Evidence for Phenyl Cation as an Intermediate in Reactions of Benzenediazonium Salts in Solution1,2

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Received May 21, 1974

Abstract: Displacements on benzenediazonium cation, C6H5N2₂⁺, in solution in the absence of strong bases, reducing agents, or light proceed by rate-determining cleavage to a singlet phenyl cation intermediate, C₆H₅⁺, rather than by the bimolecular mechanism proposed in 1969. In aqueous solution at 25°, only unarranged products are obtained, and negligible incorporation of deuterium from solvent D₂O occurs, showing that aren processes do not occur to a significant extent. The low selectivity between nucleophiles nevertheless requires a highly reactive intermediate. In the hydrolysis of C₆H₅N₂⁺, the high entropy of activation (+10.5 cal mol⁻¹ deg⁻¹) and the constancy of k₁ (within 4%) from H₂O to D₂O demonstrate that water is not involved as a nucleophile in the rate-determining step. The constancy of k₁ (within 10%) in solutions as diverse as 14–21 M H₂SO₄ and 100% CH₃CO₂H and CH₂Cl₂ is in accord with a common rate-determining step over this whole range of solvents. Para-substituent effects can be dissected into nearly equal field (predominantly transition state) and resonance constants, yielding a correlation coefficient worse than zero, although analysis using the Hammett ρσ equation, i.e., with only a single set of substituent constants, yields a correlation coefficient worse than zero.

The purpose of this work was to determine whether a weakly basic nucleophile Y (e.g., H₂O, Br⁻, Cl⁻, or F⁻), replacing the N₂⁺ group in an ordinary substitution reaction ("dediazonation") of benzenediazonium cation I in solution is in the transition state or not.6 The observed kinetics

\[
I + Y \rightarrow \ce{C6H5Y+ + N2} \\
II \rightarrow \ce{C6H4Y+ + N2} \\
III \rightarrow \ce{C6H5Y+ + N2}
\]

with benzenediazonium bromide, chloride, bisulfate, or fluoroborate in water at 5–64° is first order in diazonium salt.7 However, when Y is a solvent molecule (H₂O), the kinetics must be first order even with a bimolecular rate-determining step. When Y is a solute anion (Br⁻ or Cl⁻), a bimolecular mechanism involving Y could still give deceptive first-order kinetics because of compensating salt effects, as shown by excellent first-order kinetics for bimolecular reactions of trimethyl- or tribenzylsulfonium ion with chloride ion in 90% acetone–10% water and 16 other solvents and solvent mixtures at 18–100°.3 Analogous bimolecular possibilities for reactions of I with anions have not been eliminated in any previously published work by recourse to kinetic studies at constant ionic strength.

Possible Mechanisms. At the outset of this work, there appeared to be eight possibilities for the rate-determining step, where Y may be H₂O, Br⁻, Cl⁻, or F⁻. Mechanism I is a one-step bimolecular displacement. This simplest mech-

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III \rightarrow \ce{C6H5Y+ + N2}
\]

anism was rejected for a long time, because it appeared difficult to reconcile with the kinetics, e.g., with first-order
rate constants that vary less than 50% with hydrochloric acid concentration, while the product ratio \( \text{C}_6\text{H}_4\text{Cl}/\text{C}_6\text{H}_5\text{OH} \) changes from 0.05 to 3.\(^6\) Nevertheless, it was adopted in 1969 as the preferred mechanism for reaction of arene diazonium ions with \( \text{H}_2\text{O}, \text{SCN}^- \), \( \text{Br}^- \) or \( \text{Cl}^- \) in aqueous solution in best accord with all the evidence in much excellent published work.\(^7\)\(^8\) We too expected this mechanism or one of its stepwise addition–elimination variants (mechanisms 2 or 3)\(^9\)\(^10\) to be the one to survive further scrutiny when we began our experimental work in 1962.

Mechanism 4, first proposed in 1942 by Waters,\(^11\) does not involve \( \text{Y} \) in its transition state. This two-step mechanism proceeds through the reactive phenyl cation (IV) in which the positive charge cannot be delocalized by conventional forms of resonance. The intermediate in mechanism 2 or 3 seems much more likely, because it avoids such concentrated charge development. Singlet phenyl cation is perhaps the most implausible hydrocarbon carbonium ion that can be imagined, save for various antiaromatic cations (e.g., cyclopentadienyl), since its electron deficiency is localized in an orbital of relatively high s character (sp\(^2\)). It is generally better to give vacant orbitals maximum p character. Formally similar vinyl cation intermediates have recently been demonstrated in several reactions of acetylenes and vinyl halides and vinyl esters.\(^12\) However, \textit{ab initio} calculations\(^12b\) indicate that the preferred structure of the vinyl cation is linear at the carbonium carbon, the bent sp\(^2\) structure being higher in energy by more than 30 kcal mol\(^{-1}\). Experimentally,\(^12\)\(^d\) 1-cyclooctenyl and 2-cis-2-butenyl triflates (trifluoromethanesulfonates) solvolyze 10\(^3\) times faster than 1-cyclopentenyl triflate and 10\(^4\) times faster than 1-cyclohexenyl triflate at 50% ethanol at 100\(^\circ\)C, presumably because they can give linear carbonium ions more easily than 1-cyclopentenyl and 1-cyclohexenyl. It would be about as difficult for phenyl cation to be linear at C\(_1\) as for cyclohexenyl. A phenyl group is also more electronegative than a methyl group and unlikely to be transformed into a cation on that account also. Therefore one should be exceedingly skeptical about any interpretation requiring IV.

