chloride or ethanol). The resulting solution was layered with 75 ml of ether and refrigerated (−20°) overnight. The crystalline, nonhygroscopic product was then filtered and washed with ether. One recrystallization from ethanol–ether gave analytically pure material. The compounds isolated in this manner were as follows.

***cis*-3,3-Dimethyl-5-*p*-methylphenyl-2-phenyloxazolidinium fluoroborate (4e)** was in 78% yield: mp 146.5–147.5°; nmr (CD_2Cl_2) τ 2.3–2.6 (m, 5, Ph), 2.75 (dd, 4, J = 8 Hz, *p*-CH_3Ph), 3.99 (s, 1, PhCHO), 4.36 (t, 1, J = 8 Hz, *p*-$CH_3PhC\textit{H}CH_2N^+$), 5.62 (dd, 1, J_{gem} = 12 Hz, J_{cis} = 8 Hz, 4-H trans to 5-*p*-CH_3Ph), 6.35 (dd, 1, J_{gem} = 12 Hz, J_{trans} = 8 Hz, 4-H cis to 5-*p*-CH_3Ph), 6.74 (s, 3, $^+NCH_3$ trans to 2-Ph), 7.42 (s, 3, $^+NCH_3$ cis to 2-Ph), 7.72 (s, 3, *p*-CH_3Ph).

Anal. Calcd for $C_{18}H_{22}BF_4NO$: C, 60.87; H, 6.24; N, 3.94. Found: C, 60.71; H, 6.26; N, 3.80.

***cis*-5-*p*-Chlorophenyl-3,3-dimethyl-2-phenyloxazolidinum fluoroborate (4d)** was in 74% yield: mp 145.5–146.5; nmr (CD_2Cl_2) τ 2.2–2.44 (m, 5, Ph), 2.51 (s, 4, *p*-ClPh), 3.85 (s, 1, PhCHO), 4.18 (t, 3, J = 8 Hz, *p*-$ClPhC\textit{H}CH_2N^+$), 5.42 (dd, 1, J_{gem} = 12 Hz, J_{cis} = 8 Hz, 4-H trans to 5-*p*-ClPh), 6.22 (dd, 1, J_{gem} = 12 Hz, J_{trans} = 8 Hz, 4-H cis to 5-*p*-ClPh), 6.60 (s, 3, $^+NCH_3$ trans to 2-Ph), 7.39 (s, 3, $^+NCH_3$ cis to 2-Ph).

Anal. Calcd for $C_{17}H_{19}BClF_4NO$: C, 54.36; H, 5.10; N, 3.73; Cl, 9.44. Found: C, 54.60; H, 5.00; N, 3.81; Cl, 9.26.

***cis*-5-*p*-Bromophenyl-3,3-dimethyl-2-phenyloxazolidinium fluoroborate (4c)** was in 70% yield (based on pure starting material): mp 152–153°; nmr (CD_2Cl_2–CF_3CO_2H) τ 2.1–2.5 (m, 5, Ph), 2.30 and 2.55 (dd, 4, J = 9 Hz, *p*-BrPh), 3.96 (s, 1, PhCHO), 4.24 (t, 1, J = 8 Hz, *p*-$BrPhC\textit{H}CH_2N^+$), 5.53 (dd, 1, J_{gem} = 12 Hz, J_{cis} = 8 Hz, 4-H trans to 5-*p*-BrPh), 6.25 (dd, 1, J_{gem} = 12 Hz, J_{trans} = 8 Hz, 4-H cis to 5-*p*-BrPh), 6.62 (s, 3, $^+NCH_3$ trans to 2-Ph), 7.25 (s, 3, $^+NCH_3$ cis to 2-Ph).

Anal. Calcd for $C_{17}H_{19}BBrF_4NO$: C, 48.61; H, 4.56; N, 3.33; Br, 19.02. Found: C, 48.66; H, 4.57; N, 3.34; Br, 19.18.

