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Evidence for Phenyl Cation as an Intermediate in Reactions of Benzenediazonium Salts in Solution[1,2]

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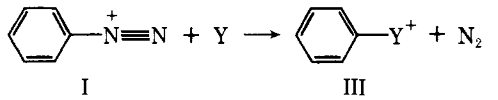
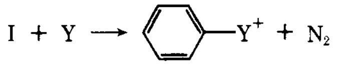
Abstract: Displacements on benzenediazonium cation, $C_6H_5N_2^+$, in solution in the absence of strong bases, reducing agents, or light proceed by rate-determining cleavage to a singlet phenyl cation intermediate, $C_6H_5^+$, rather than by the bimolecular mechanism proposed in 1969. In aqueous solution at 25°, only unrearranged products are obtained, and negligible incorporation of deuterium from solvent D_2O occurs, showing that aryne processes do not occur to a significant extent. The low selectivity between nucleophiles nevertheless requires a highly reactive intermediate. In the hydrolysis of $C_6H_5N_2^+$, the high entropy of activation (+10.5 cal mol^{-1} deg^{-1}) and the constancy of k_1 (within 4%) from H_2O to D_2O demonstrate that water is not involved as a nucleophile in the rate-determining step. The constancy of k_1 (within 10%) in solutions as diverse as 14-21 *M* H_2SO_4 and 100% CH_3CO_2H and CH_2Cl_2 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 (predominantly reactant) contributions by an analysis using dual substituent constants (previously published), with a correlation coefficient of 0.992, although analysis using the Hammett $\rho\sigma$ equation, *i.e.*, with only a single set of substituent constants, yields a correlation coefficient worse than zero.

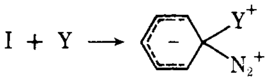
The purpose of this work was to determine whether a weakly basic nucleophile Y (*e.g.*, H_2O, Br^-, Cl^-, or F^-) replacing the N_2^+ group in an ordinary substitution reaction ("dediazoniation") of benzenediazonium cation (I) in solution is in the transition state or not.[6] The observed kinetics


I III

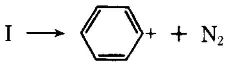
with benzenediazonium bromide, chloride, bisulfate, or fluoborate in water at 5-64° is first order in diazonium salt.[7] However, when Y is a solvent molecule (H_2O), the kinetics must be first order even with a bimolecular rate-determining step. When Y is a solute anion (Br^- or Cl^-), a bimolecular 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°.[8] 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.

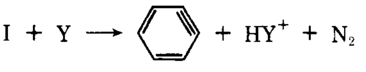
Possible Mechanisms. At the outset of this work, there appeared to be eight possibilities for the rate-determining step, where Y may be H_2O, Br^-, Cl^-, or F^-. Mechanism 1 is a one-step bimolecular displacement. This simplest mechanism was rejected for a long time, because it appeared difficult to reconcile with the kinetics, *e.g.*, with first-order

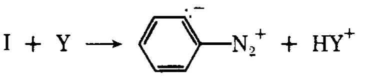

(1)
III


(2)
II

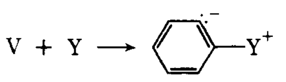
$$\text{II} \longrightarrow C_6H_5Y^+ + N_2 \tag{3}$$


(4)
IV


(5)
V


(6)
VI

$$\text{VI} \longrightarrow \text{V} + N_2 \tag{7}$$


(8)
VII

rate constants that vary less than 50% with hydrochloric acid concentration, while the product ratio C_6H_5Cl/C_6H_5OH changes from 0.05 to 3.[7c] Nevertheless, it was adopted in 1969 as the preferred mechanism for reaction of arenediazonium ions with H_2O, SCN^-, Br^- or Cl^- in aqueous solution in best accord with all the evidence in much excellent published work.[7g,9] We too expected this mechanism or one of its stepwise addition-elimination variants (mechanism 2 or 3)[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 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, *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,[12d] 1-cyclooctenyl and 2-*cis*-2-butenyl triflates (trifluoromethanesulfonates) solvolyze 10^5 times faster than 1-cyclopentenyl triflate and 10^4 times faster than 1-cyclohexenyl triflate in 50% ethanol at 100°, 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 benzyne intermediate. Other possibilities seem to be only minor variants of these eight.[14]

Products. Benzyne 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 benzyne 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 arenediazonium ions in aqueous solutions have been reported, although the reaction has been used widely for a century.[7e,15]

For I itself, the absence of benzyne mechanisms is demonstrated by negligible formation of ring-deuterated phenol during the decomposition of I BF_4^- in DCl-D_2O. As shown in Table I, the amount of phen-*d*$_1$-ol formed is only 0.05% during solvolysis for 16 hr at 25°. 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 benzyne mechanisms (0.03% from Table I) is less than 0.05% and may be essentially zero within experimental error (estimated 0.02%). That benzyne would have given rise to phen-*d*$_1$-ol is shown by the formation of greater than 90% phen-*d*$_1$-ol when benzyne is generated in D_2O containing $\leq 10^{-2}$ *M* NaOD.[20]

Table I. Deuterium Incorporation into Phenol in DCl or HCl[a]

		Time,	m/e 95/(m/e 95 + m/e 94)		
Reactant	H^+, *M*	hr	D_2O	H_2O	% D
I BF_4^-[b]	0.01	16	0.0635	0.0629	0.06
I BF_4^-[b]	0.01	16	0.0646	0.0642	0.04
C_6H_5OH	0.0087	44.5	0.0640	0.0636	0.04
C_6H_5OH	0.0434	44.0	0.0642	0.0636	0.06

[a] At 25°; hydroxyl protons exchanged before analysis. [b] Initial concentration, 0.05 *M*.