A variant of mechanism 4 involves not singlet IV but instead a triplet (biradical) phenyl cation, which might provide resonance stabilization and delocalization of the positive charge around the ring and even onto meta substituents, as was thought to be required to explain the peculiar effects of substituents on rate of dediazoniation of meta- and para-substituted benzenediazonium salts.\(^13\)

Mechanisms 5–8 all involve a benzene intermediate. Other possibilities seem to be only minor variants of these eight.\(^14\)

**Products.** Benzene mechanisms 5–8 are all excluded for decomposition of I in aqueous solutions without strong bases by the absence of isomerized products such as are formed from reactions known to proceed via a benzene intermediate under the same conditions. For example, decomposition of o-toluenediazonium chloride in water yields o-cresol but no m-cresol; likewise m-toluenediazonium ion yields m-cresol but no o-cresol, although as little as 0.1% could be detected (see Experimental Section). No rearrangements during decomposition of simple arene diazonium ions in aqueous solutions have been reported, although the reaction has been used widely for a century.\(^7\)\(^e\)\(^f\)

For I itself, the absence of benzene mechanisms is demonstrated by negligible formation of ring-deuterated phenol during the decomposition of I \( \text{BF}_4^- \) in DCI–D\(_2\)O. As shown in Table I, the amount of phen-d\(_{17}\)-ol formed is only 0.05% during solvolysis for 16 hr at 25\(^\circ\). At the acidities employed, phenol and phenoxide both undergo significant acid-catalyzed exchange.\(^19\) On the basis of control experiments, the incorporation of deuterium from exchange of the phenol under the reaction conditions is calculated as 0.02%. Thus, the contribution of benzene mechanisms (0.03% from Table I) is less than 0.05% and may be essentially zero within experimental error (estimated 0.02%). That benzene would have given rise to phen-d\(_{17}\)-ol is shown by the formation of greater than 90% phen-d\(_{17}\)-ol when benzene is generated in D\(_2\)O containing \( \leq 10^{-2} \text{M} \) NaOD.\(^20\)

The products also exclude various free radical mechanisms. Formation of phenyl radicals\(^6\) or of a triplet phenyl cation\(^13\) is ruled out by the low yields (\(\leq 2\%\)) of benzene obtained when I \( \text{BF}_4^- \) is decomposed in acetone or acetic acid, solvents that are good donors of hydrogen atoms, and by failure of any intermediate to undergo addition of bromine under our conditions. In 75% \( \text{CH}_3\text{CO}_2\text{H}–25\% \text{H}_2\text{O} \) solutions with 1–4 M \( \text{Br}_2 \) as a trap, no dibromide is formed initially. Some bromobenzene is formed, and this is later further brominated to \( \text{p-} \)dibromobenzene, but these are slower minor reactions (maximum 28%) and not zero order in \( \text{Br}_2 \) (see Experimental Section on products). Deuterium isotope effects\(^4\) also provide convincing evidence against a triplet mechanism. Thus only mechanisms 1–4, in which electrons stay paired throughout, remain.

A practical difficulty in distinguishing between mechanisms 1–4 by using reactions where \( \text{Y} \) is a solute molecule or ion, rather than the solvent, is the low selectivity between nucleophiles shown by whatever species it is (I or IV) that reacts with \( \text{Y} \) in the product-determining step. For example, hydrolysis strongly dominates and therefore obscures all other reactions in aqueous solutions. Experiments designed to influence product distribution or rate by decreasing the concentration of water had surprisingly little effect (cf. next section).

**Effect of Concentration of Water.** Tables II and III show that product distribution and rate are affected amazingly little by changes in concentration of sulfuric acid. The yields of bromobenzene and fluorobenzene are nearly constant at 11 \( \pm 2 \) and 0.9 \( \pm 0.1 \)% respectively. The major products are phenol and sulfonated derivatives of phenol.\(^2\) No doubt, the protonation of \( \text{Br}^- \) to \( \text{HBr} \) in 8–10 M \( \text{H}_2\text{SO}_4 \) decreases its reactivity and accounts for the continuing low yield of \( \text{C}_6\text{H}_4\text{Br} \). However, as a practical matter, this means that one cannot make reaction with any anion predominate over reaction with water, as would in practice be necessary if one had to choose between mechanisms 1–3 and mechanism 4 solely from kinetic order at constant ionic strength or con-

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**Table I.** Deuterium Incorporation into Phenol in DCI or HCl.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>H(^+), M</th>
<th>Time, hr</th>
<th>( m/e ) 95/(m/e 95 + m/e 94)</th>
<th>( m/e ) 94</th>
<th>% D</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{BF}_4^- )</td>
<td>0.01</td>
<td>16</td>
<td>0.0635</td>
<td>0.0629</td>
<td>0.06</td>
</tr>
<tr>
<td>( \text{BF}_4^- )</td>
<td>0.01</td>
<td>16</td>
<td>0.0646</td>
<td>0.0642</td>
<td>0.04</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5\text{OH} )</td>
<td>0.0087</td>
<td>44.5</td>
<td>0.0640</td>
<td>0.0656</td>
<td>0.04</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5\text{OH} )</td>
<td>0.0343</td>
<td>44.0</td>
<td>0.0642</td>
<td>0.0656</td>
<td>0.06</td>
</tr>
</tbody>
</table>

\(^a\) At 25\(^\circ\); hydroxyl protons exchanged before analysis. \(^b\) Initial concentration, 0.05 M.

