band column after the usual purification. The purity determined gas chromatographically was more than 99.9%. Propane obtained from Takachiho Shoji Co. was purified by several trap-to-trap distillations through a sodium mirror and stored in a storage bulb. Oxygen obtained from Awao Industrial Co. was dried by a P_2O_5 column and was used without further purification. Benzene-d_6 purchased from Merk Co., Germany, was also used without purification except drying by a sodium mirror (deuterium content, 99.5%).

Procedures. The experimental procedures were similar to those reported previously.[1] The irradiation cells were Pyrex cylinders of approximately 120 ml in volume with a break-seal. After the cells were evacuated at a pressure of 10^{-6} mm Hg overnight, the propane vapor from the storage bulb was dried by passing through a sodium mirror, and then introduced into the cells at a pressure of 100 mm. The pressure of the sample was measured by a mercury manometer. Then, a known amount of benzene or toluene, dried similarly, was introduced to the cells, in which propane was already condensed at −196°, by a trap-to-trap distillation from a cell for sampling. Finally, oxygen was introduced into the cell through a P_2O_5 column and the cells were sealed.

Samples were irradiated with γ rays from a 5000-Ci ^{60}Co source at room temperature. The dose rate to propane was determined by a ethylene dosimetry, using a G value of 1.28 for hydrogen formation[32] and correcting for the electron density of propane relative to ethylene. The irradiations were carried out at a constant dose rate of 1.85×10^{15} eV/hr μmol for propane. The G values of the product were calculated on the energy absorbed by propane alone.

After irradiation, the cell was sealed to a high vacuum line and the break-seal was ruptured after evacuation. The gases volatile at −120° (mainly propane and oxygen) were pumped off through a spiral trap kept at −120° and then the residual liquid fraction was collected into a capillary glass tube and analyzed by gas chromatographic comparison with authentic samples using several columns (Apiezon L, 6 m at 100 or 130° and Benton 34, 3 m + Apiezon L, 3 m at 130°). The yields of the products were determined by comparison of peak areas with those of known amounts of benzene, which were submitted to gas chromatography before each analysis. The calibration of the sensitivity for a flame-ionization detector was also carried out.

Competitive isopropylations of benzene and toluene or benzene-d_6 and toluene were also carried out similarly to those described above using benzene–toluene mixtures.

Acknowledgment. We thank Mr. Tamotsu Yamamoto and Mr. Tomikazu Sawai in the Radiation Laboratory for assistance in the γ irradiations.

[32] R. A. Back, T. W. Woodward, and K. A. McLauchlan, *Can. J. Chem.*, 40, 1380 (1962).

Cation–Anion Combination Reactions. II.[1] The Reactions of *p*-Nitrobenzenediazonium Ion with Hydroxide Ion in Aqueous Solution

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Abstract: The reaction of *p*-nitrobenzenediazonium ion with hydroxide ion in aqueous solution produces the *syn*-diazotate in a fast second-order reaction. The *syn*-diazotate slowly rearranges to the more stable *anti*-diazotate in a first-order process. The rate and equilibrium constants for the individual steps are evaluated and the previously proposed mechanism for the reaction is modified in several particulars.

In earlier work,[1] we noted the peculiar reactivity order $N_3^- > CH_3O^- > CN^-$ for the rates of reactions of malachite green derivatives in methanol solution. The order of azide faster than cyanide was found to be independent of solvent in methanol, dimethylformamide, and dimethyl sulfoxide. The rate order is the exact opposite of the equilibrium order for these reactions. The further observation that these nucleophiles follow the Brønsted order $CN^- > N_3^-$ in proton transfer reactions in DMSO indicates that the order for the malachite green reactions is not a characteristic of either the anions or of any solvent.

In other studies in these laboratories, attempts to measure rate and equilibrium constants for reactions of malachite green with other nucleophiles in DMSO solution have been thwarted either by rates too fast to measure (for example, thiophenoxide ion) or by unfavorable equilibria (acetate, chloride, *p*-nitrophenoxide).

Our curiosity about these reactions was heightened after a literature search failed to reveal any other reaction in which azide ion reacts faster than cyanide ion in a nucleophilic attack. On the basis of Edwards' parameters for these two anions,[2] it does not appear that any combination of basicity and polarizability could give the observed order.

