# The Reactions of Diazonium Salts with Nucleophiles. VII. p-Phenylene-bis-diazonium Ion[1,2]

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In acidic aqueous solution tetrazotized p-phenylenediamine reacts with chloride, bromide, thiocyanate and azide ions to yield the corresponding p-substituted benzenediazonium ions at rates far greater than that of any reaction of the second diazonium group. The mechanisms of these substitution reactions are believed to involve transition states with bonding to the ω-nitrogen as well as to carbon. In high concentrations iodide ion gives (with the same tetrazonium salt) p-diiodobenzene, at lower concentrations p-iodobenzenediazonium ion, and at concentrations low enough to measure rates, p-hydroxybenzenediazonium ion is produced in a reaction which is presumed to involve dissolved oxygen.

## Introduction

Aromatic diazonium salts are susceptible to nucleophilic attack on the terminal nitrogen and also at the o- and p-positions of the aromatic ring to which they are attached. In addition, one-step substitution of the diazonium group by a nucleophile activated by a p-nitro group has been reported in one case,[3] but only as a secondary reaction path to the more familiar two-step substitution by way of the aryl cation.[4] The diazonium ion group activates substitution in the o- and p-positions far more effectively than the nitro group does[5] by virtue of its extreme electron-withdrawing power.[6] We were therefore attracted to the possibility of nucleophilic attack on tetrazotized p-phenylenediamine, since bimolecular attack with displacement of $N_2$ should be more favorable in this case than in any other simple molecule. Furthermore, a possible example of such a substitution is to be found in the formation of 2-chlorotriptycene from the tetrazotization and reduction with hypophosphorous acid of 2,5-diaminotriptycene in the presence of hydrochloric acid.[7]

In a previous paper[1] it was shown that tetrazotized p-phenylenediamine reacted fairly rapidly with water both reversibly and irreversibly at all but high acidities. It is then not possible to study the reactions of nucleophiles which are present at negligible concentrations at acidities of greater than about $10^{-3}$ M $H^+$, which excludes many amines, mercaptide ions and the like.

The reactions of the p-tetrazonium ion were followed by changes in the ultraviolet absorption. In all reactions except those with iodide, the nucleophile was present in substantial excess and a first-order course was followed. Products were identified by comparison of the absorption spectrum with that of samples prepared by different routes.

Table I shows the pseudo first-order rate constants ($k_4$) for the formation of p-chlorobenzenediazonium ion from the attack of chloride ion on the tetrazonium salt. The errors listed are the average deviations from the mean of the number of runs given in parentheses.

(1) Paper VI, E. S. Lewis and M. D. Johnson, THIS JOURNAL. **82,** 5399 (1960).

(2) This work was supported by a grant from the Robert A. Welch Foundation; we acknowledge this assistance with gratitude.

(3) E. S. Lewis and W. H. Hinds, THIS JOURNAL, **74,** 304 (1952).

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

(5) (a) J. F. Bunnett and R. E. Zahler, Chem. Revs., **49,** 273 (1951); (b) E. S. Lewis and H. Suhr, THIS JOURNAL, **82,** 862 (1960).

(6) E. S. Lewis and M. D. Johnson, ibid., **81,** 2070 (1959).

(7) P. D. Bartlett. M. J. Ryan and S. G. Cohen, ibid., **64,** 2649 (1942).

### TABLE I

Rate of $ArN_2^+ + Cl^- \longrightarrow ArCl + N_2(Ar = p\text{-}^+N_2C_6H_4^-)$

| $(Cl^-)$ | $(ClO_4^-)$ | $(H^+)$ | Temp., °C. | $10^4 k\psi$, sec.$^{-1}$ | $k_2$ l./ mole sec. |
|---|---|---|---|---|---|
| 2.08 | 0.365 | 0.365 | 34.6 | 18.7 ± 2.3 (9) | 9.0 × 10⁻⁴ |
| 1.04 | 1.405 | .365 | 34.6 | 6.2 ± 0.8 (6) | 7.0 × 10⁻⁴ |
| 0.520 | 1.925 | .365 | 34.6 | 3.0 ± 0.2 (4) | 5.8 × 10⁻⁴ |
| 2.08 | 0.365 | .365 | 26.2 | 4.3 (1) | 2.1 × 10⁻⁴ |
| 2.08 | 0.365 | .365 | 24.5 | 3.8 ± 0.1 (2) | 1.8 × 10⁻⁴ |
| 1.85 | 1.30 | 1.30 | 26.2 | 4.5 (1) | 2.4 × 10⁻⁴ |