**Table II.** Yields of Halobenzenes from Dediazoniation of 0.03–0.05 M \( \text{BF}_4^- \) in Aqueous 1.0 M H\(_\text{Br}\).

<table>
<thead>
<tr>
<th>( \text{H}_2\text{SO}_4, \text{M} )</th>
<th>T, (^\circ)C</th>
<th>( \text{C}_6\text{H}_5\text{Br}, % )</th>
<th>( \text{C}_6\text{H}_5\text{F}, % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>25</td>
<td>13.4</td>
<td>0.85</td>
</tr>
<tr>
<td>2.0</td>
<td>25</td>
<td>11.9</td>
<td>0.88</td>
</tr>
<tr>
<td>10.0</td>
<td>25</td>
<td>9.7</td>
<td>0.89</td>
</tr>
<tr>
<td>0.0</td>
<td>50</td>
<td>12.0</td>
<td>0.92</td>
</tr>
<tr>
<td>2.0</td>
<td>50</td>
<td>10.9</td>
<td>0.82</td>
</tr>
<tr>
<td>8.0</td>
<td>50</td>
<td>10.1</td>
<td>0.76</td>
</tr>
</tbody>
</table>
stent high concentration of some inert salt. Fortunately, there are other ways to distinguish between them.

The selectivity of whatever species it is (I or IV) that reacts with H2O, Br-, Cl-, or F-, although very low, is nevertheless measurable. Lewis and Cooper23 reported dimensionless competition factors k_x/k_y relative to water (55 M) of 1.4 for SO42-, 3 for Cl- or the N of SCN-, and 6 for the S of SCN-), comparable to our 6 for Br-. Selectivity between nucleophiles is indicative of the structure of the intermediate (or other) species that is doing the also are intermediates like trityl cation (C6H5)3C+), that are well stabilized by resonance.23a As little as 0.0013 M NaN3 in 50% water-50% acetone solution at 25°C can intercept 90% of all trityl ions generated, although competing with 27 M water (k_Cl-/k_H2O = 280,000; k_CI-/k_H2O = 3100).23a On the other hand, benzhydryl cation is much less selective (k_CI-/k_H2O = 120), and tert-butyl has a selectivity so low that it is hard to measure (k_CI-/k_H2O = 0.4).22,24

What should one expect for I (C6H5N2+) in mechanism I?

Surely it has excellent resonance stabilization, is stabler than trityl ion, and ought to be as selective in mechanisms 1 and 3. On the other hand, in mechanism 4, the activated complex for reaction of IV (C6H5N2+) with solvent or other nucleophiles should be much closer in structure to IV than to the final product III (C6H5N2+) in accord with the very low selectivities found (e.g., k_CI-/k_H2O = 3).21 even lower than those for tert-butyl cation.

A surprising observation that excludes all mechanisms except mechanism 4 out of the eight considered is the less than 2% change in first-order rate constant (k) for hydrolysis from 80 to 105% H2SO4, in spite of the facts that (1) the activity of water changes more than 1000-fold just from 80 to 98% H2SO4, (2) HSO4- is a much poorer nucleophile than water, and (3) even HSO4- drops rapidly above 100% H2SO4.26 Evidently the extent of covalent-bond formation between carbon and the nucleophile Y (here H2O or HSO4-) at the transition state is extremely small or zero. This is confirmed by the large positive entropy of activation and by the absence of a solvent isotope effect (cf. next two sections).

Effect of Temperature. Additional evidence against covalent bonding of water to carbon at the transition state of the hydrolysis reaction can be deduced from the large entropy of activation, +10.5 ± 1.0 gibbs (cal mol-1 deg-1) for 0.1 M 1 CI- in water at 25°C.27 This is within 2 gibbs of that for tert-butyl chloride.27 where it is generally thought that water is not covalently bonded to carbon at the transition state, but 20-24 gibbs (the translational entropy of one water molecule) higher than that for hydrolysis of benzyl chloride, methyl bromide, or methyl p-toluenesulfonate, where water is bonding to carbon in the transition state. Similarly, the entropy of activation 49° for hydration of isobutylene or 1-methylcyclopetene, where the rate-determining step is formation of a carboxonium ion, and water enters only after this step, is 18-25 gibbs higher than that for crotonaldehyde, where water adds to carbon during the rate-determining step, although the overall entropies of hydration (49°) for these two hydrocarbons are within 2 gibbs of that for crotonaldehyde.27

Solvent (H2O-D2O) Isotope Effect. Rates in light and heavy water are identical within experimental error (±4%, Table III), in agreement with previous results5 for 0.1 M 1 CI- at 35°C. The best value of k_H2O/k_D2O based on all of the data is 0.98 ± 0.01. The predicted values29 are (1.5)3 = 3.4 or (1.5)2 = 2.2 for complete conversion to hydronium or phenylxonium ion at the transition state (mechanisms 7, 8, or 9) or slightly less than 3.4 or 2.2 for formation of unstable benzyne or anion intermediates (mechanisms 5, 6, or 3); (2.2)2/2 = 1.5 for a mechanism 1 transition state midway between reactants and products, or less for earlier transition states; and unity (as observed) for mechanism 4. These 1.5 factors are equilibrium constants for complete conversion of a DO+ bond to an HO+ bond, which, for example, happens six times (K = (1.5)6 = 11) in

\[ 2D_2O + 3H_2O \rightleftharpoons 3H_2O^+ + 2D_2O \]

