

The absorption spectra of polyazophenols, in which more than one phenylazo group is attached to a single phenol ring, are quite different from those of *p*-polyazophenols, which have linear conjugated systems. Some of the former have been studied in methanol solution.<sup>13</sup> Our results on benzene solution (Table II) are almost the same with minor exceptions. The introduction of a methyl group in the

(13) W. R. Brode and L. E. Herdle, *J. Org. Chem.*, **6**, 713 (1941).

position *para* to the phenylazo group causes a bathochromic and hypochromic shift, which is greater for a 2-phenylazo group than for a 4-phenylazo group.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF DOJINDO & CO., LTD., AND THE INSTITUTE OF APPLIED CHEMISTRY, KYUSHU UNIVERSITY, JAPAN]

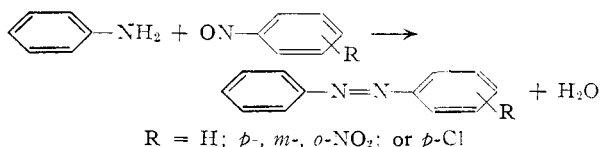
## Kinetic Study on the Condensation Reaction of Aniline and Nitrosobenzenes

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The rates of condensation reactions of aniline with nitrosobenzene and its derivatives were measured spectrophotometrically, and the differences in reactivity of the nitrosobenzenes discussed. The apparent energies of activation of these reactions were also determined.

In an investigation of the synthesis and absorption spectroscopy of polyazobenzenes,<sup>1b</sup> it was found that the rate of condensation of *p*-nitronitrosobenzene with aniline to form *p*-nitroazobenzene was far greater than that of nitrosobenzene with aniline to form azobenzene. In this paper we are reporting the kinetics of the condensation reactions of aniline with nitrosobenzene and with its nitro and chloro derivatives, the simplest examples of the general reaction



The rate of formation of azobenzenes can easily be followed spectrophotometrically because of the great difference in absorption between the reactants, aniline and the nitrosobenzenes, and the products, azobenzenes.

The initial optical density is expressed as

$$D_0 = \epsilon_a a + \epsilon_b b \quad (1)$$

where  $\epsilon_a$  and  $\epsilon_b$  are the molecular extinction coefficients of aniline and nitrosobenzene, respectively, and  $a$  and  $b$  their initial molar concentrations. Then, at any time  $t$ , the optical density of the reaction mixture is

$$D_t = \epsilon_a(a - x) + \epsilon_b(b - x) + \epsilon_c x \quad (2)$$

where  $x$  is the molar concentration of the azobenzene formed, and  $\epsilon_c$  the molecular extinction coefficient of azobenzene. From equations 1 and 2,  $x$  can be calculated as

$$x = \frac{D_t - D_0}{\epsilon_c - (\epsilon_a + \epsilon_b)} \quad (3)$$

In the above discussion it was assumed that all components obey Beer's law. Measurement of the optical densities of the individual components at 320–340  $m\mu$  (Table I) showed that light absorp-

tion by aniline is almost negligible, so that equation 3 may be simplified to

$$x = \frac{D_t - D_0}{\epsilon_c - \epsilon_b} \quad (4)$$

TABLE I

MOLECULAR EXTINCTION COEFFICIENTS OF ANILINE, NITROBENZENES AND AZOBENZENES

	320 $m\mu$	$\epsilon \times 10^{-3}$ 330 $m\mu$	340 $m\mu$
Aniline		Negligible	
Nitrosobenzene	4.44	2.11	0.85
<i>p</i> -Nitronitrosobenzene	3.78	...	2.12
<i>m</i> -Nitronitrosobenzene	2.05	1.12	0.54
<i>o</i> -Nitronitrosobenzene	3.16	...	1.36
<i>p</i> -Chloronitrosobenzene	10.25	...	2.28
Azobenzene	21.34	19.45	12.89
<i>p</i> -Nitroazobenzene	23.14	25.71	24.78
<i>m</i> -Nitroazobenzene	16.31	14.33	10.39
<i>o</i> -Nitroazobenzene	18.12	16.90	13.47
<i>p</i> -Chloroazobenzene	23.80	23.80	20.75

### Experimental

**Materials.**—Aniline was freshly distilled over zinc dust. Nitrosobenzene (m.p. 67.5–68°),<sup>2</sup> *p*-nitronitrosobenzene (119–119.5°),<sup>3</sup> *m*-nitronitrosobenzene (89.5–90°),<sup>3</sup> *o*-nitronitrosobenzene (122°),<sup>3</sup> *p*-chloronitrosobenzene (88.5–89°),<sup>4</sup> *p*-nitroazobenzene (134–135°),<sup>5</sup> *m*-nitroazobenzene (96–96.5°),<sup>5</sup> *o*-nitroazobenzene (70–70.5°)<sup>3</sup> and *p*-chloroazobenzene (90–90.5°)<sup>6</sup> were prepared as described in the literature. Azobenzene was purified by recrystallizing the commercial sample from dilute ethanol and then from petroleum ether. m.p. 67.5–68°.