Sodium perchlorate was used in addition to perchloric acid to make the ionic strength of the sodium chloride solutions about 2.44 M, except in the last entry. The rather large scatter of the runs is not an indication of a poor fit to first-order kinetics, but is a non-reproducibility which we attribute to poor temperature control in the runs. Salt effects are rather large, and we attribute the drift in $k_2$, which is $k\psi/(Cl^-)$, to a failure to eliminate these entirely by maintaining constant ionic strength, rather than indicating that the order with respect to chloride ion is greater than one. The rather limited data yield from the Arrhenius equation a rough activation energy of 25 kcal.; the $pZ$ factor of about $3 \times 10^{14}$ l./mole.sec. is not unreasonable for the reaction of oppositely charged ions in water.

### TABLE II

RATE REACTION OF $p\text{-}N_2C_6H_4N_2^{++}$ WITH SEVERAL NUCLEOPHILES AT 28.2°

| Nucleophile | Concn. of nucleophile, M | $HClO_4$, M | $k\psi \times 10^3$ sec.$^{-1}$ | $k_2$, l./ mole sec. |
|---|---|---|---|---|
| $Br^-$ | 0.96 | 0.365 | 6.6 | 6.9 × 10⁻³ᵃ |
| $Br^-$ | .24 | .365 | 2.3 | 9.4 × 10⁻³ᵃ |
| $Cl^-$ | .96 | .365 | 0.43 | 4.4 × 10⁻⁴ᵃ |
| $Cl^-$ | 2.08 | .365 | ... | 2.8 × 10⁻⁴ᵃ,ᵇ |
| $SCN^-$ | 4.0 × 10⁻³ | .79 | 26ᶜ | 6.6 |
| $N_3^-$ | 8.33 × 10⁻¹⁰ᵈ | 3.36 | 21ᵉ | 2.5 × 10⁷ |
| $N_3^-$ | 4.14 × 10⁻¹⁰ᶠ | 3.42 | 10 | 2.4 × 10⁷ |
| $ClO_4$ | 8.72 | 8.72 | 0ᵍ | 0ᵍ |
| $BF_4^-$ | 6.5 | 6.5ʰ | 0ᵍ | 0ᵍ |
| $OH^-$ | | 0.16 | | 7.0 × 10⁸ⁱ |

ᵃ These runs were at various ionic strengths. ᵇ Interpolated by the Arrhenius equation from Table I. ᶜ Average of four runs. ᵈ Added $N_3^- = 10^{-4}M$; see text. ᵉ Average of two runs. ᶠ Added $N_3^- = 5 \times 10^{-5}$ M; see text. ᵍ No perceptible reactions in several hours. ʰ $HBF_4$ rather than $HClO_4$. ⁱ $k_D k_1/k_2$ from ref. 1.

In Table II are given both the pseudo first-order constants ($k\psi$) and the second-order constants ($k_2$), obtained by dividing $k\psi$ by the nucleophile concentration. The concentration of azide was calculated from the added concentration of

azide, the acidity and the dissociation constant $2.8 \times 10^{-5}$ of hydrazoic acid.[8] The entry for hydroxide ion is taken from ref. 1, it represents the rate in the acidity region in which the rate is essentially first order in hydroxide ion; in the notation of this reference, this number is $k_D k_1/k_2$.

The reaction with iodide ion was too fast to measure when iodide was in large excess, but the reaction yielded the normal products, *p*-iodobenzenediazonium ion and *p*-diiodobenzene. In very dilute solution rate measurements were difficult, but the product was readily identified by its spectrum at different acidities as *p*-hydroxybenzenediazonium ion. With an initial mole ratio of $I^-$ to $ArN_2^+$ of 3.6 to 1, the reaction yielding this unexpected product was complete; with a ratio of 1.8 to 1, unreacted tetrazonium salt remained. Second-order rate constants based upon the stoichiometry of two iodides to one tetrazonium ion were calculated and fitted the data adequately. At $28.2°$ in 0.336 $M$ perchloric acid, with $(I^-)_0$ = $1.54 \times 10^{-5}M$ $(ArN_2^+)_0$ = $4.3 \times 10^{-6}M$, the calculated constant was $5 \times 10^3$ 1./mole.sec., the same constant was calculated in another experiment under the same conditions but with $(I^-)_0 = 7.7 \times 10^{-6}M$. Because the solutions were so dilute, and the reactions were nearly complete in one minute, neither the stoichiometry nor the rate law is more than tentatively demonstrated. It should be emphasized that the formation of *p*-hydroxybenzenediazonium ion is unquestionably catalyzed by iodide ion; at this acidity the half-life in the absence of iodide ion is several days. At these dilutions *p*-iodobenzenediazonium ion was not detected; it could only have been a minor product. In these experiments oxygen was not excluded because of experimental difficulties.

