dent process which produces II in alkaline solutions presumably involves reaction of hydroxide ion with the conjugate acid of the imidate.

The usual explanation for the dependence of imidate hydrolysis product composition on pH assumes that amine and ester are formed from a more highly protonated intermediate than that which yields amide and alcohol. A scheme involving an equilibrium between intermediates II and III satisfactorily accounts for the experimental observations (see Scheme I). Alternatively, alkaline imidate hydrolysis may resemble alkaline hydrolysis of amide acetals, in which two sets of products are formed by competing reactions of the amide acetal. The alkoxyanilinocarbinol II may form aniline and carboxylate ester by an SE2 reaction with hydronium ion, and form anilide and alcohol by dissociation to alcohol and an anilinohydroxycarbonium ion, which is converted to the anilide by loss of a proton. Amide acetals exhibit measurable electrical conductivity in polar aprotic solvents,[34,40] presumably owing to dissociation to alkoxyaminocarbonium and alkoxide ions, and a similar dissociation of alkoxyanilinocarbinol II in water seems reasonable. If this dissociation occurs, both sets of products may be formed from II. The mechanism of the product forming step in alkaline hydrolysis of imidic esters remains open.

If the uncatalyzed alkaline hydrolysis of *N*-arylimidic esters involves rate-limiting reaction of hydroxide ion with the imidate conjugate acid, it will follow the rate law of eq 9, where K_b is the basicity constant

$$k_0 = kK_bK_w \qquad (9)$$

of the imidate and K_w is the autoprotolysis constant of water. The observed activation parameters (Table V) for this reaction are thus complex quantities. From the known enthalpy and entropy of dissociation of water[41] and enthalpies and entropies of protonation of imidates estimated from those of amines (ref 36, p 14), I estimate the enthalpy of activation for the reaction of hydroxide ion with ethyl *N*-phenylformimidium ion to be about 10 kcal/mol and the entropy of activation to be about -25 eu. These values are reasonable for a bimolecular reaction of this charge type.

k_0 values for alkaline *N*-arylformimidate hydrolysis were obtained from intercepts of $k_{\exp}$ *vs.* $[\mathrm{OH}^-]$ plots, and are of low precision in the case of imidates having electron-withdrawing aryl substituents. Making allowance for this, the Hammett ρ value obtained for the imidates except the *p*-methoxy- and *p*-methyl-substituted compounds (Figure 1) is *ca.* -0.7 for the uncatalyzed reaction. The negative deviation of the points for the *p*-anisyl and *p*-tolyl compounds can be rationalized by the same argument used above for the hydrolysis reactions in acetate buffers.

The rate-limiting step of the hydroxide-catalyzed hydrolysis reaction probably involves attack by hydroxide ion on the acyl carbon of the *N*-arylformimidate. This bimolecular process, which is analogous to that involved in alkaline hydrolysis of amides and esters, should have a substantial negative entropy of activation, as is observed. The Hammett ρ value of $+1.7$ (Figure 2) for this reaction is of the expected sign and of reasonable magnitude for a nucleophilic addition to a carbon–nitrogen double bond.

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(40) G. Simchen, H. Hofmann, and H. Bredereck, *Chem. Ber.*, **101**, 42 (1968).

(41) E. A. Moelwyn-Hughes, "Physical Chemistry," 2nd ed, Macmillan, New York, N. Y., 1961, p 877.

Mechanism of the Base-Catalyzed Synthesis of Azobenzenes

ELLIS V. BROWN* AND WILLIAM H. KIPP

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506

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The base-catalyzed reaction between aniline and nitrosobenzene to form azobenzene has been investigated kinetically under homogeneous reaction conditions. Energy of activation, entropy of activation, and Hammett ρ values are calculated. The mechanism is postulated as nucleophilic attack of the negatively charged nitrogen atom of aniline on the nitrogen atom of nitrosobenzene. This is the reverse of the mechanism proposed for the same reaction in acid solution.

The base-catalyzed reaction between aniline and nitrosobenzene to form azobenzene was first utilized by Campbell[1] and coworkers. Hot concentrated sodium hydroxide was used with toluene as the solvent with the result that the reaction took place at the interface of a two-phase system. Azoxy compounds are also a minor product of this reaction. In order to investigate the kinetics and to elucidate the mechanism of this reaction, homogeneous reaction conditions are desirable. It was found that a homogeneous reaction mixture could be obtained by using tetramethylammonium hydroxide in a 80% pyridine–20% water, by volume, solution. It was then possible to follow the kinetics of the reaction spectrophotometrically.