Cation–Anion Combination Reactions. IV. Reactions of Aryldiazonium Ions with Hydroxide and Cyanide Ions in Aqueous Solution[1,2]

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Abstract: The rates and equilibria of the reactions of a series of substituted benzenediazonium ions with hydroxide and cyanide ions in aqueous solution at 23° have been studied. The rate constant for the reaction of *p*-nitrobenzenediazonium ion with water was also determined. The following Hammett equations were found to correlate the reactions of the substituted benzenediazonium ions: (1) $\log K_{CN} = 3.53\sigma + 1.82$; (2) $\log k_{CN} = 2.31\sigma + 2.32$; (3) $\log K_{O^-} = 6.58\sigma + 4.76$; and (4) $\log k_{OH} = 2.61\sigma + 3.72$; where K_{CN} and k_{CN} are the equilibrium and rate constants for formation of the *syn*-diazocyanides, and K_{O^-} and k_{OH} are the corresponding quantities for formation of the *syn*-diazotates. The ρ value for the diazocyanide reaction is significantly smaller than expected and forces us to change our previous conclusion concerning the identity of the rate-determining step in the reactions of aryldiazonium ions with azide ion. It now appears that this latter reaction involves a rapid formation of the diazoazide, followed by slow decomposition to the aryl azide and aryl pentazole. The most striking facet of the present work comes from a comparison of the relative rates of reactions of *p*-nitrobenzenediazonium and of previously studied reactions of triarylmethyl cations with the three nucleophiles, water, hydroxide ion, and cyanide ion. The entirely different cations react with any given nucleophile at rates differing by at least 10^4, but show amazingly similar selectivities for the three nucleophiles.

The present series of papers is concerned with delineating the factors affecting the reactivities of various nucleophiles in simple cation–anion combination reactions. Our curiosity was initially aroused by the fact that Malachite Green cations (specifically: bis(*p*-dimethylaminophenyl)phenylmethyl, bis(*p*-dimethylaminophenyl), *p*-nitrophenylmethyl, and tris(*p*-dimethylaminophenyl)methyl cations, which we refer to as Malachite Green, *p*-nitro Malachite Green, and Crystal Violet, respectively), in their reactions with nucleophiles to form the covalent combination products, showed the unusual rate order with azide ion reacting faster than methoxide ion, and hydroxide or methoxide ions reacting faster than cyanide ion.[3]

The two previous papers in this series have reported the results of the studies of the reactions of a series of aryldiazonium ions with azide ion in aqueous solution,[2] and of the complex reactions of *p*-nitrobenzenediazonium ion with hydroxide ion in aqueous solution.[4] In the present paper, we report the results of our studies of the rates and equilibria of the reactions of a series of aryldiazonium ions with hydroxide and cyanide ions in aqueous solution.

The products of these reactions and measurements of the equilibrium constants have been reported by other investigators. Aryldiazonium ions react with cyanide ion to form the *syn*-diazocyanides,[5] and with hydroxide ion to form the *syn*-diazotates.[6] The rate constants for these reactions have not been measured previously,

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[1] This work was supported by Grant No. GM-12832 from the National Institutes of Health, U. S. Public Health Services..

[2] Previous paper in this series: C. D. Ritchie and D. J. Wright, *J. Amer. Chem. Soc.*, **93**, 2429 (1971).

[3] C. D. Ritchie, G. A. Skinner, and V. G. Badding, *ibid.*, **89**, 2067 (1967).

[4] C. D. Ritchie and D. J. Wright, *ibid.*, **93**, 2425 (1971).

[5] E. S. Lewis and H. Suhr, *Chem. Ber.*, **92**, 3043 (1959), and earlier references cited there.

[6] E. S. Lewis and H. Suhr, *ibid.*, **91**, 2350 (1958), and earlier ref cited there.

but indications were that they would be measurable by the stop-flow techniques.

Results

The reactions of aryldiazonium ions in basic solutions were studied by both conventional spectrophotometry and stop-flow spectrophotometry. Buffered solutions, using borate, phosphate, bicarbonate, or dilute sodium hydroxide, of ionic strength ranging from 0.004 to 0.03 *M*, were prepared and mixed with a weakly acidic (*ca.* 10^{-4} *M* HCl) solution containing *ca.* 2×10^{-5} *M* of the diazonium fluoroborate. After spectrophotometric measurement, the pH of the solution was accurately measured.

