification of the method of Feigl \(^{14}\) (see experimental section). A time interval of fifteen minutes was used. (See Table 1.) These results indicate that the formation of a diazo-oxide with the elimination of one of the nitro groups is highly reasonable.

**Table 1**

Nitrite determinations in solutions of 2,4-dinitrobenzenediazonium fluoroborate.

<table>
<thead>
<tr>
<th>pH</th>
<th>type of buffer</th>
<th>color (pink indicates nitrite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.6</td>
<td>0.1M acetate buffer</td>
<td>dark pink</td>
</tr>
<tr>
<td>5.3</td>
<td>0.1M phosphate buffer</td>
<td>dark pink</td>
</tr>
<tr>
<td>6.2</td>
<td>0.1M &quot; &quot;</td>
<td>pale pink</td>
</tr>
<tr>
<td>7.0</td>
<td>0.1M &quot; &quot;</td>
<td>very pale pink</td>
</tr>
<tr>
<td>8.0</td>
<td>0.1M &quot; &quot;</td>
<td>&quot; &quot;</td>
</tr>
</tbody>
</table>

b. Synthesis of 5-nitrobenzene-2-diazole-1-oxide for comparison with decomposition product in pH 4.6 and pH 5.5 buffers.

5-nitrobenzene-2-diazole-1-oxide was synthesized according to Morgan \(^{15}\) and a spectrum of the solution was taken in the ultraviolet and visible regions. This proved to have the same maxima and minima as those obtained for the solution of 2,4-dinitrobenzenediazonium fluoroborate in pH 5.5 phosphate buffer and in pH 4.6 acetate buffer. No extinction coefficients could be calculated although the relative values or the ratio of the absorption at longest wave length over that at shortest wave length agreed for the two solutions.

Solid, isolable 5-nitrobenzene-2-diazole-1-oxide was next synthesized according to Morgan \(^{16}\). This compound gave a blue coupling product with alkaline \(\beta\)-naphthol as reported; this was in marked
contrast to the brown-orange coupling compound obtained with solutions of 2,4-dinitrobenzenediazonium ion in pH 4.6 acetate buffer. The spectra and extinction coefficients of the two solutions were also different (see Table 2). However, on standing for an hour, the aqueous solution of the diazo-oxide gave a brown-orange coupling product with pyridine and the same spectrum and extinction coefficients were obtained as those for the product of the decomposition of the diazonium salt in acetate buffers (again see Table 2). This is also the same product as that obtained in pH 5.5 phosphate buffer.

Table 2

Calculated extinction coefficients and maxima for 5-nitrobenzene-2-diazo-1-oxide in solution and for 2,4-dinitrobenzenediazonium ion in solution.

1. 5-nitrobenzene-2-diazo-1-oxide in water.

\[ \lambda_{\text{max}} = 430 \text{ nm} \]
\[ \lambda = 270 \]
\[ e = 8.1 \times 10^5 \]
\[ e = 2.20 \times 10^4 \]

2. 5-nitrobenzene-2-diazo-1-oxide in water after one hour.

\[ \lambda_{\text{max}} = 410 \text{ nm} \]
\[ \lambda = 270 \]
\[ e = 5.4 \times 10^5 \]
\[ e = 1.50 \times 10^4 \]

3. 2,4-dinitrobenzenediazonium fluoride in pH 4.6, 1M acetate buffer after ten minutes.

\[ \lambda_{\text{max}} = 410 \text{ nm} \]
\[ \lambda = 270 \]
\[ e = 5.5 \times 10^5 \]
\[ e = 1.50 \times 10^4 \]

The above information suggested the possibility that the second nitro group had been replaced giving an hydroxy diazo-oxide. As further evidence for this, solutions of 5-nitrobenzene-2-diazo-1-oxide at various pH were tested for the elimination of nitrite.