Results

In 0.10 *M* tetramethylammonium hydroxide solutions (80% pyridine–20% water by volume) with the initial concentration of aniline 0.025–0.250 *M* and that of nitrosobenzene 0.050–0.300 *M*, the rate of the reaction was found to be proportional to the product of the stoichiometric concentrations of aniline and nitrosobenzene. The pseudo-second-order rate constants, *k*, were calculated by means of a FORTRAN IV G program on an IBM 360/50 computer. The constants were satisfactory as shown in Table I.

In 80% pyridine–20% water, under the experimental conditions used, the pseudo-second-order rate constant for the formation of azobenzene is linearly related to the tetramethylammonium hydroxide concentration. The linear equation is

$$k = (0.29 + 70.4s) \times 10^{-4}\ \mathrm{l.\ mol^{-1}\ sec^{-1}}$$

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* To whom correspondence should be addressed.

(1) N. Campbell, A. W. Henderson, and D. Taylor, *J. Chem. Soc.*, 1281 (1953).

TABLE I
PSEUDO-SECOND-ORDER RATE CONSTANTS OF AZOBENZENE FORMATION IN 80% PYRIDINE–20% WATER SOLUTION (TETRAMETHYLAMMONIUM HYDROXIDE CONCENTRATION 0.10 *M* AT 30°)

Initial concentration, *M*: Aniline	Initial concentration, *M*: Nitrosobenzene	$k \times 10^4$ l. mol^{-1} sec^{-1}
0.02	0.10	7.62
0.05	0.10	7.39
0.07	0.10	7.06
0.10	0.10	7.33
0.15	0.10	7.42
0.25	0.10	7.31
0.10	0.05	7.52
0.10	0.15	7.01
0.10	0.20	7.35
0.10	0.30	7.56
	Average	7.36

where *s* is the stoichiometric concentration of tetramethylammonium hydroxide in moles. As is apparent in the equation, the *k* value at neutrality is a small positive value (Figure 1 and Table II). All of the apparent activation parameters were calculated from the apparent second-order rate constants at a temperature of 40°. A computer program using the slope of the plot of ln *k* *vs.* 1/*T* calculated the apparent activation energy (E_a), apparent activation free energy ($\Delta G^{\ddagger}_{40}$), apparent activation enthalphy ($\Delta H^{\ddagger}_{40}$), and and apparent activation entropy ($\Delta S^{\ddagger}_{40}$) for the formation of azobenzene. They were found to be 16.0, 22.4, and 15.4 kcal mol^{-1} and -22.2 cal deg^{-1} mol, respectively.

TABLE II
PSEUDO-SECOND-ORDER RATE CONSTANTS *vs.* TETRAMETHYLAMMONIUM HYDROXIDE CONCENTRATION[a]

$k \times 10^4$	[(CH$_3$)$_4$NOH] in mol/l.
7.33	1.10
5.51	0.075
3.90	0.050
2.05	0.025

[a] See Figure 1.

The rates of the reactions of aniline with substituted nitrosobenzenes and those of substituted anilines with nitrosobenzene were measured in 80% pyridine–20% water (3.10 *M* tetramethylammonium hydroxide). The results listed in Tables III–VI show that electron-attracting groups (*e.g.*, *p*-nitro) in anilines increase the rate of the reaction, while electron-releasing groups (*e.g.*, *p*-methyl) decrease the rate of the reaction. The effect is reversed for substituents of nitrosobenzene. In both cases, the relative rates of the reaction satisfy the Hammett equation. The values of ρ were calculated to be about -2.1 for the condensations of aniline with substituted nitrosobenzenes. Although the scatter is large in this case, the trend is there. The value of ρ is $+2.0$ for the condensations of substituted anilines with nitrosobenzene (see Figure 2 and Table VII).

Discussion

Since a linear relationship exists between the tetramethylammonium hydroxide concentration and the pseudo-second-order rate constant, the hydroxide ion is presumed to be involved in the transition state.