It appeared to us that the one feature of the malachite green reactions which differs drastically from other reactions which have been studied is that the anions are reacting directly with a rather nonspecifically solvated cation without the necessity of displacing any leaving group. In order to check this hypothesis, we have sought other reactions which would have this feature, but be as different from malachite green reactions as possible in other respects.

Various substituted benzenediazonium ions are known to undergo reactions of the desired type, and some rate and equilibrium data are available for these

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[1] C. D. Ritchie, G. A. Skinner, and V. G. Badding, *J. Amer. Chem. Soc.*, 89, 2063 (1967), is to be considered as paper I of the present series. We gratefully acknowledge support of this work by National Institutes of Health, Grant GM-12832.

[2] J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, 84, 16 (1962). For a tabulation of parameters, see J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 253.

Table I. Slow Reaction of *p*-Nitrobenzenediazonium Ion in Aqueous Buffer Solutions

Run	pH	A°_{260}(calcd)[a]	A°_{330}(calcd)[a]	A°_{260}(obsd)[b]	A°_{330}(obsd)[b]	k_ψ,[c] sec^{-1}
1[d]	8.21	0.812	0.075	0.780		4.6×10^{-3}
2[d]	8.56	0.812	0.075	0.810	0.140	1.2×10^{-2}
3[d]	8.78	0.812	0.075	0.662	0.123	2.8×10^{-2}
4[d]	9.08	0.812	0.075	0.413	0.100	3.9×10^{-2}
5[d]	9.46	0.812	0.075	0.270	0.215	5.2×10^{-2}
6[d]	9.68	0.812	0.075	0.187	0.295	5.1×10^{-2}
7[d]	9.82	0.812	0.075	0.215	0.295	5.0×10^{-2}
8[e]	8.65	0.730	0.070	0.60	0.11	1.7×10^{-2}
9[e]	8.79	0.730	0.070	0.58	0.17	2.5×10^{-2}
10[e]	8.96	0.730	0.070	0.46	0.24	3.4×10^{-2}
11[e]	9.12	0.730	0.070	0.38	0.26	6.7×10^{-2}
12[e]	9.31	0.730	0.070	0.32	0.26	6.6×10^{-2}
13[e]	9.47	0.730	0.070	0.29	0.29	6.9×10^{-2}
14[e]	9.60	0.730	0.070	0.28	0.29	6.9×10^{-2}
15[e]	9.64	0.730	0.070	0.28	0.31	6.9×10^{-2}

[a] Absorbances calculated from the initial concentration of diazonium ion added to the solution. [b] The initial observed absorbances are obtained by extrapolation of the first-order plots to zero time. [c] Pseudo-first-order rate constant for appearance of absorption at 330 nm or disappearance of absorption at 260 nm. [d] Runs made by conventional techniques with first observation approximately 15 sec after mixing. [e] Runs made by use of stop-flow techniques.

reactions.[3-5] In order to study a series of these reactions, first in aqueous solution, it was necessary to study the reactions of diazonium ions with hydroxide ion.

Lewis and Suhr have reported a study of the reactions of *p*-nitrobenzenediazonium ion in acidic and basic aqueous solution.[3] At pH above 7.5, they observed the disappearance of the diazonium ion at a rate which depended on the concentration of hydroxide ion to a varying degree up to a pH of about 10. At pH above 10, the disappearance of diazonium ion occurred at a rate independent of hydroxide ion concentration. They interpreted their data in terms of a mechanism involving formation of the *syn*-diazotate followed by isomerization to the *anti*-diazotate. It was suggested that the first step was rate determining at low pH, and the second at high pH. Treatment of their data according to this interpretation allowed the evaluation of the rate constant for the first step. The second-order rate constant was evaluated as 9.3×10^2 M^{-1} sec^{-1}.

In a later study using continuous flow techniques, Littler[6] estimated the rate constant for the formation of the *syn*-diazotate from *p*-nitrobenzenediazonium ion and hydroxide ion to be 2×10^5 M^{-1} sec^{-1}.

These conflicting values for the rate constant for attack of hydroxide ion on the diazonium ion necessitated a further study of the reaction of *p*-nitrobenzenediazonium ion in aqueous solution in the pH range of 7.5–10.