Evidently, even with the weak base water, the strength of Y-C bonding at the transition state is below RT and less than 2% of a normal O-C single bond. Operationally, this excludes all mechanisms except mechanism 4 of the eight considered. This evidence based on rate measurements (high activation entropy and insensitivity of hydrolytic rate to % H2SO4 or water deuteration) results of course from only the difference between transition-state and reactant structures. However, if the transition state does not bond Y, neither can any product or intermediate among the immediate products of the rate-determining step, because the descent from transition state to these first products occurs at the rate of a molecular vibration (RT/Nh), which is faster than Y can approach, if it is not already on hand and appreciably bonded. Furthermore, the evidence of at least some selectivity between nucleophiles,21 albeit low, shows that if is involved in the activated complex for the product-determining step, which must therefore be different from that for the rate-determining step. The evidence therefore specifically excludes the proposed one-step mechanism 1 and addition-elimination mechanisms 2 and 3 but still allows Water's elimination-addition mechanism 4 proceeding through the phenyl cation intermediate IV as the transition state.

Nitrogen and Aromatic Hydrogen Isotope Effects. The evidence against mechanisms 1-3 and 5-8 cited in the preceding three sections seems to us to be irrefutable. Nevertheless, we summarize here two other lines of evidence that add still more weight to the disproof of these mechanisms.

I is much less stable than III, and N2+ is a better leaving group than any Y+ that we are considering. Therefore, if the one-step mechanism 1 were correct, the transition state should be closer to I than to III in structure. Then the α-nitrogen isotope effect should be substantially less than that...
for halfway breakage of the C-N bond (1.02, based on a calculated N isotope effect of 1.04-1.045 for complete breakage of a C-N bond). If mechanism 2 or 3 were correct, the transition state should be close to the unstable intermediate II, and the α-N isotope effect should be close to unity. In the second paper following this one, we present data that show an α-N isotope effect of 1.038. This large kinetic isotope effect is inconsistent with mechanisms 1-3 but is in accord with mechanism 4 since its transition state should resemble the high-energy phenyl cation IV more closely than I, and hence the C-N bond should be extensively broken at its transition state.

The large hydrogen exchange isotope effect $k_H/k_D$ of 1.22 for each ortho hydrogen (see following paper) indicates an extremely electron-deficient transition state, as one close to the carbonium ion (IV, C$_6$H$_5^+$) in mechanism 4 would be, but one close to the resonance-stabilized diazonium ion (I, structure 9) in mechanism 1 or to the anionic intermediate (II) in mechanism 2 or 3 would not. Hyperconjugation is expected to become important only when better possibilities for stabilization by resonance, solvation, or other covalent participation by leaving, entering, or neighboring groups are all absent.

**Other Solvent Effects.** Products vary widely in different solvents, but rates vary remarkably little (Table III). In glacial acetic acid with 0-1 M LiCl added, 10$^{-3}$ M 1 BF$_2^-$ yields ≥69% phenyl acetate, 2-3% phenol, 29-0% fluorobenzene, and 0-27% chlorobenzene; in methanol, the products are 91-93% anisole, 5-6% fluorobenzene; in methylene chloride, they are 66% chlorobenzene and 34% fluorobenzene; in 3-methylsulfolane, they are 54% phenol and 17% fluorobenzene.

The similarity of rate constants shown in Table III for three solvents of widely different polarity, CH$_2$Cl$_2$ (2.2), CH$_3$CO$_2$H (2.3), and fuming H$_2$SO$_4$ (2.2), is striking. It seems to us to imply that the rate-determining step does not change, and that these solvents solvate $I^*$ and I only very feebly. The twofold decrease in rate constant in the sulfoxide acetone with 0-1 M LiCl added (Table 2) is puzzling, but it may result from tighter solvation by large ionic aggregates approaching the stability of solid I BF$_2^-$ in these solvents of especially low anion-solvating ability.

The small (twofold) increase in rate from 14 M (80%) H$_2$SO$_4$ to 10$^{-2}$ M H$_2$SO$_4$ may at first appear to suggest a change or partial change to a new mechanism in 10$^{-4}$ M H$_2$SO$_4$ in which water is involved as a nucleophile, as in mechanism 1, 2, or 3. However, this deduction is unjustified because water activity or vapor pressure increases 30-fold over this range, and this is a region already noted for large and highly specific changes in ionic activity coefficients over this range, and this is a region already noted for large and highly specific changes in ionic activity coefficients (and consequent inconstancy of rate constants for ionic reactions), in contrast to the relative constancy of activity coefficients in 93-100% H$_2$SO$_4$. This small change (doubling) of rate is in fact completely reasonable for mechanism 4, as a consequence of differing effects of water solvation on I and $I^*$. The activity coefficient of I should be lower than that of $I^*$ by increasing water activity, even though there may be the same number of water molecules in the innermost shells of I and $I^*$ at any given concentration of H$_2$SO$_4$. Because the charge in I is better delocalized by resonance ( eq 9), it benefits less from replacement of neighboring H$_2$SO$_4$ molecules by H$_2$O molecules. In short, no water is involved in the rate-determining step from 21 M H$_2$SO$_4$ down to 14 M H$_2$SO$_4$. It is weakly involved in 10$^{-4}$ M H$_2$SO$_4$ but only to an extent that is reasonably attributed to a more reduced activity coefficient for $I^*$, owing to differentially stronger solvation of $I^*$ at the highest water concentration.

A similar (twofold) increase in rate occurs in 100% acetic acid solution when 1 M LiCl is added (Table III). Since the yield of C$_6$H$_5$Cl reaches only 27%, this is again due to better solvation of $I^*$ than of I, this time with stronger solvation by Cl$^-$ ion than by CH$_3$CO$_2$H solvent molecules.