The glacial acetic acid and methanol were reagent grade and their optical transparency was checked over the range of wave length observed.

Samples of the stock solution of each component in glacial acetic acid were diluted with methanol to concentrations ranging from 10<sup>-4</sup> to 10<sup>-6</sup> mole/l., and the optical densities measured, they all obeyed Beer's law within the experimental error. The molecular extinction coefficients of each component are given in Table I.

(2) *Org. Syntheses*, **25**, 80 (1945).

(3) E. Bamberger and R. Hübner, *Ber.*, **36**, 3809 (1903).

(4) Y. Tsuzuki, T. Uemura and N. Hirasawa, *J. Chem. Soc. Japan*, **62**, 85 (1941).

(5) G. Charrier and A. Beretta, *Gazz. chim. ital.*, **54**, 977 (1924).

(6) P. Jacobson and A. Loeb, *Ber.*, **36**, 4090 (1903).

(1) (a) Department of Chemistry, Clark Univ., Worcester, Mass.; (b) K. Ueno, *THIS JOURNAL*, **74**, 4508 (1952).

**Determination of Reaction Rate.**—The stock solutions of aniline and nitrosobenzenes in glacial acetic acid were equilibrated in a constant temperature bath. At the beginning of the reaction, a sample of component was pipetted into a volumetric flask and made up volume with glacial acetic acid which had also been kept in the constant temperature bath. The reagents were mixed well and transferred to an amber glass bottle in the bath. The initial concentration of each component was about  $1-3 \times 10^{-2}$  mole/l. Every 20 to 30 minutes, a 0.1-0.2-ml. aliquot was withdrawn and diluted to 50 ml. with methanol to stop the reaction by dilution and at the same time to give the proper concentration for spectrophotometric measurements. All procedures were carried out in a half-darkened room to avoid photoisomerism of the azobenzenes, although this is not a serious problem for the particular azobenzenes under investigation. The optical densities of the methanolic solutions were measured at 320, 330 and 340  $m\mu$  in 1-cm. matched Corex cells with a Beckman model DU spectrophotometer illuminated by a tungsten lamp.

### Results and Discussion

Table II illustrates the calculation of the reaction rate; the apparent reaction rate constant was calculated from the standard equation for a second-order reaction.

TABLE II  
RATE OF REACTION OF ANILINE AND NITROBENZENE AT 21.0<sup>oa</sup>

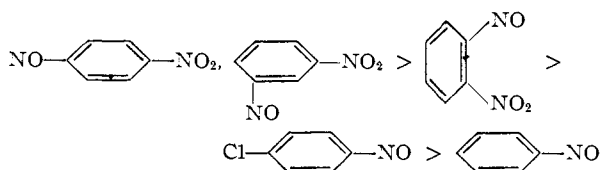
Time, min.	320 $m\mu$		$\chi \times 10^2$	$\bar{x} \times 10^2$	$k, (\text{min.})^{-1}$ (mole/l.) <sup>-1</sup>
	$D$	$330 \text{ } m\mu$			
30	0.1982		0.0831	0.0847	0.0666
		.1110	.0868		
		.0528	.0843		
60	.2282		.1719	.1748	.0733
		.1415	.1747		
		.0753	.1777		
90	.2550		.2512	.2559	.0748
		.1700	.2569		
		.0950	.2596		
125	.2775		.3178	.3253	.0742
		.1945	.3276		
		.1121	.3306		
150	.3005		.3858	.3911	.0749
		.2168	.3919		
		.1278	.3958		

Mean value = .0742<sup>b</sup>

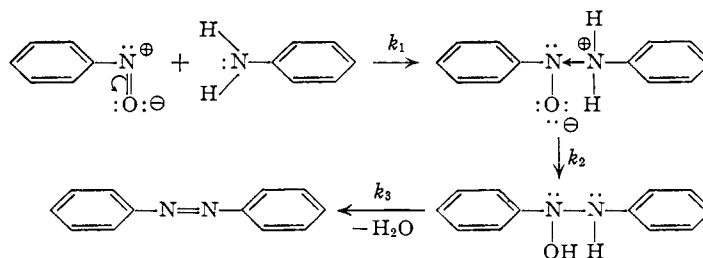
<sup>a</sup> The initial concentration of nitrosobenzene was  $1.915 \times 10^{-2}$  mole/l. and that of aniline was  $2.264 \times 10^{-2}$  mole/l. The total volume was 10 ml.; a 0.1-ml. aliquot was withdrawn every 30 minutes and diluted to 50 ml. with methanol. <sup>b</sup> The measurements made at 30 minutes were omitted.