4. Nitrite determination tests for the diazo-oxide decomposition product.

Solutions of 5-nitrobenzene-2-diazo-1-oxide at pH from
2.0-5.0, were tested for the elimination of nitrite using a modification of Feigl’s method. Positive tests were obtained for all solutions in forty-five minutes. (See Table 3 for summary of these results.)

Table 3
Nitrite determinations in solutions of 5-nitrobenzene-2-diazo-1-oxide at various pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>type of solution</th>
<th>time (min.)</th>
<th>color</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>0.1N sulfuric acid</td>
<td>30</td>
<td>none</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>pink</td>
</tr>
<tr>
<td>2.5</td>
<td>1N acetic acid</td>
<td>30</td>
<td>pink</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>1N acetic acid</td>
<td>30</td>
<td>none</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>pink</td>
</tr>
<tr>
<td>3.5</td>
<td>1N acetic acid</td>
<td>30</td>
<td>none</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>pink</td>
</tr>
<tr>
<td>4.0</td>
<td>1N acetic acid</td>
<td>30</td>
<td>none</td>
</tr>
<tr>
<td></td>
<td>1N acetic acid</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>1N acetic acid</td>
<td>30</td>
<td>none</td>
</tr>
<tr>
<td></td>
<td>1N acetic acid</td>
<td>45</td>
<td>pink</td>
</tr>
<tr>
<td>5.0</td>
<td>1N acetic acid</td>
<td>30</td>
<td>none</td>
</tr>
<tr>
<td></td>
<td>1N acetic acid</td>
<td>45</td>
<td>pink</td>
</tr>
</tbody>
</table>

The positive nitrite results obtained above indicated that either the reverse of diazotization had occurred, producing 5-nitro-2-aminophenol, or that a nitro group had been replaced. The spectrum of 5-nitro-2-aminophenol was taken. On the basis of this, the reverse diazotization process was eliminated. (See Table 4 for a comparison of spectra and relative extinction coefficients for possible decomposition products of the 2,4-dinitrobenzene-diazonium ion in solutions of 3.0-5.5.)

On the basis of the above information, the decomposition product is believed to be 5-hydroxybenzene-2-diazo-1-oxide. Several attempts were made to synthesize this compound from nonnitrosocrescnil.
These were unsuccessful (see discussion section).

Table 4

Observed maxima and relative extinction coefficients for possible decomposition products of 2,4-dinitrobenzenediazonium fluoroborate in solutions of pH 3.0-5.5.

<table>
<thead>
<tr>
<th>Product</th>
<th>λ max</th>
<th>εv/s₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-dinitroaniline</td>
<td>λ₁ = 315 nm</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>λ₂ = 260</td>
<td></td>
</tr>
<tr>
<td>2,4-dinitrophosphate ion</td>
<td>350</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td></td>
</tr>
<tr>
<td></td>
<td>shoulder at 395</td>
<td></td>
</tr>
<tr>
<td>2,4-dinitrobenzenediazonium</td>
<td>315</td>
<td>.48</td>
</tr>
<tr>
<td>Fluoroborate</td>
<td>263</td>
<td></td>
</tr>
<tr>
<td>5-nitro-2-aminophenol</td>
<td>335</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>2,4-dinitrobenzenediazotate</td>
<td>325</td>
<td>.66</td>
</tr>
<tr>
<td></td>
<td>265</td>
<td></td>
</tr>
<tr>
<td>5-nitrobenzene-2-diazo-1-oxide</td>
<td>430</td>
<td>.37</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td></td>
</tr>
<tr>
<td>Decomposition product</td>
<td>400 (av.)</td>
<td>.41</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td></td>
</tr>
</tbody>
</table>

III. Kinetic studies at intermediate pH.


Kinetic measurements of the rate of formation of the decomposition product of 2,4-dinitrobenzenediazonium ion were taken at various pH (see experimental section for details). The spectrum of the product was determined from λ = 550-250 nm at the end of each run and extinction coefficients were calculated. (The average of these are reported in Table 4.) Acetate buffers ranging from pH 4.0-5.2 and in total acetate concentration from .1M to .001M were used.
Phosphate buffers of pH 5.5, and .1M, .02M, and .001M total phosphates were used (observed rates are not reported for all of these).