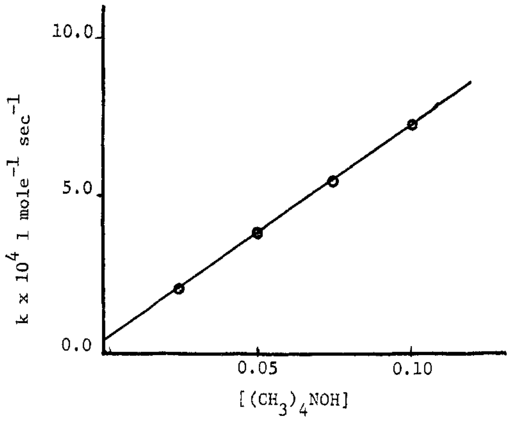
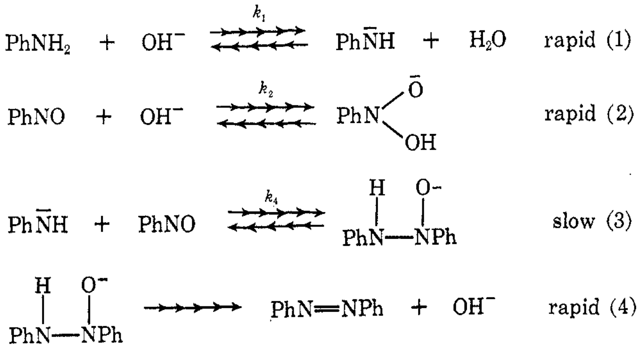


Figure 1.—Plot of pseudo-second-order rate constants *vs.* tetramethylammonium hydroxide concentration: 80% pyridine–20% water at 30° (azobenzene formation).

TABLE III
APPARENT SECOND-ORDER RATE CONSTANTS FOR THE CONDENSATION OF ANILINE WITH SUBSTITUTED NITROSOBENZENES IN 0.10 *M* TETRAMETHYLAMMONIUM HYDROXIDE, 20% WATER–80% PYRIDINE SOLUTIONS

Substituent	Temp, °C	$k \times 10^3$ l. mol^{-1} sec^{-1}
4-CH$_3$	30.0	1.4
	40.0	3.3
	50.0	5.4
3-CH$_3$	30.0	1.0
	40.0	1.9
	50.0	4.7
H	30.0	0.77
	40.0	1.6
	50.0	4.1
4-Cl	30.0	0.36
	40.0	0.50
	50.0	0.96
3-Cl	30.0	0.10
	40.0	0.19
	50.0	0.48
4-Br	30.0	0.20
	40.0	0.47
	50.0	0.99
3-Br	30.0	0.11
	40.0	0.21
	50.0	0.48
4-CH$_3$O	30.0	1.8
	40.0	1.9
	50.0	4.1
3-CH$_3$O	30.0	3.7
	40.0	7.0
	50.0	45

A probable reaction mechanism (eq 1–4) is shown for this relationship. A small contribution to the overall



$$\mathrm{PhNH_2 + OH^- \overset{k_1}{\rightleftharpoons} Ph\bar{N}H + H_2O} \quad \text{rapid (1)}$$

$$\mathrm{PhNO + OH^- \overset{k_2}{\rightleftharpoons} PhN(\bar{O})(OH)} \quad \text{rapid (2)}$$

$$\mathrm{Ph\bar{N}H + PhNO \overset{k_4}{\rightleftharpoons} PhN(H){-}N(O^-)Ph} \quad \text{slow (3)}$$

$$\mathrm{PhN(H){-}N(O^-)Ph \longrightarrow PhN{=}NPh + OH^-} \quad \text{rapid (4)}$$

TABLE IV

ACTIVATION PARAMETERS AND MEASURES OF RELIABILITY FOR THE CONDENSATION OF ANILINE WITH SUBSTITUTED NITROSOBENZENES IN 0.10 *M* TETRAMETHYLAMMONIUM HYDROXIDE, 20% WATER–80% PYRIDINE SOLUTIONS