Similar observations were made on this reaction and four others at several temperatures; the apparent reaction constants are given in Table III.

Table III shows that the order of the rate of condensation of the nitrosobenzenes with aniline is

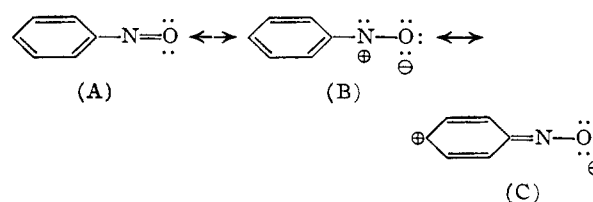


This order is understandable in terms of the electronic configuration of these nitrosobenzenes. The condensation reaction is believed to include the steps



If it is assumed that the first step is the rate-determining one, the rate of the over-all reaction should be determined by the reactivity of the nitrosobenzenes.

Of the main resonance structure of nitrosobenzene, the limiting form B should promote the reac-



tion, by coordination of the lone pair of electrons of aniline with the unsaturated shell of the nitroso nitrogen. In the case of nitrosobenzene itself, contribution of A and C seems to be predominant, thus reducing the reactivity of the molecule. However, in the case of *p*-nitronitrosobenzene C can contribute relatively little because of the electron attraction of the nitro group, while the contribution of B should be increased. This agrees with the greater reactivity of *p*-nitronitrosobenzene. The nitro group in *o*- and *m*-nitronitrosobenzenes should also exert a positive effect, but there is the possibility of steric hindrance with *o*-nitronitrosobenzene. In *p*-chloronitrosobenzene, the inductive effect of

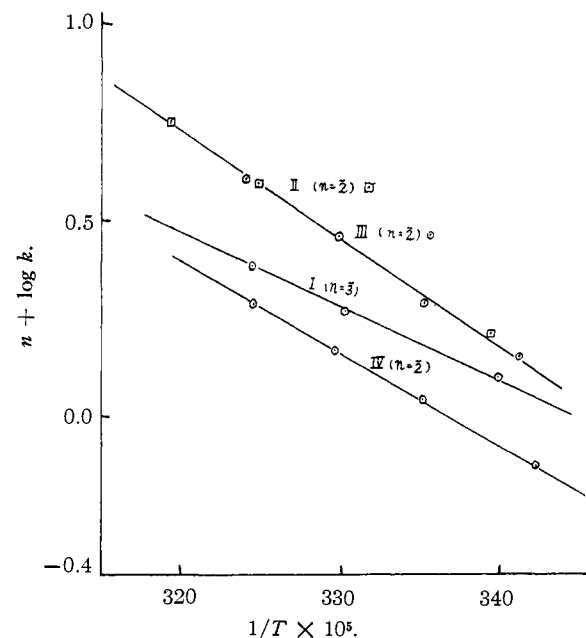


Fig. 1.—Nitrosobenzene; II, *p*-nitro-; III, *m*-nitro-; IV, *o*-nitronitrosobenzene.

TABLE III  
 RATE CONSTANTS<sup>a</sup> AND ENERGIES OF ACTIVATION

Nitrosobenzene		<i>p</i> -Nitronitrosobenzene		Reaction between aniline and <i>m</i> -Nitronitrosobenzene		<i>o</i> -Nitronitrosobenzene		<i>p</i> -Chloronitrosobenzene	
Temp., °C.	<i>k</i>	Temp., °C.	<i>k</i>	Temp., °C.	<i>k</i>	Temp., °C.	<i>k</i>	Temp., °C.	<i>k</i>
21.0	0.0742	21.4	0.966	20.0	0.852	19.0	0.448		
				25.2	1.14	25.4	.669		
29.7	.110			30.1	1.73	30.3	.872	31.1	0.192
35.1	.146	34.8	2.32	35.6	2.38	35.0	1.15		
		40.0	3.35						
Energy of activation, cal.									
8.85 × 10 <sup>3</sup>		11.8 × 10 <sup>3</sup>		11.8 × 10 <sup>3</sup>		10.6 × 10 <sup>3</sup>			

<sup>a</sup> *k*, (min.)<sup>-1</sup>(mole/l.)<sup>-1</sup>.

the *p*-Cl should stabilize form B and thus promote the reaction, although probably to a lesser extent than for a *p*-nitro group.

