

[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, THE FACULTY OF ENGINEERING, KYOTO UNIVERSITY]

**Kinetics of the Condensation of Anilines with Nitrosobenzenes to Form Azobenzenes**

BY YOSHIRO OGATA AND YASUO TAKAGI

RECEIVED DECEMBER 26, 1957

The acetic acid-catalyzed condensation of aniline with substituted nitrosobenzenes and that of substituted anilines with nitrosobenzene were kinetically investigated in 94 vol. % ethanol solutions at 72.5° by means of spectrophotometry. The rates in acetate buffers were found to be nearly proportional to the product of the stoichiometric concentrations of aniline, nitrosobenzene and acetic acid. In unbuffered solutions, the rate equation became somewhat complex. The rate constants for the condensation of aniline with substituted nitrosobenzenes and those of substituted anilines with nitrosobenzene in acetate-buffered ethanolic solution satisfy Hammett's equation, giving  $\rho$  values of +1.22 and -2.14, respectively. The energy and entropy of activation in a buffered solution were found to be 5.83 kcal. mole<sup>-1</sup> and -55.6 cal. deg.<sup>-1</sup> mole<sup>-1</sup>. The energies of activation for the condensation of aniline with substituted nitrosobenzenes are expressed as  $E_a = 5.8 - 5.2\sigma$  kcal. mole<sup>-1</sup>, and those of substituted anilines with nitrosobenzene as  $E_a = 5.8 + 6.9\sigma$  kcal. mole<sup>-1</sup>. A linear relation was observed between the energy of activation and entropy of activation. A mechanism was postulated and discussed, which involves rate-determining attacks of protonated and acid-activated nitrosobenzene on a nitrogen atom of free aniline.

The well-known condensation of anilines and nitrosobenzenes to form azobenzenes<sup>1</sup> has not been



extensively studied kinetically, in spite of the fact that the reaction is very important and is surely involved in the reduction of nitrobenzenes. The only available report<sup>1b</sup> describes simple kinetics in acetic acid without consideration of the effect of acidity.

The reaction is catalyzed by acids, but strong inorganic acids are unsatisfactory owing to the formation of tarry material. Acetic acid was therefore selected as the catalyst and, using acetate-buffered ethanol as a solvent, the kinetics of the condensation was investigated by means of spectrophotometry. The principal objectives of this investigation were to gain some insight into the effects of acidity and substituents on the reaction rate and to speculate upon probable mechanism.

**Experimental**

**Materials.**—Commercial aniline, toluidines and chloroanilines were purified by duplicate vacuum distillations. Aminobenzoic acids and nitroanilines were purified by recrystallization from water. Aniline, b.p. 85–85.5° (25 mm.); *o*-toluidine, b.p. 97–98° (24 mm.); *m*-toluidine, b.p. 99–99.5° (24 mm.); *p*-toluidine, b.p. 99–100° (26 mm.); *o*-chloroaniline, b.p. 101–102° (24 mm.); *m*-chloroaniline, b.p. 116–117.5° (22 mm.); *p*-chloroaniline, b.p. 117–118° (22 mm.); *o*-aminobenzoic acid, m.p. 145°; *p*-aminobenzoic acid, m.p. 187°; *m*-nitroaniline, m.p. 114°; *p*-nitroaniline, m.p. 147°. Nitrosobenzene, m.p. 68°, was prepared by the ferric chloride oxidation of phenylhydroxylamine obtained by the reduction of nitrobenzene with zinc, and recrystallized from methanol. Methyl<sup>2</sup> and chloro-nitrosobenzenes<sup>3</sup> were obtained by similar procedures; *m*-methylnitrosobenzene, m.p. 53°; *p*-methylnitrosobenzene, m.p. 48°; *m*-chloronitrosobenzene, m.p. 72°; *p*-chloronitrosobenzene, m.p. 90°. All these melting and boiling points agree with those in the literature.

Commercial ethanol was purified by careful rectifications, b.p. 78°, sp. gr. 0.7940 at 24°. It was used for a kinetic purpose as 94 vol. % ethanol (sp. gr. 0.8140 at 18°) by diluting it with distilled water.

**Reaction Products.**—A mixture of nitrosobenzene (1.0 g.), aniline (1.0 g.) and acetic acid (1 ml.) was dissolved in 94% ethanol and the solution was allowed to stand at 70° for 1.5 hours. When water was added to the resulting solution, a reddish-brown precipitate of azobenzene was

obtained. The yield was 1.6 g. (95%). On recrystallization from methanol it gave orange crystals melting at 68.5° (lit.<sup>4</sup> m.p. 68°).