Results

If one mixes a solution of *p*-nitrobenzenediazonium ion with an aqueous buffer solution at pH 8–10 and, within 15 sec, starts observing the disappearance of the absorption at 260 nm (*i.e.*, the $\lambda_{\max}$ for the diazonium ion) or the appearance of absorption at 330 nm ($\lambda_{\max}$ for the *anti*-diazotate) pseudo-first-order kinetics are observed. Extrapolations of the kinetic plots to zero time give, at the lower end of the pH range, the expected values for the absorption of the diazonium ion, but at the higher end of the pH range the initial absorption at 260 nm is too low, and that at 330 nm too high, to be accounted for by the added concentration of the diazonium ion.

Stop-flow experiments show clearly that two consecutive reactions are involved in these solutions. The first reaction reaches equilibrium in a time very short in comparison to the half-time of the second reaction. The sequence of reactions suggested by Lewis and Suhr[3] nicely accommodate the data, as shown.

$$\mathrm{ArN_2^+} + \mathrm{OH^-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} syn\text{-}\mathrm{ArN_2OH} \tag{1}$$

$$syn\text{-}\mathrm{ArN_2OH} + \mathrm{OH^-} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} syn\text{-}\mathrm{ArN_2O^-} + \mathrm{H_2O} \tag{2}$$

$$syn\text{-}\mathrm{ArN_2O^-} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} anti\text{-}\mathrm{ArN_2O^-} \tag{3}$$

$$syn\text{-}\mathrm{ArN_2OH} \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} anti\text{-}\mathrm{ArN_2OH} \tag{4}$$

$$anti\text{-}\mathrm{ArN_2OH} + \mathrm{OH^-} \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} anti\text{-}\mathrm{ArN_2O^-} + \mathrm{H_2O} \tag{5}$$

Table I contains the data for the slower reaction which can be observed using either conventional techniques or a slow time scale with the stop-flow techniques.

Assuming that reactions 1 and 2 are fast in comparison to reaction 3, and that no appreciable concentrations of the diazohydroxides are present in the pH range under consideration, eq 6 may be easily derived for the pseudo-first-order rate constants reported in Table I.

$$k_\psi = k_3/\{1 + [1/K_1K_2(\mathrm{OH^-})^2]\} \tag{6}$$

$$1/k_\psi = (1/k_3) + [1/K_1K_2k_3(\mathrm{OH^-})^2]$$

The plot of the reciprocal of the pseudo-first-order rate constants *vs.* $(\mathrm{OH^-})^{-2}$ is shown in Figure 1. The intercept and slope of this plot give $k_3 = 6.2 \times 10^{-2}$ sec^{-1}, and $K_1K_2 = 1.9 \times 10^{10}$ M^{-2}. A value for K_1K_2 can also be calculated independently from the observed initial absorbances at the various pH. The value calculated from these data is 2.1×10^{10} M^{-2}, in

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(3) E. S. Lewis and H. Suhr, *J. Amer. Chem. Soc.*, **80**, 1367 (1958).
(4) E. S. Lewis and H. Suhr, *Chem. Ber.*, **91**, 2350 (1958).
(5) E. S. Lewis and H. Suhr, *ibid.*, **92**, 3043 (1959).
(6) J. S. Littler, *Trans. Faraday Soc.*, **59**, 2296 (1963).

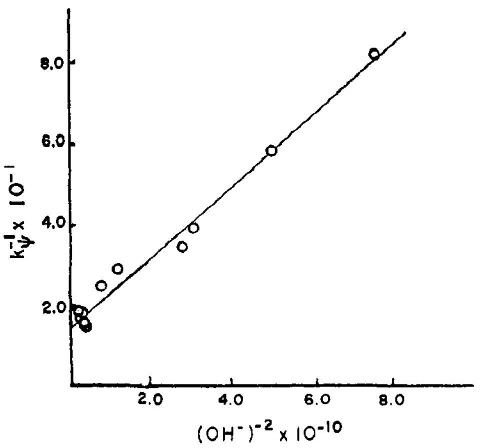

Figure 1. Treatment of the kinetic data for the formation of *anti*-diazotate according to eq 6 to determine k_3 and K_1/K_2.

good agreement with the value from treatment of the kinetic data.