The fact that the rate constant decreases no more than twofold on loss of this strong external solvation by Cl$^-$ (in 100% CH$_3$CO$_2$H) or by H$_2$O (from dilute to 100% H$_2$SO$_4$) suggests that there must be substantial compensation by some internal stabilization, such as resonance delocalization of the positive charge in the transition state $I^*$ just preceding II, obviously not as great as in 1 (eq 9) but nevertheless considerable. A mechanism for such delocalization in $I^*$ (hyperconjugation) is suggested by the kinetic secondary isotope effects observed when deuterium is present in ortho or meta positions, described in the paper immediately following this one.

**Meta- and Para-Substituent Effects.** Table IV shows observed and calculated substituent effects at 25°C. The observed log ($k/k_D$) values are those in the first major investigation of substituent effects for this reaction supplemented by two data for tert-butyl butyl26 but excluding data for anionic or partially anionic substituents. These observed rate constants range over five powers of ten, from 6 × 10$^{-5}$ sec$^{-1}$ for p-CH$_3$ to 7 × 10$^{-4}$ sec$^{-1}$ for m-C$_6$H$_4$Cl.

The calculated effects are

$$\log (k/k_D)_m = \varepsilon_m + \varepsilon_p + \varepsilon_a = (-2.74 \pm 0.20)\sigma + (-3.18 \pm 0.36)\rho + (0.27 \pm 0.12)$$

and

$$\log (k/k_D)_p = \varepsilon_m + \varepsilon_p + \varepsilon_a + i_p = (-2.60 \pm 0.16)\sigma + (0.28 \pm 0.10)$$

using $\varepsilon_m$ and $\varepsilon_p$ for "field" and "resonance" substituent constants defined and tabulated previously without any change. These $f$, $r$, and $a$ values were fitted by least-squares, and the ± numbers are their standard deviations.

For the $f_m$, $r_p$, and $a$ reaction constants represent the sensitivities of these reactions to the field constants $\varepsilon_m$ of meta and para substituents (representing all influences except those transmitted by resonance or $\sigma$ bonds). They are comparable (∼2.64 and ∼2.60) and of the expected sign and magnitude, because electron-supplying (negative $\varepsilon$) substituents should facilitate departure of N$_2$ with its previously bonding electron pair, by stabilizing the transition state $I^*$ (which is close to the electron-deficient phenyl cation IV in structure) much more strongly than the reactant I.

The $r_m$ and $r_p$ reaction constants represent the sensitivities of these reactions to the resonance constants $\sigma$ of meta and para substituents. For the ten meta substituents, resonance with electron-supplying (negative $\sigma$) substituents significantly stabilizes the transition state leading to phenyl cation by supplying negative charge to the ortho carbons. Since meta substituents are poor at stabilizing the reactant, they do not increase the double bond character of the C-N bond. Therefore the sign of this sensitivity to resonance $r_m$ due to meta substituents (∼3.18) is the same as that of $f_m$ and $f_p$ (nonresonance) sensitivities to both meta and para substituents. The % $\sigma_m$ (average relative importance of resonance) is 42.0%, which may be compared with 0% for $\sigma'$, 22% for $\sigma_m$, 53% for $\sigma_p$, and 66% for $\sigma_p^+$. For para substituents, however, resonance with electron-supplying substituents does increase the double bond character of the C-N bond in the initial reactant diazonium cation. This effect, which stabilizes the reactant and hinders cleavage of this bond, evidently considerably outweighs the

Journal of the American Chemical Society / 97:4 / February 19, 1975
kind of transition-state resonance stabilization exhibited by meta substituents and so causes \( r_p \) to be positive for para substituents (+5.08), in contrast to the otherwise negative \( f \) and \( r \) constants for these reactions. Para-resonance effects, although in the opposite direction from meta effects, are now an even larger proportion of the total substituent effects (55%). Figure 1 shows the fit for para substituents.

Both correlation coefficients are excellent: 0.984 for ten meta substituents and 0.992 for seven para substituents including hydrogen. The largest deviations calculated from observed log \( (k/k_H) \) values are for chloro (+0.36) in the meta series and for unsubstituted (-0.25) in the para series. Deviations are relatively negligible for \( p - \text{tert}-\text{butyl} \) (+0.03), \( p - \text{chloro} \) (-0.09), and \( p - \text{nitro} \) (-0.05).

The most significant aspect of these correlations is the fact that no special set of substituent constants was used to obtain these considerably better than average fits. The substituent constants used are simply the constant \( \bar{F} \) and \( \bar{R} \) values based on \( \sigma' \), \( \sigma_m \), and \( \sigma_p \) that were used previously\(^{18} \) to correlate 14 reaction series (average correlation coefficient 0.967), which did not include any diazonium ion reactions. There is thus no evidence that substituents can exert any influence on these reactions other than the two influences (field and resonance) measured by \( \bar{F} \) and \( \bar{R} \), nor that these reactions can respond to substituent changes by more than these two physical modes of interaction, characterized by \( f \bar{F} \) and \( r \bar{R} \). A two-term model is therefore quite satisfactory.

The excellent fit illustrated in Figure 1 confirms that only a single mechanism is operating over the whole range of substituents considered, because a constant pair of resonance \( (r) \) and nonresonance \( (f) \) sensitivity constants accommodates all these data.

Evidently the original reason for proposing\(^{13} \) that IV is a triplet was not valid, because substituent effects are fully explicable without involving a triplet.