**A Typical Procedure for the Rate Measurements.**—In a flask equipped with a reflux condenser, a tube for withdrawing samples and a thermometer (all of these were attached to the flask by ground joints) was placed a 94% ethanolic solution of aniline, acetic acid and in most cases 0.25 *M* sodium acetate, the flask being thermostated. An ethanolic solution (20 ml.) of nitrosobenzene similarly thermostated was introduced into the solution, to initiate the reaction.

After about 10 minutes, aliquots (1.0 ml. each) were withdrawn at regular intervals of time and each aliquot was diluted to 10 ml. with pure methanol. The optical density of this diluted solution was measured by a spectrophotometer at 750 m $\mu$  (visible region) to estimate the concentration of nitrosobenzene remaining. The rate constants were calculated from the variation of the concentration estimated from the absorption.

It was confirmed that (1) Beer's law was satisfied over the measured range of concentration, (2) azobenzene and aniline showed no absorption at this wave length, and (3) the absorption data indicated that the concentration of original reactants diminished below 5% after long reaction times. Blank tests showed that neither acetylation of ethanol and aniline nor spontaneous decomposition of nitrosobenzene takes place under these conditions.

**The Confirmation of the Reaction Product Using Vaughn's Chart.**—The optical densities were estimated with several typical runs at four wave lengths in the ultraviolet region and the diagram of Vaughn's triangular chart of three components (aniline, nitrosobenzene and azobenzene) was drawn in the same way as reported with the azoxybenzene formation.<sup>5</sup> In the chart  $D_{235}$ – $D_{298}$  was used as abscissa and  $D_{252.5}$ – $D_{320}$  as ordinate, where each  $D$  represents optical density at the subscripted wave length in m $\mu$ . The observed reaction path fitted the expected reaction line, showing that no side reaction had occurred.

**Results**

**The Rate Equation.**—In acetate buffer (0.88 *M* acetic acid and 0.25 *M* sodium acetate)<sup>6</sup> with the initial concentration of aniline of 0.025–0.250 *M* and that of nitrosobenzene of 0.050–0.300 *M*, the rate was found to be proportional to the product of the stoichiometric concentrations of aniline and nitrosobenzene. The apparent second-order rate constants  $k$  were calculated by means of the usual equation. The constants were satisfactory as shown in Table I.

However, in unbuffered solutions, the rate equation is somewhat complex, although it is nearly

(1) (a) E. Bamberger and K. Landsteiner, *Ber.*, **26**, 483 (1893); E. Bamberger, *ibid.*, **29**, 102 (1896); E. Bamberger and R. Hübner, *ibid.*, **36**, 3811 (1903); C. Mills, *J. Chem. Soc.*, **67**, 929 (1895); J. Burns, H. McCombie and H. A. Scarborough, *ibid.*, 2932 (1928); (b) K. Ueno and S. Akiyoshi, *THIS JOURNAL*, **76**, 3670 (1954).

(2) E. Bamberger and A. Rising, *Ann.*, **316**, 282, 284 (1901).

(3) R. E. Lutz and M. R. Lytton, *J. Org. Chem.*, **2**, 68 (1937).

(4) P. Griess, *Ber.*, **9**, 134 (1876).

(5) Y. Ogata, M. Tsuchida and Y. Takagi, *THIS JOURNAL*, **79**, 3397 (1957).

(6) The buffering action of sodium acetate is obvious since no appreciable change in pH was observed on addition of aniline, although the pH varied in the absence of the acetate.

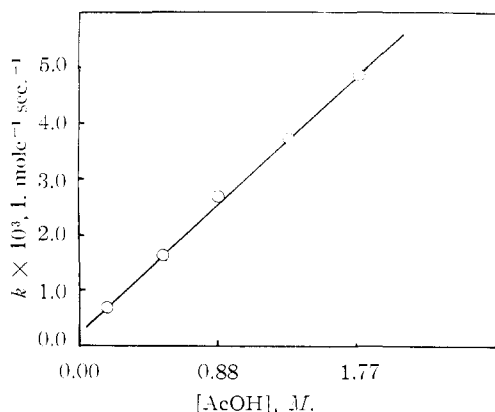


Fig. 1.—Plot of apparent second-order rate constants vs. acid concentration:  $[\text{AcONa}] = 0.25 M$ ; 94% ethanol at  $72.5^\circ$ .