The final absorbances observed after completion of the reactions give the value for $K_1K_2K_3 = 1.7 \times 10^{12}$ M^{-2}.

Lewis and Suhr[4] report $K_1K_2 = 1.3 \times 10^9$ M^{-2}, measured at an ionic strength of 1.1 M. They noted, generally, that the values for K_1K_2 for various substituted diazonium ions were larger by factors of 8–10 at an ionic strength of 0.1 M Thus, our value for K_1K_2 at an ionic strength of 0.005–0.01 M is in accordance with expectations, and is also in fair agreement with the value reported by Littler,[6] 1.6×10^{10} M^{-2}, at an ionic strength of 0.1 M.

Lewis and Suhr[3] report $K_1K_2K_3 = 8 \times 10^{12}$ M^{-2}. Their data, however, appear to show a break at pH about 7.8 (*cf.* Figure 2 of ref 3). Our value for $K_1K_2K_3$ gives points in close agreement with their data at pH above 7.8. We believe that some side reaction interferes with the measurements at low pH.

The fast pseudo-first-order disappearance of diazonium ions in solutions buffered at pH above 8.5 may be studied using stop-flow techniques. The rate constants observed are reported in Table II.

Table II. Fast Reaction of *p*-Nitrobenzenediazonium with Hydroxide Ion in Aqueous Solutions

pH	k_{ψ},[a] sec^{-1}		k_1,[b] M^{-1} sec^{-1} [b]
8.79	6.3		4.4×10^5
8.96	8.2		5.6×10^5
9.12	10.2		6.0×10^5
9.31	11.7		5.3×10^5
9.47	16.7		5.3×10^5
9.60	23		5.5×10^5
9.64	23		5.3×10^5
		Av	$5.4 (\pm 0.4) \times 10^5$

[a] Observed pseudo-first-order rate constant. [b] Rate constant for the forward direction of eq 1; calculated as discussed in text.

Assuming k_2 to be much greater than k_{-1}, eq 7 can be

$$k_{\psi} = k_1[(OH^-) + 1/K_1K_2(OH^-)] \qquad (7)$$

derived easily for the formation of the *syn*-diazotate. Values of k_1 calculated from this equation and $K_1K_2 = 2.0 \times 10^{10}$ M^{-2}, as evaluated above, are shown in the last column of Table II. The average value, $k_1 = 5.4 \times 10^5$ M^{-1} sec^{-1}, at an ionic strength of 0.005 M, may be compared with the value of 2×10^5 M^{-1} sec^{-1}, at an ionic strength of 1.0 M, estimated by Littler.[6]

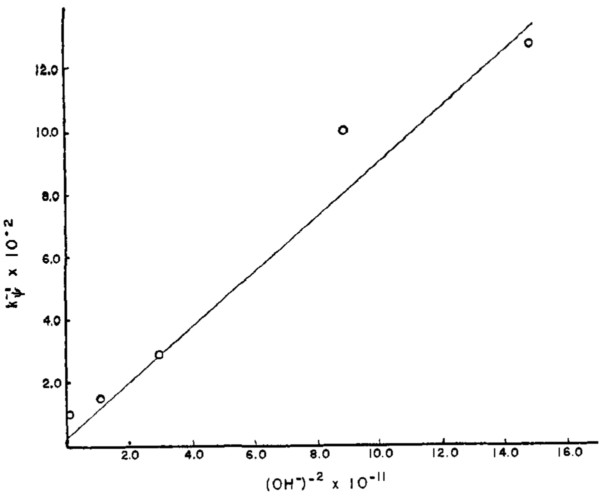

Figure 2. Comparison of data of Lewis and Suhr[3] for the formation of *anti*-diazotate (points represent observed data) with calculated data (line) from eq 6 using the values of k_3 and K_1/K_2 found in the present work.