Both conventional and stop-flow measurements of the equilibrium constants for formation of the diazotates were made for all of the compounds with the exceptions of those with the p-CO_2^-, H, and p-CH_3 substituents. For these latter compounds, side reactions were rapid enough to prevent accurate measurements by conventional spectrophotometry. Stop-flow measurements allowed observation of the diazotate formation before appreciable incursion of the side reactions.

The equilibrium constants for diazotate formation are reported in Table I and are compared to previously reported values. The values reported are not corrected for ionic strength since the variations of ionic strength employed are not great enough to cause changes outside the precision of the measurements.

Table I. Equilibrium Constants for the Reaction $XC_6H_5N_2^+ + 2OH^- \overset{K}{\rightleftarrows} syn\text{-}XC_6H_5N_2O^-$ in Aqueous Solution at 23°, μ = 0.004–0.03 *M*

		—*K*, M^{-2}—	
X	Buffer	This work[a]	Lewis and Suhr (μ = 1.0 *M*)[b]
p-NO_2[c]	Borate	2.0×10^{10}	1.3×10^9
p-CN	Borate	$3.9\ (\pm 0.3) \times 10^9$	2.9×10^8
m-CF_3	Borate, bicarbonate	$1.0\ (\pm 0.1) \times 10^8$	2.1×10^7
m-Cl	Bicarbonate	$1.9\ (\pm 0.3) \times 10^7$	4.0×10^6
p-Br	Bicarbonate, phosphate	$1.4\ (\pm 0.3) \times 10^6$	6.6×10^5
p-Cl	Bicarbonate, hydroxide	$6.7\ (\pm 0.8) \times 10^5$	3.8×10^5 (1.5×10^6)[d]
p-CO_2^-	Bicarbonate, hydroxide	$1.9\ (\pm 0.2) \times 10^5$	3.3×10^5 (1.3×10^6)[d]
H	Hydroxide	$2.8\ (\pm 0.7) \times 10^4$	1.6×10^4 (1.0×10^5)[d]
p-CH_3	Hydroxide	$2.2\ (\pm 0.7) \times 10^3$	6.6×10^2 (4.2×10^3)[d]

[a] The values and uncertainties are the average values and deviations obtained in at least four measurements at different pH. [b] Reference 6. [c] Previously reported in ref 4. [d] These values were obtained at an ionic strength of 0.1 *M*.

For the first five compounds listed in Table I, the agreement of our values with those of Lewis and Suhr[6] is as expected on the basis of the difference in ionic strengths used in the two studies. That is, our values at low ionic strength are larger by factors of two to ten than the values obtained at the much higher ionic strength. For the last four compounds listed, our values for the equilibrium constants are significantly smaller than the values reported by Lewis and Suhr for studies at an ionic strength of 0.1 *M*. It is for these compounds with less electron-withdrawing substituents, and which must be studied at high pH, that the side reactions are most bothersome. We believe that our measurements for these compounds, in which we have relied on the fast observations allowed by stop-flow techniques, have largely avoided the errors which can result from the side reactions.

Rate constants for the reactions of the aryldiazonium ions with hydroxide ion have been obtained by the usual stop-flow techniques.[3] A series of measurements at different pH for each compound verified that the reactions are first order in hydroxide ion and first order in diazonium ion concentrations. The rate constants obtained are reported in Table II. Buffer solutions were the same as for the equilibrium measurements.

Table II. Rate Constants for the Reaction of Aryldiazonium Ions with Hydroxide Ion in Aqueous Solution at 23°

$XC_6H_5N_2^+ + OH^- \overset{k}{\rightleftarrows} syn\text{-}XC_6H_5N_2OH$

X	k, M^{-1} sec^{-1} [a]
p-NO_2[b]	$5.4(\pm 0.3) \times 10^5$
p-CN	$4.2(\pm 0.2) \times 10^5$
m-CF_3	$1.6(\pm 0.2) \times 10^5$
m-Cl	$6.4(\pm 0.4) \times 10^4$
p-Br	$2.1(\pm 0.1) \times 10^4$
p-Cl	$1.6(\pm 0.1) \times 10^4$
p-CO_2^-	$5.8(\pm 0.4) \times 10^3$
H	$4.5(\pm 0.5) \times 10^3$
p-CH_3	$1.2(\pm 0.2) \times 10^3$

[a] The values and deviations shown are the average of at least four determinations at different pH. [b] Value previously reported; ref 4.