One run each at pH 3.0 in .002M perchloric and in .001M sulfuric acids was done. The reaction in these was very slow. A concentration of $10^{-5}$ M in diazonium salt was used in all cases except for two series in which $10^{-5}$ M diazonium salt was used.

b. Determination of $k_p$, the pseudo first order rate constant.

The data obtained were graphed using the method of Guggenheim.

The pseudo first order rate constants obtained for the first four minutes of reaction time appeared to be dependent on pH and on acetate concentration. The observed rate constants are independent of diazonium ion concentration. The reproducibility is within about $10^3$ in these constants. Table 5 shows a comparison of pseudo first order rate constants in .1M acetate buffers for $10^{-4}$ M and $10^{-5}$ M diazonium ion at various pH.

**Table 5**

Comparison of observed rates obtained by changing the concentration of initial diazonium salt by a factor of ten. .1M acetate buffers of varying pH were used. Temperature = 25° C.

<table>
<thead>
<tr>
<th>$10^{-4}$ M diazonium salt</th>
<th>$10^{-5}$ M diazonium salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_p$ (min$^{-1}$)</td>
<td>$k_p$ (min$^{-1}$)</td>
</tr>
<tr>
<td>4.11</td>
<td>4.11</td>
</tr>
<tr>
<td>4.52</td>
<td>4.52</td>
</tr>
<tr>
<td>4.35</td>
<td>4.36</td>
</tr>
<tr>
<td>5.25</td>
<td>5.25</td>
</tr>
</tbody>
</table>

The kinetic data obtained may be summarized as follows:

1. Phosphate buffers
   - pH 5.5
   - .01M $k_p = .40$ min$^{-1}$
   - .001M $k_p = .01$ min$^{-1}$
2. 0.001M perchloric and 0.001M sulfuric acids.

\[
\text{pH 3.0} \quad k_\text{H} = 0.025 \text{ min}^{-1}
\]

3. Acetate buffers (see Table 6).

**Table 6**

Variation of \( k_\text{H} \) with total acetate concentration and with pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>4.0</th>
<th>4.1</th>
<th>4.2</th>
<th>4.3</th>
<th>4.4</th>
<th>4.5</th>
<th>4.6</th>
<th>4.7</th>
<th>4.8</th>
<th>5.0</th>
<th>5.2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>.27</td>
<td>.26</td>
<td>.44</td>
<td>.44</td>
<td>.53</td>
<td>.48</td>
<td>.78</td>
<td>1.06</td>
<td>2.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.15</td>
<td>.37</td>
<td>.64</td>
<td>.71</td>
<td>.69</td>
<td>1.03</td>
<td>1.29</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>.50</td>
<td>.39</td>
<td>.41</td>
<td>.44</td>
<td>.53</td>
<td>.51</td>
<td>.43</td>
<td>.51</td>
<td>.48</td>
<td>.92</td>
<td>.94</td>
</tr>
<tr>
<td></td>
<td>.51</td>
<td>.39</td>
<td>.41</td>
<td>.44</td>
<td>.53</td>
<td>.51</td>
<td>.43</td>
<td>.51</td>
<td>.48</td>
<td>.92</td>
<td>.94</td>
</tr>
</tbody>
</table>

From these data, the following relation may be postulated:

\[
k_\text{H} = k_x + k_{\text{Ac}} \text{(Ac}^-)\]

in which \( k_x \) is a function of pH only.

**c. Determination of \( k_x \).**

The pseudo first order rate constants obtained above were graphed versus total acetate concentration to determine \( k_x \), the rate constant independent of acetate concentration and dependent only of pH. (See Table 7 for a summary of these results.)