Figure 2, on the other hand, shows that the same data for para substituents give an entirely random Hammett plot \( \log (k/k_H) = \rho \sigma + C \). The best line has a slope \( \rho \) of -0.7, but its correlation coefficient is so poor as to be quite imaginary (-0.16)\(^{1/2} \).\(^{40} \) No previously published alternative single set of substituent constants fits these data significantly better. Both field and resonance effects are important here. The use of dual substituent constants is always required for successful quantitative correlation whenever resonance contributions become considerable, except when the studied and defining reactions have nearly the same ratio of sensitivities \( (r/f) \) to these two kinds of substituent influences. Since they do not have the same ratio here, Figure 1 is the proper plot.

**Experimental Section**

\( \text{I (Benzenediazonium) BF}_4^- \) was prepared by diazotization of aniline in \( \text{HBF}_4 \) solution in an ice-salt bath,\(^{41} \) recrystallizing twice from saturated 25° solutions in 3% \( \text{HBF}_4 \) by chilling to 0°, and twice more by dissolving in \( \text{CH}_3_2\text{CO} \) at 25°, adding \( \text{CHCl}_3 \) until a few crystals appeared, then chilling to -20°. After being dried at 25° (1 mm) for 2 hr, it could be stored in a vacuum desiccator at 0° in the dark for several months with no sign of decomposition: ir \( \nu_{\max} \) (2% in KBr) 3100-3000, 2298, 1570, 1470, 1310, 1200-1000

Swain, et al. / Evidence for Phenyl Cation as an Intermediate
(BF₄⁻), 770, 760, 665, 535, 523, 512, and 460 cm⁻¹; uv λmax (H₂O) 260 nm (ε 12,000) and 265 (1880); nmr complex multiple δ 8.35 (20% in CDCl₃) 7.2-8.7; decays; composed slowly above 100° with evolution of BF₃ and melts into boiling C₂H₂F at 119-121° (lit. 121-122°).

Anal. Calcd for C₆H₅NBF₄; C, 37.55; H, 2.63; N, 14.60. Found: C, 37.70; H, 2.97; N, 14.68.

Solvents. Distilled water was passed through a 2-ft Pyrex column filled with Vycor Amberlite MB-1 resin (a mixture of sulfonic acid and quarternary ammonium ion resin) and sealed with a Teflon stopcock. Before use, each 1 L of water was flushed through the column. The conductivity of the water, measured in a Pyrex conductivity cell with Pt electrodes by a General Radio 1650A impedance bridge, was 2.5 × 10⁻⁷ mho cm⁻¹. This deionized H₂O was used to rinse all reaction vessels and as the solvent for all kinetic runs and product studies in aqueous or partially aqueous solutions.

H₂SO₄ used for kinetic runs and syntheses was analytical reagent 96%, diluted with the deionized H₂O. Fuming H₂SO₄ (Baker and Adamson reagent) showed a uv λmax 279-283 nm (absorbance A 0.8), attributed to SO₃·H₂O (276 nm (ε 525)). Fuming H₂SO₄ medium, 100 ml, and 0.3% H₂O (1 ml of Baker reagent grade) were refluxed 4 days in an all-glass apparatus sealed with a tube containing Drierite (CaSO₄). Destruction of SO₂ and H₂O₂ present was measured at 260 nm and 254.5 nm. The λ values for C₆H₅OCH₃ (1578, 1340, 883, 480) and C₆H₅Cl (280, 900, 600) were measured at these wavelengths. The yields of C₆H₅OCH₃, 91.5 ± 0.5%, and C₆H₅Cl, 5.5 ± 1%, were calculated from A at 277.9 and 266.5 nm. The uv was accepted for A at 260.5 and 254.5 nm against those observed with 1% H₂O. The rate constant was 8.90 ± 0.04 × 10⁻⁴ sec⁻¹ with 5.8 × 10⁻⁸ M 1 BF₄⁻ at 25°.

Products in Acetic Acid. Solutions containing approximately 10⁻² M salt and 0.0100, 0.100, and 1.00 M LiCl were decomposed at 25° for 4 days (10 half-lives). The yields of C₆H₅H, C₆H₅Cl, C₆H₅F, C₆H₅OH, and C₆H₅OAc were calculated from A of the solutions and the measured ε values at 280, 271, 265.8, 263, 260.5, and 259.5 nm. As a check, 76 mg (4 × 10⁻⁷ mol) of salt was dissolved in 10 ml of glacial HOAc containing 1.00 M LiCl. After 4 days at 25°, the solution was diluted to 100 ml and shaken with three 10-ml portions of cyclohexane. The cyclohexane solution was analyzed for C₆H₅Cl as previously described. The yield of C₆H₅Cl was 29 ± 2%. Calculated directly from A of the reaction mixture.

Products in Mercapto Chloride. When 11.6 g of salt was shaken with 100 ml of CH₃Cl₂ and allowed to stand in a dry box at 25°, the salt dissolved gradually over 2 days as the decomposition progressed. After 7 days (10 half-lives after complete solution), 90 ml of the solution was concentrated to about 1 ml by fractional distillation on a 60-cm Nester-Faust Pt spinning-band column at a reflux ratio of 7:1. The concentrate showed glc peaks for C₆H₅Cl and C₆H₅F in a ratio 3:2. The remainder of the original solution was decomposed at 25° in the dark for 42 hr (20 half-lives) and was analyzed by glc. The yields of C₆H₅F, determined from A at 266 nm (ε 170), for decomposition of 0.01-0.02% of p-HOC₆H₄CH₃Cl were calculated from A and ε of 0.025 at 270, 266.5, 260.5, and 254.5 nm. The ε values for C₆H₅CH₂Cl, C₆H₅F, and C₆H₅Cl were calculated from A at 270, 266.5, 260.5, and 255 nm. The uv was accepted for A at 260.5 and 254.5 nm against those observed with H₂O. The rate constant was 8.8 ± 0.04 × 10⁻⁴ sec⁻¹ with 5.8 × 10⁻⁸ M 1 BF₄⁻ at 25°.
Table V. Yields of Bromobenzene and p-Dibromobenzene from Dediazoniation of 0.1 M BF₄⁻ in 75% HΟAc Containing Br₂ and 0.25 M H₂SO₄ at 25°C