There is apparently a reaction with bisulfate ion, but no quantitative results were obtained.

## Discussion

Chloride, bromide, thiocyanate, azide and (over a limited range) hydroxide ions attack the tetrazonium ion with displacement of the $N_2$ group following the same rate law. It can be easily shown that all the reactions do not proceed *via* nucleophilic attack on carbon by the following argument. The nucleophilic reactivity of a reagent toward substitution on carbon may be approximated by its reactivity toward a standard substrate. Thus Swain and Scott[9] have written the general eq. 1,

$$\log k = sn + \text{const.} \qquad (1)$$

where $s$ is a reaction constant and $n$ is a measure of the nucleophilic character of the reagent. A plot of $\log k_2$ vs $n$ (from the tabulations of ref. 9) is shown in Fig. 1, a line of slope 1.5 $(s = 1.5)$ is drawn through the points for chloride and bromide ions. This value of $s$ is as large as any mentioned Swain and Scott. The points for $N_3^-$ deviates by a factor of $2 \times 10^9$, that for $SCN^-$ deviates by a factor of 40, $OH^-$ by a factor of $3 \times 10^{10}$, and $I^-$ by 5000. These deviations are enormous even when it is realized that the Swain–Scott equation is quite poor when applied to nucleophilic aromatic

(8) M. Quintin, *Compt. rend.*, **210**, 625 (1940).

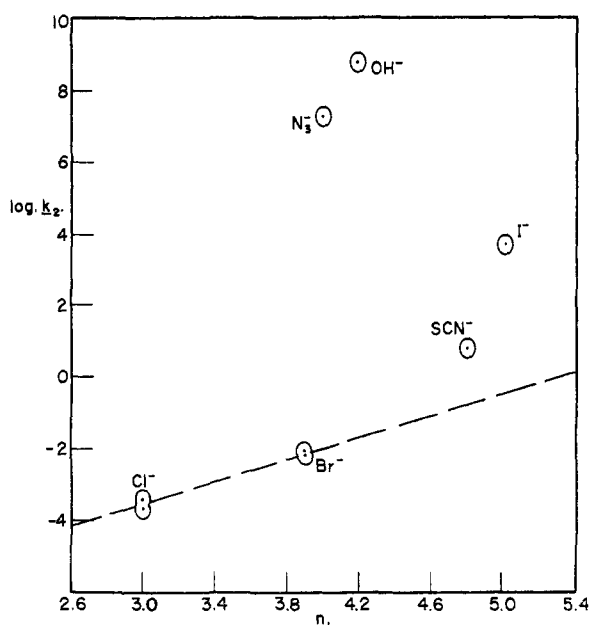(9) C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 146 (1953).



Fig. 1.—The failure of the Swain–Scott equation to fit the reaction of tetrazotized *p*-phenylenediamine with various nucleophiles.

substitution.[10] No line of positive slope can be drawn which does not miss either the $OH^-$ or the $SCN^-$ points by at least a factor of $10^4$, and those that come this close everywhere have $s$-values well outside the range previously known.

It comes as no surprise that hydroxide ion, azide ion and iodide ion are not attacking this molecule on carbon. The complex mechanism of the hydroxide ion attack, which involves prior attack on nitrogen, has been discussed elsewhere.[1] The mechanism of attack of azide ion has been shown in several cases to proceed *via* attack on nitrogen, with no attack on carbon at all.[11] The transition state for the iodide ion attack can hardly contain much carbon–iodine bond character, since there is none in the product.

A mechanism can be proposed which, with simple variations, will fit all the substitution reactions. It is suggested that there is bonding of the attacking nucleophile both to carbon and to the terminal nitrogen of the group to be displaced. The extent of the latter bonding may be correlated with the stability of the corresponding covalent diazo compound. Thus $OH^-$ and $N_3^-$ both form products of perceptible stability,[11,12] and can be expected to retain bonding to nitrogen in the reaction transition state, but $Cl^-$, $Br^-$ and $SCN^-$ show no significant covalent compound formation,[13] and therefore involve little bonding to nitrogen.

The geometry of the transition state for attack on carbon is essentially that of a heterocyclic spiro compound, with rather variable distance between

(10) Examples showing this difficulty can be found in recent re-views: J. F. Bunnett, *Quart. Revs.*, **12**, 1 (1958); ref. 5a.