Table II. Yields of Halobenzenes from Dediazoniation of 0.03–0.05 *M* I BF_4^- in Aqueous 1.0 *M* HBr

H_2SO_4, *M*	*T*, °C	C_6H_5Br, %	C_6H_5F, %
0.0	25	13.4	0.85
2.0	25	11.9	0.88
10.0	25	9.7	0.89
0.0	50	12.0	0.92
2.0	50	10.9	0.82
8.0	50	10.1	0.76

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 (<5%) of benzene obtained when I 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% CH_3CO_2H-25% H_2O solutions with 1-4 *M* Br_2 as a trap, no dibromide is formed initially. Some bromobenzene is formed, and this is later further brominated to *p*-dibromobenzene, but these are slower minor reactions (maximum 28%) and not zero order in 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 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 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 ± 2 and 0.9 ± 0.1%. The major products are phenol and sulfonated derivatives of phenol.[2] No doubt, the protonation of Br^- to HBr in 8-10 *M* H_2SO_4 decreases its reactivity and accounts for the continuing low yield of C_6H_5Br. 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-

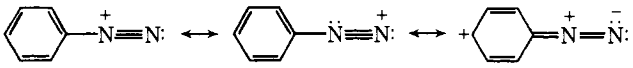
Table III. First-Order Rate Constants for Dediazoniation 0.0003–0.0015 M I BF_4^- at 25.0°

Run no.[2]	Solvent	$10^5 k_1$, sec^{-1}
25	0.001% (0.0001 M) H_2SO_4	4.59 ± 0.03
24	0.10% (0.010 M) H_2SO_4	4.55 ± 0.03
66	9.5% (1.0 M) H_2SO_4	4.12 ± 0.01
20	23% (2.7 M) H_2SO_4	3.56 ± 0.02
15	50% (6 M) H_2SO_4	2.68 ± 0.01
62	80% (14 M) H_2SO_4	2.13 ± 0.02
22	96% (18 M) H_2SO_4	2.11 ± 0.01
121	105% (21 M) H_3SO_4	2.15 ± 0.01
60	0.0001 M D_2SO_4	4.76 ± 0.04
59	0.010 M D_2SO_4	4.71 ± 0.04
67	1.0 M D_2SO_4	4.11 ± 0.07
40	100% CH_3CO_2H	2.26 ± 0.01
43	100% CH_3CO_2H + 0.13 M LiCl	3.71 ± 0.07
42	100% CH_3CO_2H + 1.0 M LiCl	4.51 ± 0.02
73	CH_2Cl_2	2.20 ± 0.05
122	3-Methylsulfolane	1.36 ± 0.03
71	97% sulfolane–3% $(C_2H_5)_2O$	1.24 ± 0.01
72	Dioxane	1.15 ± 0.02

stant 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 H_2O, Br^-, Cl^-, or F^-, although very low, is nevertheless measurable. Lewis and Cooper[21] reported dimensionless competition factors k_x/k_w relative to water (55 M) of 1.4 for SO_4^{2-}, 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 $(C_6H_5)_3C^+$, that are well stabilized by resonance.[23a] As little as 0.0013 M NaN_3 in 50% water–50% acetone solution at 25° can intercept over 90% of all trityl ions generated, although competing with 27 M water ($k_{N_3^-}/k_{H_2O}$ = 280,000; k_{Cl^-}/k_{H_2O} = 3100).[23a] On the other hand, benzhydryl cation is much less selective (k_{Cl^-}/k_{H_2O} = 120), and *tert*-butyl has a selectivity so low that it is hard to measure ($k_{Cl^-}/k_{H_2O} \simeq 4$).[22,24] What should one expect for I ($C_6H_5N_2^+$) in mechanism 1?



I

(9)

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 ($C_6H_5^+$) with solvent or other nucleophiles should be much closer in structure to IV than to the final product III ($C_6H_5Y^+$), in accord with the very low selectivities found (*e.g.*, k_{Cl^-}/k_{H_2O} = 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_1) for hydrolysis from 80 to 105% H_2SO_4, in spite of the facts that (1) the activity of water changes more than 1000-fold just from 80 to 98% H_2SO_4, (2) HSO_4^- is a much poorer nucleophile than water, and (3) even HSO_4^- drops rapidly above 100% H_2SO_4.[26] Evidently the extent of covalent-bond formation between carbon and the nucleophile Y (here H_2O or HSO_4^-) 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 I Cl^- in water at 25°.[7c] 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 ΔS^* for hydration of isobutylene or 1-methylcyclopentene, where the rate-determining step is formation of a carbonium 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 ($\Delta S°$) for these two hydrocarbons are within 2 gibbs of that for crotonaldehyde.[28]

Solvent (H_2O–D_2O) Isotope Effect. Rates in light and heavy water are identical within experimental error (±4%, Table III), in agreement with previous results[7c] for 0.1 M I Cl^- at 35°. The best value of k_{H_2O}/k_{D_2O} based on all of the data is 0.98 ± 0.01. The predicted values[29] are $(1.5)^3$ = 3.4 or $(1.5)^2$ = 2.2 for complete conversion to hydronium or phenyloxonium ion at the transition state (mechanisms 7, 8, or 4) or slightly less than 3.4 or 2.2 for formation of unstable benzyne or anionic intermediates (mechanisms 5, 6, or 3); $(2.2)^{1/2}$ = 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

$$2D_3O^+ + 3H_2O \overset{K}{\rightleftharpoons} 3H_3O^+ + 2D_2O$$

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 out of the eight considered. This evidence based on rate measurements (high activation entropy and insensitivity of hydrolytic rate to % H_2SO_4 or water deuteration) results of course from only the difference between transition-state and reactant structures. However, if the transition state does *not* bind 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 Y *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[9] and addition–elimination mechanisms 2 and 3[10] but still allows Water's elimination–addition mechanism 4 proceeding through the phenyl cation intermediate IV.[11]

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 N_2^+ 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,[5] 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 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 kinetic hydrogen secondary isotope effect k_H/k_D of 1.22 for each ortho hydrogen (see following paper[4]) indicates an extremely electron-deficient transition state, as one close to the carbonium ion (IV, $C_6H_5^+$) 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 this 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).[2] In glacial acetic acid with 0–1 M LiCl added, 10^{-3} M I BF_4^- 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.[30]

The similarity of rate constants shown in Table III for three solvents of widely different polarity, CH_2Cl_2 (2.2), CH_3CO_2H (2.3), and fuming H_2SO_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 sulfolanes and dioxane is puzzling, but it may result from tighter association into large ionic aggregates approaching the stability of solid I BF_4^- in these solvents of especially low anion-solvating ability.

The small (twofold) increase in rate from 14 M (80%) H_2SO_4 to 10^{-4} M H_2SO_4 may at first appear to suggest a change or partial change to a new mechanism in 10^{-4} M H_2SO_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 (and consequent inconstancy of rate constants for ionic reactions), in contrast to the relative constancy of activity coefficients in 83–100% H_2SO_4.[26] 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 lowered less 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_2SO_4. Because the charge in I is better delocalized by resonance (eq 9), it benefits less from replacement of neighboring H_2SO_4 molecules by H_2O molecules. In short, *no* water is involved in the rate-determining step from 21 M H_2SO_4 down to 14 M H_2SO_4. It is weakly involved in 10^{-4} M H_2SO_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.[31]

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_6H_5Cl 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_3CO_2H 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_3CO_2H) or by H_2O (from dilute to 100% H_2SO_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 I (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.[4]

Meta- and Para-Substituent Effects. Table IV shows observed and calculated substituent effects at 25°. The observed log (k/k_H) values are those determined in the first major investigation of substituent effects for this reaction[7c] supplemented by two data for *tert*-butyl[2,36] but excluding data for anionic or partially anionic substituents.[37] These observed rate constants range over five powers of ten, from 6×10^{-9} sec^{-1} for p-OCH_3 to 7×10^{-4} sec^{-1} for m-t-C_4H_9.