The kinetic behavior clearly shows that the rate-determining step of these reactions is the formation of *syn*-diazohydroxide, and that the conversion to the *syn*-diazotate is rapid.[6]

We have also been interested in determining the rate constant for the reaction of water with aryldiazonium ions. The reaction sequence

$$ArN_2^+ + OH^- \overset{k_1}{\rightleftarrows} syn\text{-}ArN_2OH \qquad (1a)$$

$$syn\text{-}ArN_2OH + OH^- \underset{\text{fast}}{\overset{K_2}{\rightleftarrows}} syn\text{-}ArN_2O^- \qquad (1b)$$

$$ArN_2^+ + H_2O \overset{k_3}{\rightleftarrows} syn\text{-}ArN_2OH_2^+ \qquad (1c)$$

$$syn\text{-}ArN_2OH_2^+ + OH^- \underset{\text{fast}}{\overset{K_4}{\rightleftarrows}} syn\text{-}ArN_2OH \qquad (1d)$$

gives eq 2 for the pseudo-first-order rate constants for disappearance of diazonium ion in buffered solution.

$$\begin{aligned} k_{\text{obsd}} &= k_1[(OH^-) + 1/K_1K_2(OH^-)] + \\ &\qquad k_3[1 + 1/K_1K_2(OH)^2] \qquad (2) \\ &= k_1[1 + 1/K_1K_2(OH^-)^2][(OH^-) + k_3/k_1] \end{aligned}$$

Inspection of this equation shows that the determination of k_3 requires the study of the rates in a rather narrow pH range where the equilibrium will be essentially complete to the diazotate, but where the hydroxide ion concentration is small enough that the rate of the reaction with hydroxide ion is not much greater than the rate of the reaction with water. For the p-nitrobenzenediazonium ion, we have carefully studied the

Table III. Rates of Formation of *syn-p*-Nitrobenzene Diazotate in Aqueous Buffers

pH	k_{obsd}, sec^{-1}	k_{calcd},[a] sec^{-1}	k_{calcd},[b] sec^{-1}
9.206	12.5	12.7	11.1
9.304	14.5	14.2	13.1
9.403	16.0	16.7	15.9
9.487	21.2	19.2	18.7
9.582	25.5	22.9	22.9
9.682	28.1	28.1	28.6
9.760	30.7	32.9	33.9
9.874	37.2	41.8	43.8
9.900	46.0	44.2	46.4
9.950	50.8	49.2	51.9
10.024	59.8	58.0	61.8

[a] Calculated from eq 2 with $K_1K_2 = 2.0 \times 10^{10}\ M^{-2}$, $k_1 = 5.24 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$, and $k_3 = 2.2\ \mathrm{sec}^{-1}$. [b] Calculated from eq 2 with $K_1K_2 = 2.0 \times 10^{10}\ M^{-2}$, $k_1 = 5.80 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$, and $k_3 = 0.00$.

rates of reaction in borate buffers in the range from pH 9.2 to 10.0 with the results reported in Table III.

Using the value of K_1K_2 ($= 2.0 \times 10^{10}\ M^{-2}$) previously reported, a plot of $k_{\mathrm{obsd}}/[1 + 1/K_1K_2(\mathrm{OH}^-)^2]$ *vs.* (OH^-) gives slope of k_1 and intercept of k_3. Since both the rate and pH measurements give nearly constant percentage errors rather than absolute errors, we have treated the data by a weighted least-squares treatment[7] to obtain the values $k_1 = 5.24 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$, and $k_3 = 2.2\ \mathrm{sec}^{-1}$. These values lead to the calculated values of k_{obsd} shown in the third column of Table III. An indication of the reliability of the value for k_3 is obtained by comparing the observed values of the first-order rate constants with those shown in column four of Table III which were calculated assuming that $k_3 = 0$. Although the evaluation of k_3 depends heavily on the rates at the lower pH only, we do not think that the value obtained is likely to be in error by more than a factor of two.