Discussion

Lewis and Suhr[3] studied the rates of reaction of *p*-nitrobenzenediazonium ion with hydroxide ion over the pH range from 7.0 to 13. In the range above pH about 10, the change in absorbance observed after 17 sec is quite small, and the rate constants obtained using conventional techniques are subject to large error. Treatment of Lewis and Suhr's data for the pH range from 8.0 to 10.0 according to eq 6, using the values of k_3 and K_1K_2 found in the present study, yields the plot shown in Figure 2. The agreement with our data is quite satisfying. The plot includes data which Lewis and Suhr excluded from their interpretation because of differences in ionic strength.

In the pH range below 8, two complications arise in the kinetic behavior of this system. First, as the pH is lowered, the reaction becomes incomplete and the reverse reaction must be taken into account. Second, reactions 2 and 5 may be incomplete, and, therefore, reaction 4 may begin to contribute appreciably to the overall rate. Lewis and Hanson[7] have evaluated $K_5 = 7.2 \times 10^7$ M^{-1}, and have interpreted their data to suggest that $k_{-4} = 4.8 \times 10^{-3}$ sec^{-1}. Reasonably assuming that reactions 1, 2, and 5 are at equilibrium throughout the course of the reaction,[8] eq 8 can be derived for the pseudo-first-order rate constant in buffered solutions:

$$\begin{aligned} k_{\psi} = {} & K_1K_2k_3(OH^-)^2 + K_1k_4(OH^-) + \\ & [k_{-3}K_5(OH^-) + k_{-4}]/[1 + K_5(OH^-)] = \\ & K_1K_2k_3(OH^-)^2 + K_1K_2K_3k_{-4}(OH^-)/K_5 + \\ & [k_{-3}K_5(OH^-) + k_{-4}]/[1 + K_5(OH^-)] \qquad (8) \end{aligned}$$

Using the values of the rate constants and equilibrium constants already given, eq 8 allows the calculation of rate constants shown in Table III.

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

(8) The assumption that reaction 1 is at equilibrium can be shown to be correct from the known rate and equilibrium constants.

Table III. Rate Constants Calculated from Equation 8

pH	k(calcd)	k(obsd)[a]
7.91	1.7×10^{-3}	7.9×10^{-4}
7.66	1.2×10^{-3}	5.3×10^{-4}
7.21	1.2×10^{-3}	2.4×10^{-4}
7.01	1.2×10^{-3}	2.6×10^{-4}

[a] Data reported by Lewis and Suhr, ref 3.

The agreement of the calculated and observed rate constants is not as good as might have been hoped for, but it must be remembered that the extent of conversion of the diazonium ion to the diazotate is quite small at the two lower pH values. The agreement within a factor of 2 for the two higher values is all that could have been expected on the basis of the disagreement of the equilibrium constants, particularly $K_1K_2K_3$, and the differences in ionic strength in our work and that of Lewis and Suhr. It might also be pertinent that Lewis and Suhr noted appreciable side reactions at low pH for their reactions.

Lewis and Suhr interpreted their data as indicating that the formation of the *anti*-diazotate proceeded by rate-limiting formation of the *syn*-diazotate at low pH, and by rate-limiting isomerization of the *syn*-diazotate at the higher pH. The present work makes this interpretation untenable. The rate constant for reaction 1 is orders of magnitude larger than would be required for this reaction to be rate limiting at the low pH. It is somewhat surprising that Lewis and Suhr obtained linear plots of $k_\psi/(\mathrm{OH^-})$ *vs.* $(\mathrm{OH^-})^{-2}$. Equation 8 indicates that this would happen only if the following conditions were fulfilled: (a) $K_5(\mathrm{OH^-}) > 1$; (b) $k_{-4} > k_{-3}K_5(\mathrm{OH^-})$; and (c) $K_1K_2K_3k_{-4}/K_5 > K_1K_2k_3(\mathrm{OH^-})$. From the value of K_5 given above, condition a is fulfilled for pH above *ca.* 7. Using the values of the equilibrium and rate constants given above, however, conditions b and c are not fulfilled; instead, the inequality signs should be replaced by approximately equal signs at pH 7.

Our values for the equilibrium constant $K_1K_2K_3$ indicate that the extent of conversion of diazonium ion to *anti*-diazotate is extremely small at pH 7.01 and 7.21. It seems quite possible that the rates actually measured by Lewis and Suhr at these pH were rates of some side reaction, and that the fit of the data to their interpretation was fortuitous. The excellent agreement of the data above pH 8 with eq 6, and the direct measurement of the rate of reaction 1 in the present work, leave little doubt that Lewis and Suhr's interpretation is incorrect.