The calculated effects are

$$\log (k/k_H)_m = f_m\mathcal{F} + r_m\mathcal{R} + i_m = (-2.74 \pm 0.20)\mathcal{F} + (-3.18 \pm 0.36)\mathcal{R} + (0.27 \pm 0.12)$$

and

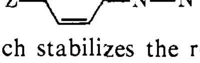
$$\log (k/k_H)_p = f_p\mathcal{F} + r_p\mathcal{R} + i_p = (-2.60 \pm 0.16)\mathcal{F} + (5.08 \pm 0.37)\mathcal{R} + (-0.25 \pm 0.10)$$

using $\mathcal{F}$ and $\mathcal{R}$ ("field" and "resonance") substituent constants defined and tabulated previously,[38] without any change. These f, r, and i values were fitted by least-squares, and the ± numbers are their standard deviations.[39]

The f_m and f_p reaction constants represent the sensitivities of these reactions to the field constants $\mathcal{F}$ of meta and para substituents (representing all influences except those transmitted by resonance or π bonds). They are comparable (−2.74 and −2.60) and of the expected sign and magnitude, because electron-supplying (negative $\mathcal{F}$) 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 $\mathcal{R}$ of meta and para substituents. For the ten meta substituents, resonance with electron-supplying (negative $\mathcal{R}$) 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 its 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 % $\mathcal{R}$ (average relative importance of resonance) is 42.0%, which may be compared with 0% for σ', 22% for σ_m, 53% for σ_p, and 66% for σ_p^+.[38]

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

Table IV. Effect of Substituents on Rate of Dediazoniation of I at 25°[a]

Substituent	Substituent constant $\mathcal{F}$	Substituent constant $\mathcal{R}$	Values of log (k/k_H) for Meta position Obsd	Meta position Calcd	Para position Obsd	Para position Calcd
H	0.000	0.000	0.000	0.272	0.000	−0.251
CH_3	−0.052	−0.141	0.650	0.864	−0.930	−0.832
C_2H_5	−0.065	−0.114	0.930	0.814		
$C(CH_3)_3$	−0.104	−0.138	1.250	0.997	−0.710	−0.682
C_6H_5	0.139	0.088	0.398	0.171	−1.252	−1.060
OH	0.487	−0.643	1.088	0.981		
OCH_3	0.413	−0.500	0.708	0.729	−3.842	−3.866
Cl	0.690	−0.161	−1.465	−1.109	−2.773	−2.865
Br	0.727	−0.176	−1.205	−1.163		
NO_2	1.109	−0.155	−3.063	−3.265	−2.401	−2.351

[a] Chloride salts in 0.1 *M* HCl (pH 1.7).[2,7c,37]

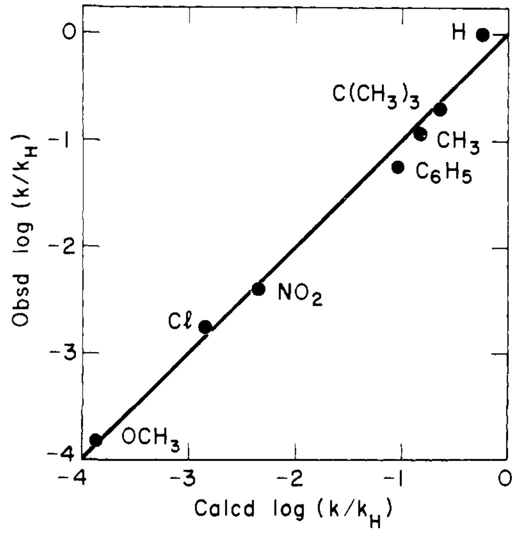


Figure 1. Dual substituent constant $(f\mathcal{F} + r\mathcal{R} + i)$ plot of para-substituent effects on rate of dediazoniation of I Cl^- in 0.1 *M* HCl at 25°.

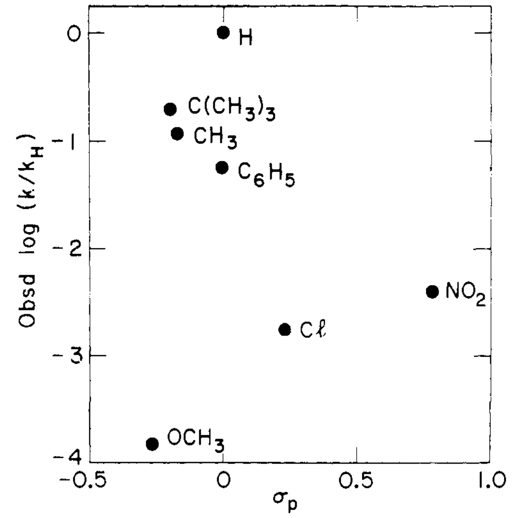


Figure 2. Hammett $(\rho\sigma)$ plot of para-substituent effects on rate of dediazoniation of I Cl^- in 0.1 *M* HCl at 25°.

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*-methoxy (−0.02), *p-tert*-butyl (+0.03), *p*-chloro (−0.09), and *p*-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 $\mathcal{F}$ and $\mathcal{R}$ values based on σ', σ_m, and σ_p that were used previously[38] 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 $\mathcal{F}$ and $\mathcal{R}$, nor that these reactions can respond to substituent changes by more than these two physical modes of interaction, characterized by $f\mathcal{F}$ and $r\mathcal{R}$. 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 (ρ) 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

I (Benzenediazonium) BF_4^- was prepared by diazotization of aniline in HBF_4 solution in an ice-salt bath,[41] recrystallizing twice from saturated 25° solutions in 5% HBF_4 by chilling to 0°, and twice more by dissolving in $(CH_3)_2CO$ at 25°, adding $CHCl_3$ 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 ν_{max} (2% in KBr) 3100-3000, 2298, 1570, 1470, 1310, 1200-1000

(BF_4^-), 770, 760, 665, 535, 523, 512, and 460 cm^{-1}; uv λ_{max} (H_2O) 260 nm (ϵ 12,000) and 295 (1880); nmr complex multiplet δ_{TMS} (20% in CH_3CN) 7.2-8.8; decomposes slowly above 100° with evolution of BF_3 and melts into boiling C_6H_5F at 119-121° (lit.[42] 121-122°).