Substituent	E_a, kcal/mol	$\Delta G^{\ddagger}_{40}$, kcal/mol	$\Delta H^{\ddagger}_{40}$, kcal/mol	$\Delta S^{\ddagger}_{40}$, eu/mol	Coefficient of variation[a]	Standard deviation[a]
4-CH_3	13.03	21.92	12.41	−30.37	1.40	0.081
3-CH_3	14.98	22.25	14.35	−25.20	1.21	0.074
H	16.03	22.36	15.41	−22.21	1.32	0.084
4-Cl	9.61	23.10	8.99	−45.05	1.39	0.104
3-Cl	15.12	23.69	14.50	−29.35	1.20	0.101
4-Br	15.42	23.14	14.80	−26.62	0.13	0.010
3-Br	14.40	23.63	13.78	−31.45	0.63	0.053
4-CH_3O	8.10	22.26	7.48	−47.22	3.49	0.210
3-CH_3O	24.05	21.45	23.43	6.32	8.25	0.376

[a] Measures the variability between the experimental points plotted (ln *k*) and the least-squares value as calculated for a line drawn through these points.

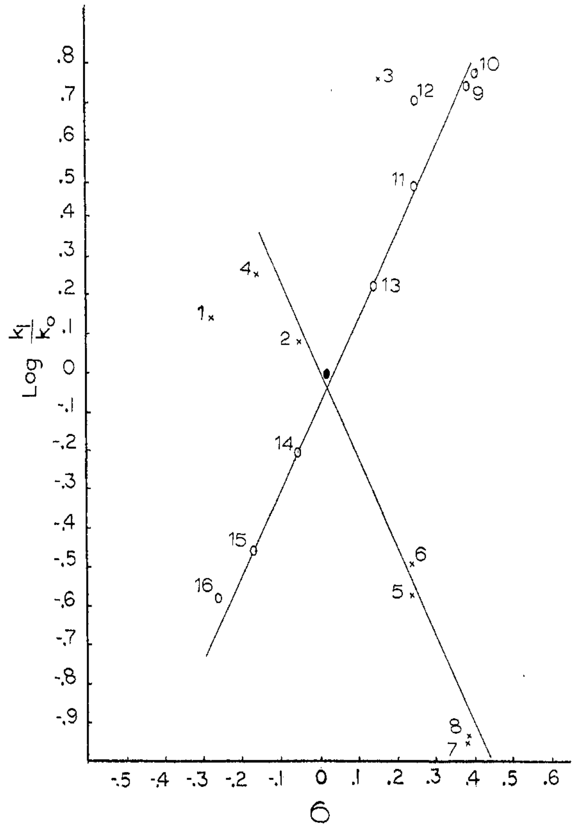


Figure 2.—Plot of log (k/k_0) *vs.* σ, [$(CH_3)_4NOH$] = 0.10 *M* (80% pyridine–20% water at 40°): ●, unsubstituted; ×, aniline with substituted nitrosobenzenes; ○, substituted anilines with nitrosobenzenes; 1, 1-CH_3; 2, 3-CH_3; 3, 3-CH_3O; 4, 4-CH_3; 5, 4-Br; 6, 4-Cl; 7, 3-Cl; 8, 3-Br; 9, 3-Cl; 10, 3-Br; 11, 4-Cl; 12, 4-Br; 13, 3-CH_3O; 14, 3-CH_3; 15, 4-CH_4; 16, 4-CH_3O.

k is conceivable from the reaction between neutral molecules in the presence of the solvent, aqueous pyridine, as was shown in the relation between *k* and acidity. Equation 1 shows how electron withdrawal from aniline increases the rate of condensation, and eq 2 shows how electron donation to nitrosobenzene increases the rate of condensation.

The substituent effects on nitrosobenzene (ρ = −2.1) and the effect on aniline (ρ = +2.0) are consistent with the above mechanism of a nucleophilic attack of the negatively charged nitrogen atom of aniline on the nitrogen atom of nitrosobenzene. This is just the reverse substituent effect as seen in the mechanism for the acid-catalyzed condensation of anilines with nitrosobenzenes. This was found to be an electrophilic attack of the nitrogen atom of activated nitrosobenzene on the nitrogen atom of aniline.[2]

TABLE V

APPARENT SECOND-ORDER RATE CONSTANTS FOR THE CONDENSATION OF SUBSTITUTED ANILINES WITH NITROSOBENZENE IN 0.10 *M* TETRAMETHYLAMMONIUM HYDROXIDE, 20% WATER–80% PYRIDINE SOLUTIONS