<table>
<thead>
<tr>
<th>Br₂, M</th>
<th>C₆H₅Br, %</th>
<th>p-C₆H₄Br₂, %</th>
<th>Total %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.44</td>
<td>7.7</td>
<td>0</td>
<td>7.7</td>
</tr>
<tr>
<td>1.1</td>
<td>12.2</td>
<td>0.1</td>
<td>12.2</td>
</tr>
<tr>
<td>2.2</td>
<td>12.1</td>
<td>5.9</td>
<td>18.0</td>
</tr>
<tr>
<td>3.0</td>
<td>0.8</td>
<td>21.5</td>
<td>22.3</td>
</tr>
<tr>
<td>4.0</td>
<td>0</td>
<td>28.0</td>
<td>28.0</td>
</tr>
</tbody>
</table>

Products in 75% Acetic Acid Containing Bromine. 1 BF₄⁻ (1.0 g, 0.005 mol) was dissolved in 100 ml of 75% HΟAc-25% H₂O containing 0.50 M Br₂ (Mallinkrodt reagent). After 48 hr at 25°C in the dark, the solution was filtered, and 0.67 g (30%) of bromanil was dried over Drierite and examined by glc on the Apiezon L column and analyzed for C₆H₅Br (13% yield) and p-ChH₄Br₂ (11% yield) by glc with a 6-ft 20% Apiezon L on Chromosorb W column at 150°C and 14 psi of He. To five 50-ml glass-stoppered erlenmeyer flasks painted black to exclude light were added 25 ml of 75% HΟAc-25% H₂O, 100 ml of concentrated H₂SO₄, and 32.0 g of Br₂ (0.20 M). The solutions were fitted to 25°C for 60-72 hr. The solutions were analyzed for C₆H₅Br and p-ChH₂Br₂ by glc (Table V). No o-C₆H₄Br₂ was detected, although an authentic sample was cleanly separated from p-ChH₂Br₂.

In order to determine whether C₆H₅Br is converted to p-ChH₂Br₂ under these reaction conditions, 29 g (0.18 mol) of Br₂ and 2.0 g (0.013 mol) of C₆H₅Br were added to 50 ml of 75% HΟAc containing 0.25 M H₂SO₄. The resulting 3.0 M Br₂ solution was allowed to stand at 25°C in the dark. Analysis of a 10-ml sample withdrawn after 10 hr showed a 98% yield of p-ChH₂Br₂.

Finally, a solution containing 0.124 M 1 BF₄⁻, 0.24 M H₂SO₄, and 0.95 M Br₂ was prepared from 5.00 g of 1 (0.026 mol), 150 g of glacial HΟAc, 50 g of 1.00 M H₂SO₄, and 32.0 g of Br₂ (0.20 mol). The solution was poured into a 250-ml glass-stoppered erlenmeyer flask painted black to exclude light and placed in a constant-temperature bath at 25°C. At 1-3 hr intervals, 25-ml samples were withdrawn and analyzed for C₆H₅Br and p-ChH₂Br₂. The half-life for C₆H₂Br₂ formation was about 7 hr vs. 5 hr for dediazoniation in the absence of Br₂.

If the diradical intermediate had a finite lifetime, Br₂ should readily attack it, forming o- and p-dibromobenzene but no C₆H₅Br. When 1 BF₄⁻ was decomposed in 75% HΟAc containing 0.44-4.0 M Br₂ and 0.25 M H₂SO₄, the initial product was C₆H₅Br. In solutions of Br₂ greater than 1 M, C₆H₅Br is subsequently brominated to p-ChH₂Br₂. The other products, C₆H₄OH and C₆H₄OAc, are converted to a mixture of 2,4,6-tribromophenol and bromoanil. Cα₆H₄Br₃ is the initial product, the reaction does not proceed through a diradical.

Products in Concentrated and Fuming Sulfuric Acid. First, 0.459 g of 1 BF₄⁻ was dissolved in 25 ml of 96% H₂SO₄ (0.096 M solution) and kept at 25°C for 1 week (16 half-lives). The resulting solution was extracted repeatedly with CHCl₃. The CHCl₃ solution was dried over Drierite and examined by glc on the Apiezon L column. No volatile products were detected. Next, 0.241 g was dissolved in 25 ml of 105% H₂SO₄ (0.05 M solution) and kept at 25°C for 7 days (16 half-lives). The solution was diluted to 250 ml, and three 50-ml aliquots were treated with excess Br₂ for 14 days at 25°C and filtered. The average yield was 59 mg of a yellow solid, mp 235°-240°, 275°-280° after recrystallization from benzene-Treatment with more Br₂ for 2 hr at 95°C produced an additional 15 mg of yellow crystals, mp 290°-295°, total yield 74 mg (70%). The ir spectrum of both fractions was identical with that of bromobenzene and absence of volatile products confirm that the original products were sulfonated derivatives of phenol.