Anal. Calcd for $C_6H_5N_2BF_4$: 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 Fisher analytical grade Amberlite MB-1 resin (a mixture of sulfonic acid and quarternary ammonium ion resin) and sealed with a Teflon stopcock. Before use each day, at least 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 H_2O was used to rinse all reaction vessels and as the solvent for all kinetic runs and product studies in aqueous or partially aqueous solutions.

H_2SO_4 used for kinetic runs and syntheses was analytical reagent 96%, diluted with the deionized H_2O. Fuming H_2SO_4 (Baker and Adamson reagent) showed a uv λ_{max} 279-283 nm (absorbance *A*, 0.8), attributed to SO_2, λ_{max} (H_2O) 276 nm (ϵ 525).[43] Fuming H_2SO_4, 100 ml, and 30% H_2O_2 (1 ml of Baker reagent grade) were refluxed 4 days in an all-glass apparatus sealed with a tube containing Drierite ($CaSO_4$). Destruction of SO_2 and H_2O_2 was quantitative: a 1-ml portion of the acid failed to decolorize 100 ml of 10^{-6} *M* $KMnO_4$. The *A* of the purified acid was 0.030 at 280 nm *vs.* 96% H_2SO_4, and its concentration, by titration with standard NaOH, was 105.4 ± 0.2% H_2SO_4 (28% SO_3 by weight).

D_2SO_4 was prepared by Jones[44] by reaction of SO_3 (Baker and Adamson reagent) with 99% D_2O. Titration with standard NaOH corresponded to 97.0% D_2SO_4.

Acetic acid (reagent glacial) was titrated with standard NaOH, indicating 99.7 ± 0.3% HOAc. This material was used for most purposes without further purification. The CH_3CO_2H used in some of the kinetic runs and for the product studies using LiCl was refluxed for 10 hr over CrO_3 and distilled through a 30-cm Vigreux column. The middle 80% was redistilled from triacetylborate,[45] bp 117°, mp 16.2°.

Cyclohexane (Baker reagent, 2.5 l.) was stirred with four 400-ml portions of 96% H_2SO_4 for at least 2 hr each. The last two portions remained colorless. The cyclohexane was washed with 1 l. of H_2O, 1 l. of 0.1 *M* NaOH, and three 1-l. portions of H_2O, dried overnight over Drierite, and distilled through a 30-cm Vigreux column. The middle 80%, bp 80.3°, n_D^{25} 1.4232 was used. Methanol (Fisher reagent) was used without further purification.

Methylene chloride (Fisher reagent) was purified by the same procedure as cyclohexane, except that after drying over Drierite, it was dried over Fisher reagent grade molecular sieves (3-mm pellets of a sodium calcium aluminum silicate with a pore size of 4 Å) for at least 30 min, then distilled through a 60-cm column packed with glass helices. The middle 80% of the distillate, bp 40.3°, n_D^{25} 1.4209, was stored in the dark and used for kinetic runs within a week.

Sulfolane (tetrahydrothiophene 1,1-dioxide, Shell Development) was distilled through a 60-cm column packed with 3-mm Pyrex beads. The middle 80% was redistilled twice without the fractionating column. Redistilled sulfolane was colorless and odorless, bp 90° (1 mm), n_D^{25} 1.4825. Analysis by glc on a 6-ft 20% Apiezon L on Chromosorb W column at 25-300° and 14 psi of He showed 0.1% volatile impurity. Since sulfolane solidifies at 28°, 3.3% Et_2O (Mallinckrodt reagent) was added to depress the melting point below 25°. 3-Methylsulfolane was purified by the procedure of Alder and Whiting,[46] with the exception that CaO was used instead of P_2O_5 as the drying agent. The purified material, bp 83° (0.2 mm), when analyzed by glc on the Apiezon L column showed less than 0.1% volatile impurities. The *A* of a 1-cm cell of 3-methylsulfolane *vs.* air was 0.124 at 315 nm, 0.155 at 295 nm, 0.233 at 270 nm and increased gradually at lower wavelengths.

Determination of Yields of Halobenzenes from Dediazoniation of I BF_4^-. Three 80-mg samples of I BF_4^- were dissolved in 10 ml of HBr or HCl solution in 25-ml volumetric flasks. Cyclohexane (10 ml) was added, and the flasks were shaken, sealed, and placed in a constant-temperature bath at 25 or 50° for at least 3 days at 25° or 1-2 hr at 50° (10 half-lives). The acid layer was separated and extracted with two more 5-ml portions of cyclohexane. The combined cyclohexane solutions were extracted thrice with 0.1 *M* NaOH and once with 1 *M* H_2SO_4, then diluted to 25 ml. The absorbance *A* of the C_6H_5Br solutions was measured at 265.6 and 261.5 nm. The yields were calculated from the extinction coefficients of C_6H_5Br [265.6 nm (ϵ 211), 261.5 (182)] and C_6H_5F [265.6 nm (ϵ 613), 261.5 (800)]. The yield of C_6H_5Cl was calculated from *A* at 264.6 nm. Since *A* was measured at only one wavelength, the yield of C_6H_5F could not be calculated but was assumed to be 1%, in agreement with the C_6H_5Br solutions. The yields of C_6H_5F, determined from *A* at 266 nm (ϵ 1070), for decomposition of 0.03-0.05 *M* salt in 1.0 and 7.0 *M* H_2SO_4 with no added halide were 1.2-1.4 and 0.8-1.0%, respectively. When solutions were extracted with cyclohexane immediately after dissolution, the yield was 0.2-0.5%. Part of the C_6H_5F therefore arises from decomposition of the salt in the solid phase.

Products in Methanol. Solutions containing 0.016-0.028 *M* salt in CH_3OH were decomposed at 25° in the dark for 42 hr (20 half-lives). The solutions showed absorption at 260-400 nm equivalent to formation of 0.01-0.02% of *p*-$HOC_6H_4N_2C_6H_5$. The solutions were diluted 25-50-fold and *A* measured at 277.9, 266.5, 260.5, and 254.5 nm. The ϵ values for $C_6H_5OCH_3$ (1578, 1340, 883, 480) and C_6H_5F (2, 800, 900, 600) were measured at these wavelengths. The yields of $C_6H_5OCH_3$, 91.5 ± 0.5%, and C_6H_5F, 5.5 ± 1%, were calculated from *A* at 277.9 and 266.5 nm. The values calculated for *A* at 260.5 and 254.5 nm agreed with those observed within 1%. The rate constant was 9.80 ± 0.04 × 10^{-5} sec^{-1} with 6.8 × 10^{-4} *M* I BF_4^- at 25°.