Substituent	Temp, °C	$k \times 10^3$, l. mol^{-1} sec^{-1}
4-CH_3	30.0	0.29
	40.0	0.62
	50.0	1.4
3-CH_3	30.0	0.57
	40.0	1.0
	50.0	2.4
4-CH_3O	30.0	0.21
	40.0	0.40
	50.0	1.0
3-CH_3O	30.0	1.4
	40.0	2.6
	50.0	6.0
H	30.0	0.80
	40.0	1.6
	50.0	4.1
4-Cl	30.0	3.2
	40.0	4.4
	50.0	9.9
4-Br	30.0	3.3
	40.0	9.8
	50.0	16
3-Br	30.0	4.9
	40.0	7.8
	50.0	24
4-NO_2	30.0	110
3-NO_2	40.0	54
3-Cl	30.0	4.3
	40.0	8.5
	50.0	20

Experimental Section

Commercial aniline, 3- and 4-chloroanilines, 3- and 4-methylanilines, and 3- and 4-methoxyanilines were purified by vacuum distillation. Commercial 3- and 4-nitroaniline were recrystallized from water and commercial 4-bromoaniline was recrystallized from ethanol. The following boiling and melting points were obtained: aniline, bp 85–85.5° (25 mm); 3-chloroaniline, bp 99–100° (10 mm); 4-chloroaniline, bp 104–105° (11 mm);

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[2] Y. Ogata and Y. Takagi, *J. Amer. Chem. Soc.*, **60**, 3591 (1958).

TABLE VI

ACTIVATION PARAMETERS AND MEASURES OF RELIABILITY FOR THE CONDENSATION OF SUBSTITUTED ANILINES WITH NITROSOBENZENE IN 0.10 *M* TETRAMETHYLAMMONIUM HYDROXIDE, 20% WATER–80% PYRIDINE SOLUTIONS

Substituent	E_a, kcal/mol	$\Delta G^{\ddagger}_{40}$, kcal/mol	$\Delta H^{\ddagger}_{40}$, kcal/mol	$\Delta S^{\ddagger}_{40}$, eu/mol	Coefficient of variation[a]	Standard deviation
4-CH_3	15.11	22.96	14.49	−27.04	0.21	0.016
3-CH_3	13.93	22.66	13.31	−29.87	1.51	0.103
4-CH_3O	15.36	23.23	14.73	−27.11	1.09	0.085
3-CH_3O	14.47	22.08	13.85	−26.27	1.28	0.075
H	16.03	22.36	15.41	−22.21	1.32	0.084
4-Cl	10.85	12.74	10.23	−36.74	2.94	0.154
4-Br	15.50	21.24	14.88	−20.32	3.11	0.150
3-Br	15.53	12.38	14.91	−20.67	4.52	0.209
4-NO_2						
3-NO_2						
3-Cl	14.86	21.33	14.24	−22.64	1.21	0.057

[a] Measures the variability between the experimental points plotted (ln *k*) and the least squares value as calculated for a line drawn through these points.

TABLE VII

VALUES OF LOG k_{40}/k_{040} *vs.* σ IN 0.10 *M* TETRAMETHYLAMMONIUM HYDROXIDE 20% WATER–80% PYRIDINE SOLUTIONS[a]

Substituent	Registry no.	σ, ρ, or m	log $\frac{k_{40}}{k_{040}}$
Condensation of Aniline with Substituted Nitrosobenzenes			
4-CH_3	623-11-0	−0.17	0.23
3-CH_3	620-26-8	−0.07	0.07
H	586-96-9		0.00
4-Cl	932-98-9	+0.23	−0.50
3-Cl	932-78-5	+0.37	−0.92
4-Br	3623-23-2	+0.23	−0.58
3-Br	13125-68-3	+0.39	−0.89
4-CH_3O	1516-22-8	−0.27	0.13
3-CH_3O	26595-63-1	+0.12	0.79
Condensation of Substituted Anilines with Nitrosobenzenes			
4-CH_3	106-49-0	−0.17	−0.45
3-CH_3	108-44-1	−0.07	−0.20
4-CH_3O	104-94-9	−0.27	−0.60
3-CH_3O	536-90-3	+0.12	0.20
H	62-53-3		0.00
4-Cl	106-47-8	+0.23	0.47
4-Br	106-40-1	+0.23	0.67
3-Br	591-19-5	+0.39	0.75
3-Cl	108-42-9	+0.37	0.71

[a] See Figure 2.