(11) K. Clusius and H. Hürzeler, *Helv. Chim. Acta*, **37**, 798 (1954); R. Huisgen and I. Ugi, *Chem. Ber.*, **90**, 2914 (1957).
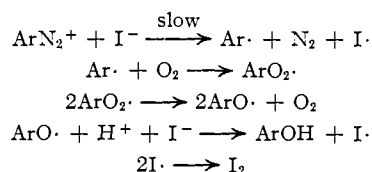
(12) (a) E. S. Lewis and H. Suhr, *ibid.*, **91**, 2350 (1958); (b) I. Ugi, H. Perlinger and L. Behringer, *ibid.*, **91**, 2324 (1958).

(13) (a) W. B. Davidson and A. Hantzsch, *Ber.*, **31**, 1612 (1898); (b) R. E. Kunetka, M.A. Thesis, The Rice Institute, 1952; H. Suhr and E. S. Lewis, unpublished work.
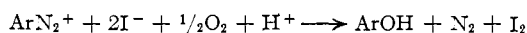
the attacking nucleophile and the terminal diazo nitrogen. It does not appear important whether or not there is a perceptibly stable *syn*-diazo compound formed on the way to the crucial transition state. Of course in the case of azide ion reaction can take place from a covalent *syn*-diazo compound without destroying the planarity of the system by two different routes, one of direct attack on the terminal nitrogen, the other *via* the arylpentazole,[11] so the higher energy non-planar system is never attained. A transition state with bonding to two different electron-deficient centers has been invoked also to explain the high reactivity of $\alpha$-haloketones toward nucleophilic substitution.[14]

While this mechanism is by no means clearly demonstrated, it does seem satisfactory to explain the very wide variation in reaction rates, and it makes a continuous transition from the SNi reaction proposed for the substitution by hydroxide[1] and the normal activated nucleophilic substitution previously proposed for bromide attack in a different situation.[3]

The reaction with iodide ion is particularly interesting. The only reasonable fate for iodide ion, which is consumed but is not incorporated into the organic molecule, is oxidation to iodine. Only oxygen can reasonably accomplish this without being detected. The following reaction series has been selected because it effectively couples the oxidation of iodide to the substitution of OH for $N_2^+$, and can reasonably fit the probable stoichiometry and the kinetics. It is not conclusively demonstrated.

$$ArN_2^+ + I^- \xrightarrow{slow} Ar\cdot + N_2 + I\cdot$$

$$Ar\cdot + O_2 \longrightarrow ArO_2\cdot$$

$$2ArO_2\cdot \longrightarrow 2ArO\cdot + O_2$$

$$ArO\cdot + H^+ + I^- \longrightarrow ArOH + I\cdot$$

$$2I\cdot \longrightarrow I_2$$

The net reaction of this series would then be

$$ArN_2^+ + 2I^- + {}^1/_2O_2 + H^+ \longrightarrow ArOH + N_2 + I_2$$

The observed formation of *p*-iodobenzenediazonium ion at higher concentrations may mean that the substitution reaction is higher order in I⁻, or it may merely mean that the supply of $O_2$ is limited, and with more iodine and iodide the reaction is

$$Ar\cdot + I\cdot \longrightarrow ArI$$

or

$$Ar\cdot + I_2 \longrightarrow ArI + I\cdot$$
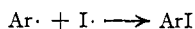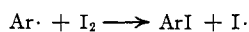
Further experiments to study this tentative proposal have not yet been made.

## Experimental

**Materials.**—Sodium chloride, bromide, iodide, azide and thiocyanate and the acid used were reagent grade materials. Solutions of known concentrations of the salts were made up by weighing the dry salt, except that sodium thiocyanate solutions were standardized argentimetrically. Sodium perchlorate was prepared by neutralization of perchloric acid with sodium carbonate, and evaporation to dryness. The solution was analyzed by titration of the acid formed on percolation through a hydrogen form cation exchange resin. *p*-Phenylene-bis-(diazonium fluoroborate) was prepared by

the tetrazotization of *p*-phenylenediamine following the procedure of Lewis and Johnson.[6]