Products in Acetic Acid. Solutions containing approximately 10^{-3} *M* salt and 0, 0.0100, 0.100, and 1.00 *M* LiCl were decomposed at 25° for 4 days (10 half-lives). The yields of C_6H_6, C_6H_5Cl, C_6H_5F, C_6H_5OH, and C_6H_5OAc were calculated from *A* of the solutions and the measured ϵ values at 280, 271, 265.8, 263.5, 260.5, and 259.5 nm. As a check, 76 mg (4 × 10^{-4} 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 C_6H_5Cl as previously described. The yield of C_6H_5Cl was 29 *vs.* 27% calculated directly from *A* of the reaction mixture.

Products in Methylene Chloride. When 11.6 mg of salt was shaken with 100 ml of CH_2Cl_2 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 C_6H_5Cl and C_6H_5F in a ratio 3/2. The remainder of the original solution was used for spectrophotometric measurements. The products of decomposition of saturated solutions in CH_2Cl_2 were also analyzed spectrophotometrically. The yields of C_6H_6 (2 ± 2%), C_6H_5F (33 ± 3%), and C_6H_5Cl (65 ± 3%) were calculated from the *A* and ϵ at 270, 266.5, 264.5, 264, 262.5, 261, 260, 258, and 255 nm. Presumably CH_2ClF was formed equivalent to the C_6H_5Cl, but it was not isolated because of its volatility.

Products in Acetone. When 0.493 g, in 25 ml reagent $(CH_3)_2CO$ was decomposed at 25° for 4 days, the resulting solution was deep purple, with an unpleasant odor. Analysis of the solution by glc on a 6-ft 20% Apiezon L on Chromosorb W S-60-80 column at 130° and 20 psi of He showed 13 ± 2% C_6H_5F and 100 ± 15% C_6H_5OH. Estimation of the area of the C_6H_5OH peak was less accurate because the peak tailed badly. 4-Hydroxy-4-methyl-2-pentanone (2.73 mol per mol of salt) and other higher molecular weight condensation products were also formed.

Products in 3-Methylsulfolane. I (0.194 g, 1.01 × 10^{-3} mol) was decomposed in 10 ml of 3-methylsulfolane at 25.00 ± 0.02° for 11 days (16 half-lives). The solution analyzed by glc showed four peaks, C_6H_5F, 0.31, (17% yield); unknown, 0.24; unknown, 0.24; unknown, 0.16; C_6H_5OH, 1.0 (57% yield). When 90% of the solvent was distilled at 95° (1 mm), no phenol appeared in the distillate and the residue showed the same peaks by glc. The uv of the solution had λ_{max} 266 nm (ϵ 178), 260 (258), and 255 (251) but no peaks for phenol at 280 nm (ϵ 1500) or 273 (1800). The product was postulated to be a sulfoxonium salt which decomposed to yield phenol during glc analysis. Attempts to isolate the salt were unsuccessful. Chalkley, *et al.*,[47] have subsequently confirmed the existence of the sulfoxonium salt and prepared samples of it by decomposition of I in sulfolane at 70-80°.

Table V. Yields of Bromobenzene and *p*-Dibromobenzene from Dediazoniation of 0.1 *M* I BF_4^- in 75% HOAc Containing Br_2 and 0.25 *M* H_2SO_4 at 25°

Br_2, *M*	C_6H_5Br, %	*p*-$C_6H_4Br_2$, %	Total %
0.44	7.7	0	7.7
1.1	12.2	0.1	12.2
2.2	12.1	5.9	18.0
3.0	0.8	21.5	22.3
4.0	0	28.0	28.0

Products in 75% Acetic Acid Containing Bromine. I BF_4^- (1.0 g, 0.005 mol) was dissolved in 100 ml of 75% HOAc-25% H_2O containing 0.50 *M* Br_2 (Mallinckrodt reagent). After 48 hr at 25° in the dark, the solution was filtered, and 0.67 g (30%) of bromanil (tetrabromo-1,4-benzoquinone), mp 291° uncor, was obtained after recrystallization from C_6H_6: ν_{max} (2% in KBr) 1690, 1560, 1220, 1070, 1030, 710, and 640 cm^{-1}. The filtrate was diluted with 200 ml of H_2O and treated with excess $NaHSO_3$. The curdy white precipitate was extracted with $CHCl_3$ and the $CHCl_3$ layer with 10% NaOH. Neutralization of the solution gave 0.93 g (54% crude yield) of 2,4,6-tribromophenol, identified by ir, mp 96°, crystallized from EtOH-H_2O. The $CHCl_3$ solution was dried over Drierite and analyzed for C_6H_5Br (13% yield) and *p*-$C_6H_4Br_2$ (11% yield) by glc with a 6-ft 20% Apiezon L on Chromosorb W column at 150° and 14 psi of He.

To five 50-ml glass-stoppered erlenmeyer flasks painted black to exclude light were added 25 ml of 75% HOAc-25% H_2O, 0.25 *M* in H_2SO_4, 0.50 g (0.0026 mol) of I BF_4^-, and Br_2 for 0.44-4.0 *M* Br_2. The flasks were shaken, sealed tightly, and allowed to stand at 25° for 60-72 hr. The solutions were analyzed for C_6H_5Br and *p*-$C_6H_4Br_2$ by glc (Table V). No *o*-$C_6H_4Br_2$ was detected, although an authentic sample was cleanly separated from *p*-$C_6H_4Br_2$.

In order to determine whether C_6H_5Br is converted to *p*-$C_6H_4Br_2$ under these reaction conditions, 29 g (0.18 mol) of Br_2 and 2.0 g (0.013 mol) of C_6H_5Br were added to 50 ml of 75% HOAc containing 0.25 *M* H_2SO_4. The resulting 3.0 *M* Br_2 solution was allowed to stand at 25° in the dark. Analysis of a 10-ml sample withdrawn after 10 hr showed a 98% yield of *p*-$C_6H_4Br_2$.

Finally, a solution containing 0.124 *M* I BF_4^-, 0.24 *M* H_2SO_4, and 0.95 *M* Br_2 was prepared from 5.00 g of I (0.026 mol), 150 g of glacial HOAc, 50 g of 1.00 *M* H_2SO_4, and 32.0 g of Br_2 (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°. At 1-3 hr intervals, 25-ml samples were withdrawn and analyzed for C_6H_5Br and *p*-$C_6H_4Br_2$. The half-life for C_6H_5Br formation was about 7 hr *vs.* 5 hr for dediazoniation of I in the absence of Br_2.