3-methylaniline, bp 99–99.5° (24 mm); 4-methylaniline, bp 115–116° (13 mm); 3-nitroaniline, mp 112–113°; 4-nitroaniline, mp 147–148°; nitrosobenzene mp 68°. 3-Methylnitrosobenzene,[2] mp 53°, was prepared by the ferric chloride oxidation of 3-methylphenylhydroxylamine which was obtained by the reduction of 3-nitrotoluene with zinc. The crude product was steam distilled and the distillate recrystallized from ethanol. 4-Methylnitrosobenzene,[3] 3- and 4-chloronitrosobenzene,[4] 3-[5] and 4-bromonitrosobenzene,[6] and 3-[7] and 4-methoxynitrosobenzenes[8] were prepared by similar procedures. The following melting points were obtained: 4-methylnitrosobenzene, mp 48°; 3-chloronitrosobenzene, mp 72°; 4-chloronitrosobenzene, mp 90°; 3-bromonitrosobenzene, mp 78°; 4-bromonitrosobenzene, mp 92°; 3-methoxynitrosobenzene, mp 48°; 4-methoxynitrosobenzene, mp 35°. 3-Bromoaniline was prepared by catalytic hydrogenation of 3-bromonitrobenzene and was purified by vacuum distillation, bp 122–124° (10 mm).

ACS analyzed pyridine, bp 115.5°, and distilled reagent grade toluene, bp 110.5°, were used in the kinetic runs. All melting and boiling points agree with those in the literature.

Reaction Products.—A mixture of nitrosobenzene (0.53 g), aniline (0.47 g), and tetramethylammonium hydroxide (0.9 g) was dissolved in a mixture of 40 ml of pyridine and 10 ml of distilled water and the solution was allowed to stand at room temperature for 4 hr. The solution was then extracted with toluene, the toluene was removed under vacuum, and a reddish orange precipitate of azobenzene was obtained. The yield was 0.82 g (90%). On recrystallization from ethanol, orange crystals were obtained melting at 68° (lit.[9] mp 68°). 3- and 4-chloroazobenzenes, 3- and 4-methylazobenzenes, 3- and 4-methoxyazobenzenes, and 3- and 4-nitroazobenzenes were prepared by similar procedures. The following melting points were obtained: 3-chloroazobenzene, mp 67.5° (lit.[10] mp 89°); 3-bromoazobenzene, mp 69° (lit.[10] mp 69°); 4-bromoazobenzene, mp 91° (lit.[10] mp 90–91°); 3-methylazobenzene, mp 18° (lit.[11] mp 18°); 4-methylazobenzene, mp 71–72°) (lit.[12] mp 72°); 3-methoxyazobenzene, mp 33° (lit.[13] mp 32.5–33.5°); 4-methoxyazobenzene, mp 64° (lit.[14] mp 64°); 3-nitroazobenzene, mp 95–96° (lit.[15] mp 96°); 4-nitroazobenzene, mp 134–136° (lit.[15] mp 134–135°).

A Typical Procedure for the Rate Measurement.—To 25 ml of a 0.2 *M* solution of aniline (20 ml of pyridine–5 ml of water) thermostated at 30° was added 25 ml of a 0.2 *M* solution of nitrosobenzene (20 ml of pyridine–5 ml of water) similarly thermostated. The 0.1 *M* tetramethylammonium hydroxide pentahydrate was added to initiate the reaction and stirring was begun. At 5-min intervals a 1-ml aliquot was removed and extracted with four 10-ml portions of toluene. The toluene extracts were then diluted to exactly 50 ml. The absorbance at the wavelength of maximum absorption in the visible region (442 mμ) of the azobenzene product was measured with a Cary 15 spectrophotometer. The rate constants were calculated from the variation of the concentration estimated from the absorption.

It was determined that (1) Beer's law was satisfied over the measured range of concentration, (2) nitrosobenzene and the anilines showed no absorption at this wavelength, and (3) the reaction was better than 95% complete after long reaction times.

Registry No.—4-Nitroaniline, 100-01-6; 3-nitroaniline, 99-09-2.

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