Experimental Section

Materials. Boric acid was a commercial product used without further purification.

The preparation of *p*-nitrobenzenediazonium tetrafluoborate has been described previously.[4] The uv spectrum of the product agreed closely with that reported ($\lambda_{\max}$ 260 nm, log ϵ 4.207).

All solutions were prepared from distilled water stored under argon, and were protected from the atmosphere throughout the experiments.

Equilibrium and Rate Constant Measurements. All measurements were carried out at room temperature of 22–24°.

Buffer solutions were prepared from master solutions (7.81×10^{-2} *M* NaOH, 9.92×10^{-2} *M* H_3BO_3) by placing 6.50 ml of the sodium hydroxide solution in a 50.0-ml volumetric flask, adding the calculated volume of boric acid solution for the desired pH, and diluting to the mark with water. The solutions obtained have a constant ionic strength of $1.02 \times 10^{-2}M$.

For measurements of the equilibrium and rate constants by conventional techniques, the reactions were followed spectrophotometrically on a Cary Model 14 spectrophotometer. Approximately 18–20-mg samples of the diazonium salt were accurately weighed on a Cahn electrobalance, and were dissolved in 25.0 ml of water to which 1 drop of 0.1 *M* HCl had been added to stabilize the solutions. (On dilution in the buffered solutions, the concentration of added acid is insignificant.)

Exactly 3.0 ml of the appropriate buffer solution was placed in the spectrophotometer cell and 50 μl of the diazonium salt solution was added with a micropipet. The cell was stoppered, shaken, and placed in the spectrophotometer; the absorbance of the solution at fixed wavelength was followed with time. Separate runs were made at 260 nm ($\lambda_{\max}$ for the diazonium salt) and at 330 nm ($\lambda_{\max}$ of the *anti*-diazotate). The reference cell in each case was filled with the same buffer solution used for the reaction. The first observation of absorbance was within 15–20 sec after mixing of the solutions. When the absorbance at fixed wavelength became constant, the entire spectrum from 220 to 400 nm was recorded.

The pH of the remaining portion of the buffer solution was measured potentiometrically using a Beckman Model 1019 pH meter equipped with a Corning triple-purpose glass electrode and a calomel reference electrode which had been standardized at pH 9.000 with a commercial buffer mixture.

The reaction solutions at equilibrium showed isosbestic points at 240 and 280 nm.

Measurements in the pH range from 8.2 to 9.8 allowed the calculation of the equilibrium constant for the *anti*-diazotate. The usual first-order kinetic plots of absorbance of the reacting solutions at both wavelengths were linear and the rate constants obtained at the two different wavelengths agreed within 10% for all runs. The average of the two values obtained at each pH is reported in Table **I**, for runs 1–7.

The stop-flow experiments utilized buffers prepared as described above. Diazonium ion solutions were accurately prepared at concentrations of *ca.* 5×10^{-5} *M*. In the actual reacting solutions, since equal volumes of the buffer and the diazonium ion solutions are mixed, the ionic strength is 5.0×10^{-3} *M*, and the initial concentration of the diazonium is *ca.* 2.5×10^{-5} *M*. The observation chamber of the stop-flow apparatus has a 2.0 cm path. Reactions were followed at both 260 and 330 nm in separate runs for each buffer. After proper flushing of the system, two runs were made at each wavelength. In the first run, the time scale was adjusted to allow observation for 200 msec, permitting the fast reaction to be followed almost to completion. In the second run, the time scale was adjusted to allow observation for a total time of 50 sec, permitting the slow reaction to be followed. The first reaction was sufficiently faster than the second that equilibrium was completely established before any appreciable interference from the slow reaction.

Table I, runs 8–15, contains the data for the absorbance of the solutions when the first reaction had essentially reached equilibrium. These data allow the calculation of the equilibrium constant for the formation of the *syn*-diazotate.

The usual first-order plots of the data for both the fast and slow reactions gave the rate constants reported in Tables I and II.

The spent reaction solution from the stop-flow experiments was collected under argon, and the pH of each solution was determined as described above.