If the diradical intermediate had a finite lifetime, Br_2 should readily attack it, forming *o*- and *p*-dibromobenzene but no C_6H_5Br. When I BF_4^- was decomposed in 75% HOAc containing 0.44-4.0 *M* Br_2 and 0.25 *M* H_2SO_4, the initial product was C_6H_5Br. In solutions of Br_2 greater than 1 *M*, C_6H_5Br is subsequently brominated to *p*-$C_6H_4Br_2$. The other products, C_6H_5OH and C_6H_5OAc, are converted to a mixture of 2,4,6-tribromophenol and bromanil. Catalysis of dediazoniation by Br_2 does not occur, because the rate of formation of C_6H_5Br is slower than the rate of dediazoniation in HOAc solutions in the absence of Br_2. Since C_6H_5Br rather than *p*-$C_6H_4Br_2$ is the initial product, the reaction does not proceed through a diradical.

Products in Concentrated and Fuming Sulfuric Acid. First, 0.459 g of I BF_4^- was dissolved in 25 ml of 96% H_2SO_4 (0.096 *M* solution) and kept at 25° for 1 week (16 half-lives). The resulting solution was extracted repeatedly with CH_2Cl_2. The CH_2Cl_2 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% H_2SO_4 (0.05 *M* solution) and kept at 25° for 7 days (16 half-lives). The solution was diluted to 250 ml, and three 50-ml aliquots were treated with excess Br_2 for 14 days at 25°, then filtered, average yield 59 mg of a yellow solid, mp 235-240°, 275-280° after recrystallization from benzene. Treatment with more Br_2 for 2 hr at 95° 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 bromanil. The formation of bromanil 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°, 6.9 g (0.10 mol) of $NaNO_2$ in 15 ml of water was added dropwise with stirring. After diazotization was complete, the flask was removed from the ice bath and 100 ml of concentrated H_2SO_4 was added. The heat of dilution of the H_2SO_4 was sufficient to cause rapid decomposition. After evolution of N_2 had ceased, the mixture was diluted with 300 ml of water and extracted thrice with CH_2Cl_2. The CH_2Cl_2 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*-Toluidine was converted to *m*-cresol by the same procedure. No *o*-cresol was detected by glc of the reaction mixture.

Deuterium Incorporation into Phenol. I BF_4^- (0.001 mol) was dissolved in 20 ml of 0.01 *M* DCl in D_2O (Columbia Organic Chemicals) or 0.01 *M* HCl in H_2O and kept at 25° for 16.0 hr (3.8 half-lives). The mixture was extracted with three 10-ml portions of CH_2Cl_2, which were then extracted successively with three 20-ml portions of water and one 20-ml portion of saturated NaCl. The CH_2Cl_2 layers were combined, dried over Na_2SO_4, and evaporated at low pressure. For investigation of D exchange of C_6H_5OH, 0.001 mol of C_6H_5OH (Fisher reagent grade) was dissolved in 0.0087 or 0.0434 *M* DCl in D_2O and maintained at 25° for the designated periods of time, then isolated as described above.

The isotopic composition of the phenol samples was determined on an Atlas CH4 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 (± 10%) inlet pressures, and the amplifier attenuator 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 1-cm silica cells containing 3 ml of solution were placed in the water-jacketed cell block of a Zeiss Model PMQ-II spectrophotometer maintained at 25.00 ± 0.03°. The absorbance *A* at 295 nm (ϵ 1650), 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 $A_t = A_\infty + (A_0 - A_\infty)e^{-kt}$ by the method of least-squares. Computations were performed on an IBM 7094 computer.[48] The observed values of A_0 and A_∞ and a value of *k* calculated from the apparent half-life were submitted as initial estimates; the correct values for A_0, A_∞, and *k* were calculated by repeated iterations of the experimental data. The corrected values of A_0, A_∞, and *k* after each iteration were used as the estimates for the next iteration. After the fourth iteration, the values of A_0, A_∞, and *k*, the standard deviations of these values, and ($A_{calcd} - A_{obsd}$) for each point were printed out. Observed A_∞ values were generally less than 1% of A_0 and agreed with calculated A_∞ values within ±0.005 or ±1% of A_0.

References and Notes

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

(2) For a review of the literature and for further experimental details, *cf.* J.E.S., Ph.D. Thesis, Massachusetts Institute of Technology, December 1965, 198 pp. Deuterium tracer experiments were performed subsequently by K.G.H.

(3) Presented in part by J.E.S. at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, Abstract ORGN-34.

(4) For aromatic hydrogen isotope effects, see accompanying paper: C. G. Swain, J. E. Sheats, D. G. Gorenstein, and K. G. Harbison, *J. Amer. Chem. Soc.*, **97**, 791 (1975).

(5) For nitrogen isotope effects, see accompanying paper: C. G. Swain, J.

E. Sheats, and K. G. Harbison, *J. Amer. Chem. Soc.*, **97,** 796, (1975).

(6) We have concentrated our study on the mechanism of the homogeneous, dark, 0–100° thermal decomposition of neutral diazonium salts in aqueous solution when only weakly basic nucleophiles like H_2O, Br^-, Cl^-, or F^- are present. There seem to be as many actual mechanisms for denitrogenation (dediazoniation) of diazonium salts as for dehydrogenation of alcohols or decarboxylation of carboxylic acids. However, in this paper, we purposely exclude consideration of mechanisms that may operate with strong bases or with nucleophiles that bond to nitrogen (*e.g.*, in the Gomberg–Bachmann reaction, probably initiated by $I + HO^- \rightleftarrows C_6H_5N_2OH \rightarrow C_6H_5\cdot + N_2 + HO\cdot$), in reactions with reducing agents (*e.g.*, the Sandmeyer reaction or the Meerwein condensation, $C_6H_5N_2^+ + CuCl_2^- \rightarrow C_6H_5\cdot + N_2 + CuCl_2$), on metal surfaces (*e.g.*, the Gattermann reaction on powdered Cu), in the solid state, or in photodecompositions. Studies of systems where polar and free radical mechanisms for decomposition coexist (*e.g.*, in methanol or glyme) have been made by D. F. DeTar and T. Kosuge, *J. Amer. Chem. Soc.*, **80,** 6072 (1958), by J. F. Bunnett and H. Takayama, *ibid.*, **90,** 5173 (1968), by T. J. Broxton, J. F. Bunnett, and C. H. Paik, *Chem. Commun.*, 1363 (1970), and by L. Friedman and J. F. Chlebowski, ref 9, and personal communication from L. Friedman.