Search for a Rearranged Product. To 14.4 g (0.10 mol) of o-toluidine and 60 ml of 4 M HCl in a 1-l. round-bottomed flask at 0°C, 6.9 g (0.10 mol) of NaNO₂ in 15 ml of water was added dropwise with stirring. After diazotization was complete, the flask was moved from the ice bath and 100 ml of concentrated H₂SO₄ was added. The heat of dilution of H₂SO₄ was sufficient to cause rapid decomposition. After evolution of N₂ had ceased, the mixture was diluted with 300 ml of water and extracted thrice with CH₂Cl₂. The CH₂Cl₂ solution was dried over Drierite and analyzed by glc. Peaks for o-cresol and o-chlorotoluene were observed in a ratio of 5:1, but no peak for m-cresol was observed. Tests with a mixture of o- and m-cresol showed that as little as 0.5% of either substance could be detected in the presence of the other. m-Toluol was converted to m-cresol by the same procedure. No o-cresol was detected by glc of the reaction mixture.

Deuterium Incorporation into Phenol. 1 BF₄⁻ (0.001 mol) was dissolved in 20 ml of 0.01 M DCI in D₂O (Columbia Organic Chemicals) or 0.01 M HCl in H₂O and kept at 25°C for 16 hr (3.8 half-lives). The mixture was extracted with three 10-ml portions of CH₂Cl₂, which were then extracted successively with three 20-ml portions of water and one 20-ml portion of saturated NaCl. The CH₂Cl₂ layers were combined, dried over Na₂SO₄, and evaporated at low pressure. For investigation of D exchange of C₆H₅OH, 0.001 mol of C₆H₅OH (Fisher reagent grade) was dissolved in 0.0087 or 0.034 M DCI in D₂O and maintained at 25°C for the designated periods of time, then isolated as described above.

The isotopic composition of the phenol samples was determined on an Atlas CH14 mass spectrometer at 20 eV by scanning the molecular ion peaks repeatedly. The exit slit was 1 mm, which gave flat-topped but resolved peaks. The reaction products and corresponding reference samples were introduced at similar (± 1%) inlet pressures, and the amplifier attenuation settings were adjusted identically for each sample and such as to give the maximum readable chart value for each m/e value. Because of slow equilibration of the instrument (half-life 1.5 min), it was pumped out for 15 min between samples, and the samples were introduced 15 min before measurements were begun.

Kinetic Measurements. Solutions about 0.001 M in I were prepared by dissolving 4 mg of salt in 25 ml of solvent. Glass-stoppered silica columns containing 3 ml of solution were placed in the water-jacketed cell block of a Zeiss Model PMQ-II spectrophoto meter maintained at 25.00 ± 0.03°C. The absorbance A at 295 nm (ε 1630), or at 315-325 nm if products or solvent absorbed, was measured every 20-30 min for 8-12 hr, then after an 8-10 hr break for another 4-5 hr. An additional measurement was made after at least 10 half-lives. An average of 15-25 measurements was made in each run. The half-lives of the reactions studied varied from 2 to 17 hr.

Experimental data were fitted to An = A₀ + (An - A₀) e⁻kt by the method of least-squares. Computations were performed on an IBM 7094 computer. The observed values of A₀ and Aₐ and of a value of k calculated from the apparent half-life were submitted as initial estimates; the correct values for A₀, Aₐ, and k were calculated by repeated iterations of the experimental data. The correct values of A₀, Aₐ, and k after each iteration were used as the estimates for the next iteration. After the fourth iteration, the values of A₀, Aₐ, and k, the standard deviations of these values, and (Aₐcalc - Aₐobs) for each point were printed out. Observed Aₐ values were generally less than 1% of A₀ and agreed with calculated Aₐ values within ±0.005 or ±1% of A₀.

References and Notes

(1) Supported in part by research grants from the Atomic Energy Commission, the National Institute of Health, and the National Science Foundation, and NSF Predoctoral fellowships to J.E.S. and K.G.H.


Swain, et al. / Evidence for Phenyl Cation as an Intermediate

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Although selectively mediated by analysis of products formed during solvolysis may be affected by trapping of species at various degrees of ionization, this relative is relatively small in the systems that have been studied to date for this purpose.


Ethers were found previously to be the principal products in alcohols: cf. DeTar and Kogwe, ref. 6.


C. F. Bernasconi, MTP Int. Rev. Sci.: Org. Chem., Ser. 1, 3, 35 (1973). A more complicated variant of this mechanism improves the rapidly forming a substituted anion, because the denitration reaction is not affected by the presence of free nucleophilic centers as NaBF is increased from 0 to 8.0 M. However, this and other published interpretations are based on the questionable assumption that the ion is a single entity formed or else change critically on addition of 0.5-8.0 M concentrations of salt. We would expect the activity coefficient of the ion to have a lower sensitivity to added salts than that of ion in solution and thus favor the tetravalent assumption, because the product may be consistent with the small (2-5%) changes observed in the experimental first-order rate constant.

Most nonaromatic nucleophilic substitution reactions in the absence of strong bases appear to proceed by an "SNAr" mechanism (2 or 3) rather than by 1 or 4 [J. F. Bunnett and R. E. Zahler, J. Amer. Chem. Soc., 81, 425 (1969); F. Pietra, Quart. Rev. Chem. Soc., 34, 254 (1969); J. F. Chlebowski, ref 9, and per-}


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E. Deveze and R. M. Harris, Jr., J. Amer. Chem. Soc., 93, 1365 (1971). DOH-COOH and -OH are excluded, because calculations from estimated pK values are not available.


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