**Table 7**

Variation of \( k_x \) with pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>( k_x ) (min(^{-1}))</th>
<th>([H^+])</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>.025</td>
<td>(10^{-3})</td>
</tr>
<tr>
<td>4.0</td>
<td>.23</td>
<td>(7.9 \times 10^{-5})</td>
</tr>
<tr>
<td>4.1</td>
<td>.37</td>
<td>(4.0 \times 10^{-5})</td>
</tr>
<tr>
<td>4.2</td>
<td>.43</td>
<td>(3.2 \times 10^{-5})</td>
</tr>
<tr>
<td>4.3</td>
<td>.48</td>
<td>(2.5 \times 10^{-5})</td>
</tr>
<tr>
<td>4.4</td>
<td>.48</td>
<td>(1.6 \times 10^{-5})</td>
</tr>
<tr>
<td>4.5</td>
<td>.54</td>
<td>(1.0 \times 10^{-5})</td>
</tr>
<tr>
<td>5.0</td>
<td>.92</td>
<td>(6.3 \times 10^{-5})</td>
</tr>
<tr>
<td>5.2</td>
<td>.94</td>
<td>(1.0 \times 10^{-5})</td>
</tr>
</tbody>
</table>

To determine the effects of pH, \( 1/k_x \) versus hydrogen ion concentration was graphed. (\( k_x \) versus hydroxide ion concentration was
also graphed.) See graphs 1 and 2. The non-linearity of the rate versus hydroxide ion concentration suggests an effect of pH on rate parallel to that of the phenol-forming reaction of the tetrazonium salt. This requires a plot of $1/k_{\text{obs}}$ versus hydrogen ion concentration to be linear and a reasonable fit to this is shown in Graph 2.

d. Determination of $k_{\text{Ac}}$

$k_{\text{Ac}}$; the acetate dependent rate constant was determined by plotting true acetate concentration versus $k_{\text{obs}} - k_{k}$. Although the fit to a straight line in Graph 5 is poor, a trend toward increase in rate with acetate concentration is indicated. The linear relation predicted by the equation for the over-all rate given above is adequate for the experimental precision.

Table 8 given below shows a comparison of the observed and calculated $k_{k}$ as they vary with pH. (See discussion section for the calculation of $k_{k}$.)

<table>
<thead>
<tr>
<th>pH</th>
<th>$k_{k}$ obs. (min.$^{-1}$)</th>
<th>$k_{k}$ calc. (min.$^{-1}$)</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>0.26</td>
<td>0.26</td>
<td>0.00</td>
</tr>
<tr>
<td>4.1</td>
<td>0.31</td>
<td>0.37</td>
<td>0.06</td>
</tr>
<tr>
<td>4.5</td>
<td>0.48</td>
<td>0.55</td>
<td>0.07</td>
</tr>
<tr>
<td>4.6</td>
<td>0.54</td>
<td>0.62</td>
<td>0.03</td>
</tr>
<tr>
<td>4.8</td>
<td>0.92</td>
<td>0.75</td>
<td>0.17</td>
</tr>
<tr>
<td>5.0</td>
<td>0.94</td>
<td>0.86</td>
<td>0.08</td>
</tr>
<tr>
<td>5.2</td>
<td>0.94</td>
<td>0.95</td>
<td>0.01</td>
</tr>
<tr>
<td>5.0</td>
<td>0.02</td>
<td>0.05</td>
<td>0.005</td>
</tr>
</tbody>
</table>
DISCUSSION

1. Assignment of molecular species present at different pH.

On the basis of their ultraviolet and visible spectra, and by analogy with other diazonium salts, the following compounds are assumed to be present at the pH indicated:

<table>
<thead>
<tr>
<th>pH</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-3.5</td>
<td>2,4-dinitrobenzenediazonium ion</td>
</tr>
<tr>
<td>4.0-5.6</td>
<td>decomposition product of 2,4-dinitrobenzenediazonium ion and of 5-nitro-2-diazo-1-oxide</td>
</tr>
<tr>
<td>6.2-8.0</td>
<td>2,4-dinitrobenzenediazotate ion</td>
</tr>
</tbody>
</table>

Evidence for the diazotate being present at pH 6.2-8.0, rather than the diazohydracide is based on pKₐ measurements of p-nitrobenzenediazotate done by Lewis and Suhr. The addition of an ortho nitro group should give a pKₐ in the region 5-6 by analogy to the p-nitro compound, and therefore, the concentration of 2,4-dinitrobenzenediazohydracide at pH 6.2-8.0, would be very small.