(7) For previous kinetic studies, *cf.* (a) J. Hausser and P. T. Muller, *Bull. Soc. Chim. Fr.*, [3] **7,** 721 (1892); (b) H. A. H. Pray, *J. Phys. Chem.*, **30,** 1417, 1477 (1926), and references cited there; (c) M. L. Crossley, R. H. Kienle, and C. H. Benbrook, *J. Amer. Chem. Soc.*, **62,** 1400 (1940); (d) E. A. Moelwyn-Hughes and P. Johnson, *Trans. Faraday Soc.*, **36,** 948 (1940); (e) H. Zollinger, "Azo and Diazo Chemistry," Interscience, New York, N.Y., 1961, pp 137–142; (f) S. D. Ross, *Progr. Phys. Org. Chem.*, **1,** 34 (1963); (g) H. Zollinger, *Accounts Chem. Res.*, **6,** 338 (1973).

(8) C. G. Swain and L. E. Kaiser, *J. Amer. Chem. Soc.*, **80,** 4089 (1958).

(9) E. S. Lewis, L. D. Hartung, and B. M. McKay, *J. Amer. Chem. Soc.*, **91,** 425 (1969); F. Pietra, *Quart. Rev., Chem. Soc.*, **23,** 504 (1969); J. F. Chlebowski, "Carbonium Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1970, p 770.

(10) *Mechanism 2 (or 3, with 2 as a prior equilibrium)* was proposed by E. S. Lewis and W. H. Hinds, *J. Amer. Chem. Soc.*, **74,** 304 (1952), for reaction of *p*-nitrobenzenediazonium ion with bromide ion, because rate of dediazoniation doubles as NaBr is increased from 0 to 8.0 *M*. However, this and other published interpretations are based on the questionable assumption that activity coefficients for I and the transition state I* of the phenyl cation mechanism 4 should be constant or else change identically on addition of 0.5–8.0 *M* concentrations of salt. We would expect the activity coefficient of I to have a lower sensitivity to added salts than that of I* of mechanism 4, because the charge in I is better delocalized by resonance; thus mechanism 4 may be compatible with the small (twofold or smaller) changes observed in the experimental first-order rate constant k_1.

Most nonaryne nucleophilic aromatic 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, *Chem. Rev.*, **49,** 295 (1951); S. D. Ross, ref 7f, p 37 ff; C. F. Bernasconi, *MTP Int. Rev. Sci.: Org. Chem., Ser. 1,* **3,** 35 (1973)]. A more complicated variant of mechanism 2 involves the rapidly formed but relatively unstable cis adduct of Y to the terminal nitrogen of I as an additional intermediate between I and II. This mechanism is allowed by orbital symmetry, although the one-step rearrangement of this cis azo compound to III [proposed by A. Hantzsch, *Chem. Ber.*, **27,** 1702 (1894); **33,** 2517 (1900); cited by K. H. Saunders, "Aromatic Diazo Compounds," 2nd ed, Edward Arnold, London, 1949, p 145] is not.

(11) W. A. Waters, *J. Chem. Soc.*, 266 (1942).

(12) (a) M. Hanack, *Accounts Chem. Res.*, **3,** 209 (1970); (b) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91,** 5350 (1969); (c) G. Modena and U. Tonellato, *Advan. Phys. Org. Chem.*, **9,** 185 (1971); (d) W. D. Pfeifer, C. A. Bahn, P. v. R. Schleyer, S. Bocher, C. E. Harding, K. Hummel, M. Hanack, and P. J. Stang, *J. Amer. Chem. Soc.*, **93,** 1513 (1971); (e) L. R. Subramanian and M. Hanack, *Angew. Chem., Int. Ed. Engl.*, **11,** 714 (1972); (f) R. H. Summerville, C. A. Senkler, P. v. R. Schleyer, T. E. D. Dueber, and P. J. Stang, *J. Amer. Chem. Soc.*, **96,** 1100, 1110 (1974).

(13) R. W. Taft, *J. Amer. Chem. Soc.*, **83,** 3350 (1961); R. A. Abramovitch and J. G.Saha, *Can. J. Chem.*, **43,** 3275 (1965); R. A. Abramovitch and F. F. Gadallah, *J. Chem. Soc. B*, 497 (1968); R. J. Cox, P. Bushnell, and E. M. Evleth, *Tetrahedron Lett.*, 209 (1970).

(14) For example, in the Schiemann reaction (decompositions of arenediazonium fluoborates), reaction of BF_4^- (with either I or II) might give $C_6H_5F + BF_3$ in one step (either the only step or the second step); alternatively, because the equilibrium $BF_4^- \rightleftarrows BF_3 + F^-$ is rapid, I or II might react with F^- rather than with BF_4^-. We shall demonstrate which of these alternatives is correct in a following paper: C. G. Swain and R. J. Rogers, *J. Amer. Chem. Soc.*, **97,** 799 (1975).

(15) Benzyne is formed in the decomposition of benzenediazonium-2-carboxylate in aprotic solvents [M. Stiles and R. G. Miller, *J. Amer. Chem. Soc.*, **82,** 3802 (1960); M. Stiles, R. G. Miller, and U. Burckhardt, *ibid.*, **85,** 1792 (1963)], but a reaction like (4) may still be the first and rate-determining step [S. Yaroslavsky, *Chem. Ind. (London)*, 765 (1965); R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N.Y., 1967, pp 73–77]. Arynes have also been demonstrated as intermediates in decompositions of diazonium ions containing ortho sulfinic[16] or boronic[17] acid functions or from decompositions of various *N*-nitrosoacetanilides in aprotic solvents.[18]

(16) G. Wittig and R. W. Hoffmann, *Chem. Ber.*, **95,** 2718 (1962).

(17) L. Verbit, J. S. Levy, H. Rabitz, and W. Kwalwasser, *Tetrahedron Lett.*, 1053 (1966).

(18) J. I. G. Cadogan and P. G. Hibbert, *Proc. Chem. Soc., London*, 338 (1964); R. W. Franck and K. Yanagi, *J. Amer. Chem. Soc.*, **90,** 5814 (1968); D. L. Brydon, J. I. G. Cadogan, D. M. Smith, and J. B. Thomson, *Chem. Commun.*, 727 (1967); G. W. Clark, III, Ph.D. Thesis, University of Rochester, Rochester, N.Y., 1971; *Diss. Abstr.*, **32,** 1442B (1971).