The studies of the reactions of the diazonium ions with cyanide ion were carried out in solutions buffered at pH such that the diazotate formation would not interfere. Potassium cyanide dissolved in buffer solutions was mixed with the solution of aryldiazonium ion, and after spectrophotometric measurements of the formation of the diazocyanide, the pH of the reaction solution was determined accurately. Low ionic strength (0.06–0.02 *M*) was maintained for all solutions and the concentration of cyanide ion was calculated from the known p*K* of 9.14 for HCN in aqueous solution. Ionic strength corrections were not applied since the variation of ionic strength was small enough that such corrections would not be significant within the precision of the measurements. There are a number of side reactions that cause difficulty in the determination of the equilibrium constants for diazocyanide formation.[5] Only in the cases of the *p*-Cl, *p*-Br, and *m*-Cl substituted benzenediazonium ions were we able to obtain precise results by the use of conventional spectrophotometry. For all other compounds, the stop-flow techniques were required for rapid observation of the initial equilibrium before the side reactions caused trouble.

Table IV. Rate and Equilibrium Constants for the Reaction $\mathrm{XC_6H_5N_2^+} + \mathrm{CN^-} \rightleftarrows$ *syn*-$\mathrm{XC_6H_5N_2CN}$ Aqueous Solution at 23°, $\mu = 0.035\ M$

	K, M^{-1}		
X	This work[c]	Lewis and Suhr[b]	k, $M^{-1}\ \mathrm{sec}^{-1}$ [c]
p-$\mathrm{NO_2}$	$6.0(\pm 0.5) \times 10^4$	1.0×10^5	$1.7(\pm 0.2) \times 10^4$
p-CN	$1.4(\pm 0.2) \times 10^4$	5.0×10^4	$7.4(\pm 0.8) \times 10^3$
m-$\mathrm{CF_3}$	$4.8(\pm 0.7) \times 10^3$	4.0×10^3	$3.9(\pm 0.5) \times 10^3$
p-$\mathrm{C_6H_5CO}$	$1.9(\pm 0.3) \times 10^3$		$1.7(\pm 0.1) \times 10^3$
m-Cl	$1.6(\pm 0.2) \times 10^3$	1.9×10^3	$1.8(\pm 0.2) \times 10^3$
p-Br	$3.7(\pm 0.2) \times 10^2$	6.1×10^2	$6.5(\pm 0.4) \times 10^2$
p-Cl	$4.5(\pm 0.9) \times 10^2$	6.9×10^2	$6.8(\pm 0.4) \times 10^2$
p-$\mathrm{CO_2^-}$	$1.3(\pm 0.1) \times 10^2$	4.3×10^2	$1.9(\pm 0.2) \times 10^2$
H[a]	$5.1(\pm 0.6) \times 10$	4.6×10	$2.6(\pm 0.2) \times 10^2$
p-$\mathrm{CH_3}$[a]	$1.5(\pm 0.2) \times 10$		$9.0(\pm 0.9) \times 10$

[a] Ionic strength 0.06 *M*. [b] Ionic strength 1.1 *M*; ref 5. [c] The values and deviations are the averages of at least four determinations at different concentrations of cyanide ion.

The reaction kinetics were all shown to be first order with respect to cyanide and first order with respect to diazonium ion concentrations. The rate and equilibrium constants obtained are reported in Table IV. Equilibrium measurements previously reported by Lewis and Suhr[5] for much higher ionic strengths (1.1 *M*), and obtained by conventional spectrophotometry, are shown for comparison. The agreement of the values to within a factor of *ca.* two is all that could be expected considering the differences in ionic strength and the difficulties in conventional measurements caused by the side reactions. We believe that our use of the stop-flow technique, the use of low ionic strength, and the accurate determination of pH leads to the more accurate values.