The plot of log *k* against 1/*T* is in accord with the Arrhenius equation as shown in Fig. 1; the apparent activation energies of these reac-

tions are given in Table III.

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[CONTRIBUTION FROM THE HAND CHEMICAL LABORATORY, MISSISSIPPI STATE COLLEGE]

## Position Isomerism in the Azoxybenzenes

BY LYELL C. BEHR

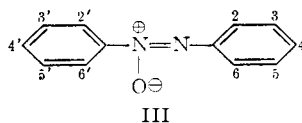
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Because the azoxy group is unsymmetrical, the rings in azoxybenzene are different and position isomerism can occur in unsymmetrically substituted azoxybenzenes. The assignment of structure to these isomers has in the past been made on the basis of certain substitution reactions, but assumptions have been necessary. The structures of the two *p*-bromoazoxybenzenes and the two *p*-ethoxyazoxybenzenes have now been established by synthesis, the procedure involving the vigorous oxidation of indazole oxides of known structure, followed by decarboxylation of the resultant azoxybenzene-2'-carboxylic acids. In this way the structures previously proposed for the two pairs of isomers have been confirmed.

The proof that the azoxy group is unsymmetrical<sup>1</sup> pointed up the problem of the synthesis of the two possible position isomers (I and II), and the determination of their structure. The preparation of the two isomers had in a number of cases been



accomplished by Angeli and his school<sup>2</sup> chiefly by peroxyacetic acid oxidation of unsymmetrical azo compounds. Assignment of structure to the two isomers has in general been made by comparison of their substitution reactions. Thus the bromination of azoxybenzene yields a single *p*-bromoazoxy-



benzene, which is probably 4-bromoazoxybenzene<sup>3</sup> since substitution would likely occur there in preference to the 4'-position (see formula III<sup>3</sup>) which is in an electronically deficient ring.<sup>4</sup> Further, of the

two *p*-bromoazoxybenzenes, the so-called  $\beta$ -isomer<sup>5</sup> undergoes substitution readily in the *para* position whereas the  $\alpha$ -isomer does not undergo substitution readily. The conclusion<sup>4</sup> is that the  $\alpha$ -isomer is 4-bromoazoxybenzene and the  $\beta$ -isomer 4'-bromoazoxybenzene. By similar arguments, structures have been assigned to the two *p*-nitroazoxybenzenes<sup>6</sup> and the two *p*-ethoxyazoxybenzenes.<sup>7,8</sup>

In order to provide a firmer basis for the assignment of structures to the position isomers and to supply a method for the assignment of structures where the substitution methods are not applicable a synthetic method was sought. This was found in the vigorous oxidation of indazole oxides,<sup>9</sup> followed by decarboxylation of the acids produced, and has been applied to the two *p*-bromoazoxybenzenes and the two *p*-ethoxyazoxybenzenes. It can be seen that barring rearrangements (see below), this scheme provides an unequivocal route to the azoxybenzenes, since the oxygen which appears in the azoxy group comes originally from the nitro group of the aldehyde. As an example of the procedure, there may be cited the synthesis of 4-bromoazoxy-

(5) The prefix " $\beta$ " has been used generally in the literature to denote the isomer more readily substituted.

(6) A. Angeli and L. Alessandri, *Atti accad. naz. Lincei, Rend., Classe sci. fis. mat. e nat.*, [5], **20**, II, 170 (1911).

(7) A. Angeli and B. Valori, *ibid.*, [5] **21**, I, 729 (1912).

(8) A. Angeli, *ibid.*, [5] **23**, I, 557 (1914).

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- (1) T. Chu and C. S. Marvel, *THIS JOURNAL*, **58**, 2841 (1933).  
 (2) See A. Angeli, *Ahrens Sammlung*, **19**, 447 (1913), and D. Bigiavi, *Gazz. chim. ital.*, **64**, 900 (1934), and leading references therein.  
 (3) The numeration in this paper is that used in *Chemical Abstracts*.  
 (4) A. Angeli and B. Valori, *Atti accad. naz. Lincei, Rend., Classe sci. fis. mat. e nat.*, [5], **21**, I, 155 (1912).