From the positive tests obtained for the elimination of nitrite from the solutions of both 2,4-dinitrobenzenediazonium ion and 5-nitrobenzene-2-diazo-1-oxide, and by comparison of the ultraviolet and visible spectra of these solutions with each other and with the spectra of other possible products, the decomposition product present at pH 4.0-5.6, is probably 5-hydroxybenzene-2-diazo-1-oxide.
Tables 1, 2, 3, 4). Therefore, a synthesis of this compound was attempted.

II. Attempted synthesis of decomposition product.

The synthesis of 5-hydroxybenzene-2-diazo-1-oxide from resorcinol via the mononitroso-derivative was attempted. Unfortunately, this was unsuccessful. 6-aminoresorcinol was synthesized but could not be obtained in pure form as it is very susceptible to air oxidation. It was thought that the dibenzoate of 6-aminoresorcinol would hinder oxidation of the amine, but attempted nitration of resorcinol dibenzoate went in very low yield. Attempted diazotization of crude 6-aminoresorcinol was unsuccessful. Since nitrous acid can act as a nitrosating and oxidizing agent in addition to diazotizing amines, it appeared that the amine had either been oxidized, or more probably, nitrosated in the course of the attempted diazotization. Evidence for the nitrosation rather than diazotization having occurred is found in the work of Kaufmann and dePay who state that attempted diazotization of 2-aminoresorcinol gave only a nitroso compound:

A similar reaction for 6-aminoresorcinol would not be unreasonable.

As further evidence for the proposed structure of the decomposition product, previous literature on the diazo-oxides was consulted.

III. Previous literature on the diazo-oxides.

From the literature, it is found that diazonium salts of poly-nitro substituted aromatic amines are very prone to form diazo-oxides with the elimination of a nitro group. Some examples of
diazo-oxides are:

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

The first diazonium salt synthesized by Griess (1858),\textsuperscript{19} that of picramic acid, formed a diazo-oxide.

The structure of the diazo-oxides has been the subject of much discussion. Morgan and Porter\textsuperscript{15} favored a cyclic structure (I) on the basis of observed physical properties. However, they stated that a quinonoid structure (II) could not be eliminated entirely. Klemenc\textsuperscript{20} believed that the diazonium structure (III) most closely accounted for the observed properties.

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\text{II} & \quad \text{III} \\
\end{align*}
\]

Recently, Glowiak\textsuperscript{21} studied the infra-red spectra of some substituted ortho-diazo-oxides. He stated that on the basis of dipole studies, the cyclic structure (I) may be discarded. He suggests that the quinonoid and diazonium structures (II and III) are interchangeable, and that one or the other may be predominant, depending on the substituents present:

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\end{align*}
\]
He took the infra-red spectrum of a known diazo-oxide and compared this with the spectra of the corresponding amine, diazonium salt, and an analogous orthoquinone. He correlated his findings with solubility data. Glowiak observed that the quinonoid form as determined by its spectrum is fairly soluble in organic media and is affected by acid. The diazonium form is only slightly soluble in organic solvents and is unaffected by acids. Methyl and hydroxyl groups appear to favor the quinonoid structure; carboxyl, the diazonium form (two nitro groups were present in the molecule in all cases observed). These observations can be interpreted in a reasonable and obvious manner even though it is clear that the two structures are extreme contributing structures of a resonance hybrid.

The formation of diazo-oxides has been observed under the following conditions: 15

1. Diazotization of an amine containing ortho or para hydroxyl, nitro, methoxy, or bromo substituents. Dilute acid or acetic acid is commonly used in the diazotization.