Discussion

Hammett plots[8] of the data for the rates and equilibria of reactions with hydroxide and cyanide ions showed good correlations. Least-squares treatment gives the equations

$$\log K_{\mathrm{O^-}} = 6.58\sigma + 4.76 \tag{3}$$

$$\log k_{\mathrm{OH}} = 2.61\sigma + 3.72 \tag{4}$$

$$\log K_{\mathrm{CN}} = 3.53\sigma + 1.82 \tag{5}$$

$$\log k_{\mathrm{CN}} = 2.31\sigma + 2.32 \tag{6}$$

The ρ value for the equilibrium constants for diazotate formation is in excellent agreement with the value of 6.3 which Lewis and Suhr obtained from their data at 1 *M* ionic strength. As was pointed out, this large ρ value is the sum of the ρ values for formation of the diazohydroxides and for the ionization of the diazohydroxides to form the diazotates.[9,10] The ρ values for both the rates of formation of the diazotates and the rates of formation of the diazocyanides are quite comparable to

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(7) Defining: $k' = k_{\mathrm{obsd}}/[1 + 1/K_1K_2(\mathrm{OH}^-)^2]$, $k' = k_1(\mathrm{OH}^-) + k_3$. We have carried out the minimization of $\Sigma\{[k_i' - k_1(\mathrm{OH}^-)_i - k_3]/k_i'\}]^2$, with respect to k_1 and k_3.

(8) The σ values used are those reported by C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964), and listed as "simple" σ (*i.e.*: fourth column of Table I, p 336). The choice of σ values is quite arbitrary, but it is important to be consistent when comparing ρ values for similar reaction series, as we do in the present paper.

(9) The very high ρ value for diazotate formation requires some further comment. Lewis and Hanson[10] have reported that the ρ value for the ionization of *anti*-diazohydroxides to *anti*-diazotates is 1.4. If this value applied to the *syn*-diazohydroxide ionization, we would calculate a ρ value of 5.2 for the formation of the *syn*-diazohydroxides from the diazonium ions. This value is much higher than expected for such a reaction. It seems quite likely, and rationalizable, that the ionization of the *syn*-diazohydroxides to the *syn*-diazotates exhibits a much larger ρ value than the corresponding anti compounds.

(10) E. S. Lewis and M. P. Hanson, *J. Amer. Chem. Soc.*, **89**, 6268 (1967).

the ρ value of 2.4 found for the rates of formation of diazosulfones in methanol solution.[11] The values, however, are considerably smaller than the ρ value for the rates of reaction of the diazonium ions with azide ion (3.2) which we previously reported,[2] and are smaller than expected on the basis of the arguments presented in that paper.

The arguments presented in connection with the azide reaction were based on the ρ value of 4.7 for the equilibrium formation of *syn*-diazocyanides which had been reported by Lewis and Suhr.[5] The value of 3.53 found in the present study requires a reexamination of those arguments. From a comparison of the ρ value of 3.2 for the rates of the azide reaction with the value of 4.7 expected, in analogy to the cyanide reaction, for the equilibria of formation of the diazoazides, we concluded that it was unlikely that the decomposition of the diazoazides could be the rate-determining step in the reaction to form aryl azides and aryl pentazoles. Our present data show clearly that the ρ value for the rates of the azide reactions is larger than can be attributed to the rates for the formation of the diazoazides, and is only slightly smaller than expected for equilibrium formation of the diazoazides. It seems quite likely, then, that the azide reactions involve a rapid preequilibrium formation of the diazoazide followed by rate-determining decomposition to aryl azide and aryl pentazole.[2] Thus, the rate constants for formation of the diazoazides must be larger than the observed second-order rate constants. This provides a rational explanation of the fact that the rate constant for azide reaction is greater than that for hydroxide in the case of *p*-nitrobenzenediazonium ion, while the reverse is true for benzenediazonium ion. It is almost certain that the rate constants for formation of the diazoazides are greater than those for formation of the diazohydroxides in all cases.