**Kinetic Measurements.**—The tetrazonium salt was added to the reaction mixture in the form of a solution about $2 \times 10^{-3}M$ in concentrated perchloric acid. The reaction with chloride ion was followed by the absorbance at 284 m$\mu$ of a solution made by adding 0.1 ml. of the tetrazonium salt solution to 2.29 ml. of an appropriate mixture of sodium perchlorate and sodium perchlorate and sodium chloride in a 1-cm. square cell. Temperature was controlled by circulating thermostated water through the walls of the cell compartment, and solutions were brought to temperature in the thermostat before mixing. This temperature control is not very good; the remaining measurements were made by setting the thermostat temperature at 28.2° (which was fairly close to the room temperature) to minimize this error. Rate constants were calculated from the change in absorbance with time by the method of Guggenheim.[15] The reaction with bromide ion was followed similarly using the absorbance at 295 m$\mu$; the reaction with thiocyanate was followed using the absorbance at 242 m$\mu$ for two runs, and 325 m$\mu$ for two others. The reaction with azide ion was followed by adding 0.05 ml. of the tetrazonium salt solution to a mixture of 10 ml. of 8.72 $M$ perchloric acid, 15 ml. of water and 1.0 (or 0.5 ml.) of 2.61 × 10⁻³ $M$ sodium azide solution. Change in absorbance at 335 m$\mu$ was followed in a 10-cm. cell. The reaction with iodide was similarly followed (at 310 m$\mu$) in a 10-cm. cell as soon as possible after mixing 0.05 ml. of tetrazonium salt solution with a mixture of 25 ml. 1.6 × 10⁻⁵ $M$ sodium iodide (or in another experiment 8 × 10⁻⁶ $M$ sodium iodide) and 1 ml. of 8.72 $M$ perchloric acid. The extent of reaction was calculated from the absorbance at various times, and the second-order rate constant, $k_2$ was calculated from the equation

$$k_2t = (2.303/(B_0 - 2A_0)) \log (A_0B/B_0A)$$

where $A_0$ is the initial concentration of tetrazonium salt, $B_0$ is the initial concentration of iodide ion, and $A$ and $B$ are the corresponding concentrations at the time $t$.

The reaction in sulfuric acid solution was followed by the change in absorption at 310 m$\mu$, the absorption maximum of *p*-hydroxybenzenediazonium ion. No reactions were carried to completion and the products were not identified, but the change in absorbance was faster in 3.8 $M$ sulfuric acid than it was in 0.5 $M$ or in concentrated sulfuric acid, and in all solutions change was faster than in concentrated perchloric acid. These results conform to the suggestion of attack by bisulfate ion, but it is not demonstrated.

**Product Identification.**—The diazotization of commercially available *p*-chloroaniline, *p*-bromoaniline and *p*-iodoaniline furnished samples of diazonium salts for comparison with the products of reaction of chloride, bromide and iodide ions, respectively. In the first two and in the cases mentioned later, the shapes of the peaks and the wave lengths of maxima and minima agreed. No attempt to get agreement of extinction coefficients was made because of the difficulty of getting pure samples of any diazonium salts. *p*-Thiocyanatobenzenediazonium ion was prepared from the rapid reaction of excess sodium thiocyanate with *p*-bromobenzene-diazonium ion in 95% by volume *t*-butyl alcohol and water.[5b] The synthesis of a solution of *p*-azidobenzenediazonium salt started with *p*-aminobenzenediazonium fluoborate,[6] which was dissolved in 0.1 $M$ perchloric acid containing an excess of sodium azide. After several hours the solution was made alkaline and the resulting *p*-aminophenyl azide was extracted into ether. It was then extracted again into 0.1 $M$ perchloric acid and treated with sodium nitrite. The solution had a conspicuous absorption maximum at 335 m$\mu$, not distinguishable from that of the product of reaction of the tetrazonium salt with azide ion. Treatment with sodium azide caused a change at a rate proportional to the azide ion concentration to a solution with a maximum absorption at 270 m$\mu$. Concentrated iodide solutions yielded with the tetrazonium salt a substance not identified (but presumably *p*-diiodobenzene) with maxima at 300 and 350 m$\mu$. Lower concentrations yielded a product with $\lambda_{max}$ 327 m$\mu$, the same as independently synthesized *p*-iodobenzenediazonium ion. At the very low iodide concentrations, the product had $\lambda_{max}$ 310 in the acid solutions and at pH 5, the maximum shifted to 350 m$\mu$. The spectrum was essentially that of independently synthesized *p*-hydroxybenzenediazonium salt.[6]

(14) The arguments for this explanation are studied by P. D. Bartlett and E. N. Trachtenberg, THIS JOURNAL, **80**, 5808 (1958).

(15) E. A. Guggenheim, *Phil. Mag.*, Ser. **7**, **2**, 538 (1926).