2. Diazotization in strong acid of an amine containing ortho or para nitro or methoxy groups. The diazotization mixture is then diluted with water and made slightly alkaline, or the diazonium salt is isolated and then added to water or to a slightly alkaline solution. In some cases aqueous acetic acid may be basic enough.
Moldola and co-workers studied the formation of diazo-oxides on diazotization of various nitro substituted p-anisidines. The structures of the diazo-oxides obtained were based on elemental analyses of the \( \beta \)-napthol coupling products. The diazotizations were done in acetic acid with the exception of trinitro-p-anisidine which was diazotized in cold concentrated sulfuric acid and the resulting solution diluted with water. Moldola found that a methoxy group was displaced preferentially if activated by an ortho nitro group; otherwise, a nitro group was displaced by hydroxyl to give the diazo-oxide.

Morgan and co-workers have done a variety of work on the diazo-oxides. The properties they observed may be summarized as:

1. In general, the diazo-oxides are sparingly soluble in organic media.

2. They are relatively stable in acid solution.

3. Diazo-oxides have a pronounced color both as a solid and in solution.

4. They couple readily with alkaline \( \beta \)-napthol; the coupling product with \( \beta \)-napthol was the means of identifying each diazo-oxide studied by Morgan and co-workers. They observed the color, melting point, and did an elemental analysis of the coupling product. In some cases, the latter were not too accurate. For example, for the coupling product of 5-nitrobenzenes-2-diazo-1-oxide with \( \beta \)-napthol, 13.59\% nitrogen was calculated and 12.71\% nitrogen was obtained experimentally. This difference may be accounted for if one assumes that a reaction in which a nitro group in the diazo-oxide
has been replaced has already occurred to some extent.

5. The diazo-oxides are light-sensitive.

6. They are somewhat inert as far as replacement of the
diazo group is concerned; one observes primarily replacement
of substituents on the aryl nucleus.

Thus 5-hydroxybenzene-2-diazo-1-oxide as the decomposition
product of 2,4-dinitrobenzenediazonium ion and of 5-nitrobenzene-2-
diazo-1-oxide is a reasonable assumption.

IV. Interpretation of kinetic data.

From previous work with diazonium salts, the reaction studied
is assumed to be first order in 2,4-dinitrobenzene diazonium ion.
Further evidence for the correctness of this assumption is that
changing the initial concentration of the diazonium salt by a
factor of ten resulted in little or no change in observed rate (see
Table 5).

a. Discussion of the observed rate constant, $k_\psi$.

In obtaining the observed or pseudo first order rate
constants, $k_\psi$, the first four minutes of reaction time were used.
After this time, a first order course may no longer be assumed since
reverse diazotate formation and other side reactions probably occur.
From comparison of the rates, a definite dependence on pH and some
dependence on acetate concentration is observed. From this, the
following equation may be set up:

$$k_\psi = k_x + k_{OAc} \cdot [OAc^-]$$

where $k_x$ is a function only of pH.

b. Determination of $k_x$, a rate constant dependent only on pH.
$k_n$, the acetate independent rate constant was obtained
by extrapolation of the pseudo first order rate constants to zero
acetate concentration at constant pH. A plot of $k_n$ versus hydroxide
ion concentration gave a curve similar to that obtained for the bis-
diazonium salt.\footnote{See Graph 1} By analogy with this, the following
reaction sequence may be postulated:

\[
\text{diazonium salt} \xrightleftharpoons[OH^-]{\overset{\text{H}^+}{\leftrightarrow}} \text{diazohydroxide} \xrightarrow{\text{H}^+} \text{product} \xrightarrow{\text{H}^+} \text{diazotate}
\]