The most interesting, and we suspect fundamental, conclusion to come from the present work arises in the comparison of the present data with the previously reported data for reactions of Malachite Green cations with cyanide ions, hydroxide ions, and water in aqueous solution.[3] In the introduction, we called attention to the unusual order of nucleophilicities: $OH^- > CN^-$, and $N_3^- > CH_3O^- > CN^-$, found for those reactions. We now find that the diazonium ions give the similar rate order: $N_3^- > OH^- > CN^-$, even though the absolute rate constants for the different classes of cations are widely different. As can be seen from the comparison of the rate constants for the reaction of *p*-nitrobenzenediazonium ion with those for reactions of *p*-nitro Malachite Green, shown in Table V, it appears that this similarity may be more than qualitative.

Table V. Comparison of Rate Constants for Reactions of *p*-Nitro Malachite Green and of *p*-Nitrobenzenediazonium Ion in Aqueous Solution

Nucleophile	$k(ArN_2^+)$[a]	$k(Ar_3C^+)$[b]
OH^-	$5.2 \times 10^5\ M^{-1}\ sec^{-1}$	$5.6\ M^{-1}\ sec^{-1}$
CN^-	$1.7 \times 10^4\ M^{-1}\ sec^{-1}$	$1.1\ M^{-1}\ sec^{-1}$
H_2O	$2.2\ sec^{-1}$	$1.8 \times 10^{-4}\ sec^{-1}$

[a] Rate constant for *p*-nitrobenzenediazonium ion. [b] Rate constant for reaction of *p*-nitro Malachite Green. See ref 3.

Experimental Section

Materials. Diazonium fluoroborates were prepared from the corresponding amines by standard methods and were recrystallized from methanol–acetone to constancy of their ultraviolet spectra. The diazonium fluoroborates in tightly sealed vials were stored at −20° and showed no decomposition over a period of several months.

Potassium cyanide, sodium bicarbonate, sodium phosphate, and boric acid were commercial products used without further purification. Water used in all experiments was distilled and stored protected from carbon dioxide.

Buffer component solutions were prepared at concentrations approximately ten times those used for reaction studies and were mixed and diluted to the appropriate concentrations immediately before use. For pH above 11, sodium hydroxide was used.

Equipment. All studies were carried out in an air-conditioned room maintained at 23 ± 1°. pH measurements were made with a Beckman Model 1019 pH meter equipped with glass and saturated calomel electrodes standardized immediately before use with commercial standard buffers within one pH unit of the pH to be measured.

A Cary Model 14 spectrophotometer with 1.0-cm quartz cells was used to obtain spectra. The stop-flow apparatus has been described previously.[3]

Reactions with Aqueous Base. The techniques used for both equilibrium and rate measurements were similar to those previously described for reactions of *p*-nitrobenzenediazonium ion.[4] Solutions were collected from the stop-flow or Cary 14 spectrophotometers under an inert atmosphere. The pH of each reaction solution was measured after the reaction was complete.

Each diazonium ion was studied over a range of at least fivefold variation in (OH^-), and in most cases tenfold. Potassium perchlorate was used to maintain constant ionic strength.

Reactions with Cyanide Ion. Boric acid–sodium borate buffers were used for all measurements of the cyanide reactions. Potassium cyanide was weighed and dissolved in a known volume of the appropriate buffer, and this solution was then mixed with a solution of the diazonium fluoroborate (*ca.* $2 \times 10^{-5}\ M$) in $10^{-4}\ M$ hydrochloric acid. The buffer capacity was at least $10^{-3}\ M$ in all cases. Ionic strength was maintained with potassium perchlorate.

Spectrophotometric measurements with either the Cary 14 or the stop-flow were analogous to those for the reactions with aqueous base. The reaction solutions were collected under an inert atmosphere after spectrophotometric measurements and the pH of the solution was measured. The concentration of cyanide ion was calculated from the known total concentration of cyanide ion and hydrocyanic acid, the measured pH, and the known pK of 9.14 for hydrocyanic acid.

Each diazonium ion was studied over a range of at least fivefold variation in cyanide ion concentration.

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(11) C. D. Ritchie, E. S. Lewis, and J. Saltiel, *J. Amer. Chem. Soc.*, 83, 4601 (1961).