(19) P. Bellingham, C. D. Johnson, and A. R. Katritzky, *J. Chem. Soc. B*, 1226 (1967).

(20) K. G. Harbison and C-S. Chang, *J. Amer. Chem. Soc.* submitted for publication; C.-S. Chang, Ph.D. Thesis, University of Rochester, Rochester, N.Y., 1971; *Diss. Abstr.*, **32,** 3248B (1971).

(21) E. S. Lewis, *J. Amer. Chem. Soc.*, **80,** 1371 (1958); E. S. Lewis and J. E. Cooper, *ibid.*, **84,** 3847 (1962).

(22) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **9,** 751, 759 (1970).

(23) (a) C. G. Swain, C. B. Scott, and K. H. Lohmann, *J. Amer. Chem. Soc.*, **75,** 136 (1953); (b) C. G. Swain and C. B. Scott, *ibid.*, **75,** 141 (1953).

(24) Although selectivity measurements determined by analysis of products formed during solvolysis may be affected by trapping of species at various degrees of ionization, this effect is relatively small in the systems that have been studied (*ca.* a factor of 2 for bis(4-methoxyphenyl)methyl mesitoate with azide in MeOH) and should not confound the interpretation of selectivities that differ by large factors.[25]

(25) C. D. Ritchie, *J. Amer. Chem. Soc.*, **93,** 7324 (1971); C. D. Ritchie and P. O. I. Virtanen, *ibid.*, **94,** 4966 (1972).

(26) For leading references, *cf.* C. G. Swain and A. S. Rosenberg, *J. Amer. Chem. Soc.*, **83,** 2154 (1961).

(27) S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, **79,** 5940 (1957).

(28) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **74,** 5375 (1952).

(29) C. G. Swain, D. A. Kuhn, and R. L. Schowen, *J. Amer. Chem. Soc.*, **87,** 1554 (1965).

(30) Ethers were found previously to be the principal products in alcohols: *cf.* DeTar and Kosuge, ref 6. A chlorobenzene was found previously as a product in chloroform: T. Cohen and J. Lipowitz, *Tetrahedron Lett.*, 3721 (1964). For products in dimethyl sulfoxide, acetonitrile, and aromatic solvents, *cf.* K. Ishida, N. Kobori, M. Kobayashi, and H. Minato, *Bull. Chem. Soc. Jap.*, **43,** 285 (1970); M. Kobayashi, H. Minato, E. Yamada, and N. Kobori, *ibid.*, **43,** 215 (1970); M. Kobayashi, H. Minato, and N. Kobori, *ibid.*, **43,** 219 (1970); N. Kobori, M. Kobayashi, and H. Minato, *ibid.*, **43,** 223 (1970). For products with sulfones and aryl sulfonates, *cf.* G. R. Chalkley, D. J. Snodin, G. Stevens, and M. C. Whiting, *J. Chem. Soc. C*, 682 (1970).

(31) Our conclusion that even this reaction has a carbonium ion intermediate does not, however, imply agreement with a 1969 proposal[32] that all displacements on saturated carbon are two step, and that even methyl halides and sulfonates undergo displacement *via* $CH_3^+X^-$ ion-pair intermediates. This seems unlikely in view of arguments[33] that the rate and product data on secondary alkyl sulfonates that led to this proposal are still consistent with concurrent one- and two-step processes and evidence[34] on the small magnitude of substituent effects on a primary bromide, as well as by the disproof[8] of a mechanism involving methyl cations proposed earlier, and the repeated failure to generate spectroscopically observable methyl cations in solution even in the most acidic and nonnucleophilic media so far devised.[35]

(32) R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, **91,** 362, 6031 (1969); R. A. Sneen and H. M. Robbins, *ibid.*, **91,** 3100 (1969); R. A. Sneen, *Accounts Chem. Res.*, **6,** 46 (1973).

(33) B. J. Gregory, G. Kohnstam, M. Paddon-Row, and A. Queen, *J. Chem. Soc. D*, 1032 (1970); D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93,** 4821 (1971); D. J. Raber and J. M. Harris, *J. Chem. Educ.*, **49,** 60 (1972).

(34) J. L. Kurz and J. C. Harris, *J. Amer. Chem. Soc.*, **92,** 4117 (1970), compared rates of displacements on $BrCH_2CO_2H$ and $BrCH_2CO_2^-$.

(35) G. A. Olah, J. R. DeMember, and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **91,** 2112 (1969).

(36) E. S. Lewis and E. B. Miller, *J. Amer. Chem. Soc.*, **75,** 429 (1953).

(37) SO_3^- is excluded because of untypical negative charge, and because it has so seldom been tested in other reaction series; *m*- and *p*-COOH and *p*-OH are excluded, because calculations from estimated pK_a values of 2.55, 2.41, and 3.40 show them to be 15, 20, and 2% ionized under the conditions of this reaction.[2]

(38) C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90,** 4328 (1968).

(39) We wish to thank Dr. Stefan Unger for performing these calculations.

(40) The coefficient of determination or square of the correlation coefficient for this simple correlation is $1 - \{[\Sigma(z_{\text{calcd}} - z_{\text{obsd}})^2/(n-2)]/[\Sigma(z_{\text{obsd}} - [\Sigma z_{\text{obsd}}/n])^2/(n-1)]\} = 1 - \{[10.513/5]/[10.896/6]\} = -0.16$. It represents the fraction of the variations of z_{obsd} that is statistically attributable to variations in the factor represented by the Hammett σ constant, and it would be zero for an infinite number of randomly distributed points. It is even less than zero here because of the finite number of points ($n = 7$).

(41) (a) M. F. W. Dunker, E. B. Starkey, and G. L. Jenkins, *J. Amer. Chem. Soc.*, **58,** 2309 (1936); (b) D. T. Flood, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N.Y., 1943, p 295.

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(43) D. Devèze and P. Rumpf, *C.R. Acad. Sci.*, **258,** 6135 (1964).

(44) L. B. Jones, Ph.D. Thesis in Chemistry, Massachusetts Institute of Technology, 1964, p 65.

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(46) R. W. Adler and M. C. Whiting, *J. Chem. Soc.*, 4710 (1964).

(47) G. R. Chalkley, D. J. Snodin, G. Stevens, and M. C. Whiting, *J. Chem. Soc. C*, 682 (1970).

(48) Program written by K.G.H. A full description of a similar program is given in R. P. Wood, "NLSS:A704 Program for Fitting Nonlinear Curves by Least Squares," AEC Research and Development Report K-1440, Union Carbide Nuclear Co., Oak Ridge, Tenn., Jan 28, 1960.