$1/k_n$ versus hydrogen ion concentration was next graphed, as suggested
by eqs. (6) and (15) of reference 1. The results are summarized in
Table 3 (see results section). By analogy to the bis-diazonium salt\footnote{See Graph 2}, an equation
of the form

\[
l/k_n = a[H^+] + b
\]

where $a$ and $b$ are constants, was used to determine $k_n$ calc. The
constants, $a$ and $b$, were calculated analytically using intermediate
points on the graph. The following values for $a$ and $b$ were obtained:

\[
a = 0.50 \\
b = 0.36
\]

$k$ calc. differ from $k$ obs. by about 12% on the average.

\begin{itemize}
  \item c. Determination of $k_{\text{Ac}}$
  
  $k_{\text{Ac}}$, the acetate dependent rate constant, was determined
  by plotting true acetate concentration versus $k$. See Graph 3.
  The slope is equal to $k_{\text{Ac}}$, or
  \[
k_{\text{Ac}} = 0.05 \text{ min}^{-1}
  \]
\end{itemize}

d. Interpretation of observed differences in rate using acetate
buffers and phosphate buffers.
It was observed that the pseudo first order rate constants found in acetate and in phosphate buffers differed markedly. Those observed in the phosphate buffers were much slower. This difference in rate may be attributed to steric and possibly electronic effects. The acetate (and carbonate ions used by Morgan\textsuperscript{15}) are planar in structure; the phosphate ions are tetrahedral. Thus, it can be seen that from the figures below the steric hindrance would be a reasonable explanation for the difference in rates found if one assumes this sort of intermediate, which, on the basis of other work with diazonium salts,\textsuperscript{1} is reasonable.

The observed difference in rates obtained on changing the concentration of the phosphate buffers was not studied in detail so no conclusions may be drawn from these results.

On the basis of the above structural and kinetic evidence, the following reaction scheme may be postulated. See following page.
* acetate, carbonate, phosphate ions may also be used.
** this transition state is suggested by analogy with the tetrazonium salt.
*** postulated decomposition product on the basis of structural evidence available.
EXPERIMENTAL

A. Syntheses.

1. 2,4-dinitrobenzenediazonium sulfate was synthesized by the method of Gilman. The fluoroborate salt was then precipitated and collected according to Hinds. It was stored in a desiccator in the dark and appeared to be relatively stable up to three months under these conditions.

The spectrum of 2,4-dinitrobenzenediazonium fluoroborate in 6M and in 3M sulfuric acid was observed in the ultra-violet and visible regions. (See Table 4.)

2. 2,4-dinitrodobenzene was synthesized by the method of Beckwith, Miller, and Leaky. Yellow crystals, mp. 83.5-39° C. were obtained. The ultra-violet and visible spectrum in water gave

\[ \lambda_{\text{max}} = 270 \text{ nm} \quad \varepsilon = 15,000 \]

3. 2,4-dinitrophenol was prepared by heating 2,4-dinitrochlorobenzene with concentrated sodium hydroxide for 15-30 minutes. The mixture was cooled and acidified. The solid which separated was collected and recrystallized from water. Yellow-green crystals, mp. 113.2-113.6° C. were obtained. The ultra-violet and visible spectrum in pH 8.0 phosphate buffer was taken. (See Table 4.)

4. 5-nitrobenzene-2-diazo-1-oxide in solution was synthesized by the method of Morgan. No \( \beta \)-naphthol coupling product was made.

The spectrum of the aqueous solution is reported in Table 4.
5. 5-nitrobenzene-2-diazo-1-oxide was prepared as the solid according to Morgan from 2-amino-5-nitrophenol. The visible and ultra-violet spectrum in aqueous solution did not vary with pH 2.0-7.0. It is reported in Table 2.

On standing in aqueous solution for 45 minutes to an hour, nitrite was evolved and a change in spectrum was observed. (Again see Table 2.)

6. The synthesis of 5-hydroxybenzene-2-diazo-1-oxide was attempted. Mononitrosoresorcinol was prepared from amyl nitrite and resorcinol by the method of Henrich. The aminoresorcinol was prepared by catalytic hydrogenation of the nitroso compound. The hydrochloride of the amine was prepared by pouring an ethanolic solution of the amine on a mixture of ice and hydrochloric acid. The brown solid which separated was collected. Diazotization of this substance was then attempted (see discussion section). This was unsuccessful. Diazotization of the amine hydrochloride in glacial acetic acid with sodium nitrite gave a mixture. Maxima were observed at

\[ \lambda_{max} = 395 \text{ (shoulder)} \]

No extinctions were calculated. No conclusions can be drawn from this as the purity of the sample is very questionable.

B. Preparation of Buffer Solutions.

1. 0.1M phosphate buffers from pH 5.4-8.0, were prepared according to Hiller and Golder. Dilutions were made of these.

2. 0.01M acetate buffers from pH 4.0-5.2, were prepared according to Willard, Furman, and Bricker. Dilutions were made of these.
C. Nitrite Determinations.

Nitrite determinations for the diazonium salt and for the diazo-oxide in different solutions were done using a variation of the method of Feigl.\(^1\) Filter paper containing two drops each of the reagent solutions was held over the mouth of the flask containing the solution to be tested. The flask was then heated slightly. A pink coloration indicated nitrite.

D. Spectral Determinations.

Spectral determinations were done in the ultra-violet and visible regions from \( \lambda = 550-250 \text{ nm} \), using an automatic recording spectrophotometer (Cary model 14) and one centimeter cells. In most cases, one milligram of solid was dissolved in 25 milliliters of solution. In other cases, where the solid could not be isolated, the spectrum of the solution was taken.

E. Kinetic Studies.

Kinetic studies were carried out as follows: 25 ml. of the desired buffer solution was pipetted into a 50 ml. Erlenmeyer flask containing approximately 1 mg. of 2,4-dinitrobenzenediazonium fluoroborate accurately weighed on a Cahn electrobalance. Timing was started from the beginning of addition of buffer. (In the cases of \( 10^{-5} \) M diazonium salt, 0.5 mg. in 50 ml. buffer solution was used.) A sample of the mixed solution was withdrawn and put in a one centimeter cell which had been rinsed with methanol and dried. The cell was then placed in a Cary model 14 automatic recording spectrophotometer, and the change in absorbance with time at \( \lambda = 400 \text{ nm} \) was recorded. In most cases, a maximum of 45 seconds was required.
from the addition of buffer to the beginning of recording of change in absorbance. Each run took ten minutes. At the end of this time, a spectrum from \( \lambda = 550-230 \) nm was taken to check the compound produced. Buffers of pH ranging from 4.0-5.2, and total acetate concentration from \( \text{.1M-.001M} \) were used. Phosphate buffers, pH 5.5, \( \text{.1M, .01M, and .001M} \) were used. One run each was done using \( \text{.001M perchloric and .001M sulfuric acid, pH 5.0} \). Temperatures ranged from 21°, 25°, 29° C. There seemed to be little effect of changing temperature. The majority of runs were done at 25° C. Different series of runs were done to determine the effects on observed rate of changing the concentration of diazonium salt, hydrogen ion concentration, and total acetate concentration. The results of the kinetic runs for the first four minutes were graphed by the method of Guggenheim using plotting log of change in absorbance versus time.
BIBLIOGRAPHY

The reactions of the 2,4-dinitrobenzenediazonium ion in solutions at various pH were studied. In particular, the product produced in the pH range 4.0-5.5 was studied to determine the structure of the decomposition product and to suggest a possible mechanism for the reaction. The kinetics of formation of this product were also studied. The decomposition product is suggested to be 5-hydroxybenzene-2-diazolo-1-oxide on the basis of available structural and theoretical evidence. The observed kinetics are found to fit the following equation:

\[ k' = k_x + k_{QAc} (QAc^-) \]

where \( k' \) is the observed pseudo first order rate constant
\( k_x \) is dependent only on pH as follows:
\[ \frac{1}{k_x} = a[H^+] = b \]
\( k_{QAc} \) is dependent only on acetate concentration and is 0.05 min.\(^{-1}\).