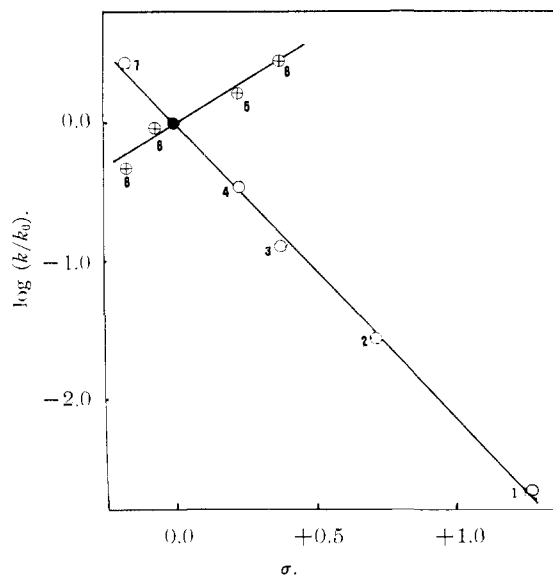


Fig. 2.—Plot of  $\log (k/k_0)$  vs.  $\sigma$ ;  $[\text{AcOH}] = 0.88 M$ ;  $[\text{AcONa}] = 0.25 M$ ; 94% ethanol at  $72.5^\circ$ : ●, unsubstituted; ⊕, aniline with substituted nitrosobenzenes; ○, substituted anilines with nitrosobenzene; 1, *p*-NO<sub>2</sub>; 2, *m*-NO<sub>2</sub>; 3, *m*-Cl; 4, *p*-Cl; 5, *p*-Cl; 6, *m*-Cl; 7, *p*-CH<sub>3</sub>; 8, *m*-CH<sub>3</sub>; 9, *p*-CH<sub>3</sub>.

TABLE I  
SECOND-ORDER RATE CONSTANTS OF AZOBENZENE FORMATION IN BUFFERED 94% ETHANOL SOLUTIONS  
 $[\text{AcOH}] = 0.88 M$ ;  $[\text{AcONa}] = 0.25 M$

Aniline	Initial concentration, M Nitrosobenzene	$k \times 10^3$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>
0.025	0.100	2.10
.050	.100	2.83
.075	.100	2.75
.100	.100	2.93
.150	.100	2.70
.250	.100	2.63
.200	.050	2.68
.200	.150	2.63
.200	.200	2.73
.200	.300	2.83

Average 2.68

second-order with respect to both reactants in each run, if more than two-equivalents of aniline were used against the nitrosobenzene. The apparent second-order constants estimated from the slope of the plot of  $t$  vs.  $\ln b(a-x)/[a(b-x)]$  tended to be small with increasing initial concentration of aniline in various runs. Moreover, if an excess of aniline was not employed, the second-order equation no longer was obeyed, and the order with aniline became smaller with increasing initial concentration of aniline.

**The Effect of Acidity.**—In buffered solutions, the apparent rate constant  $k$  is linearly related to the acetic acid concentration, at least under these experimental conditions.

$$k = (0.20 + 2.65s) \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1} \quad (1)$$

Here  $s$  is the stoichiometric concentration of acetic acid in  $M$ . As is apparent in the equation, the  $k$  value at neutrality is a small positive value (Fig. 1).

**The Apparent Energy and Entropy of Activation.**—The temperature dependence of the  $k$  value was estimated using various substituted anilines and nitrosobenzenes in a buffered solution. From the slope of the plot of  $k$  vs.  $1/T$ , energy of activation,  $E_a$ , and entropy of activation,  $\Delta S^\ddagger$ , for unsubstituted aniline and nitrosobenzene were calculated to be 5.83 kcal. mole<sup>-1</sup> and  $-55.6$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>, respectively.

**The Effect of Substituent.**—The rates of the reaction of aniline with substituted nitrosobenzenes and those of substituted anilines with nitrosobenzene were measured in acetate-buffered ethanol solution (0.88  $M$  acetic acid and 0.25  $M$  sodium acetate). The results are listed in Tables II and III, which show that electron-releasing groups (*e. g.*, *p*-methyl) in anilines facilitate the reaction, while electron-attracting groups (*e. g.*, *p*-nitro) decrease the rate. The effect is reversed with the substituents in the nitrosobenzene. In both cases, the relative rates satisfy Hammett's equation, the values of  $\rho$  being calculated to be  $+1.22$  for the condensations of aniline with substituted nitrosobenzenes and  $-2.14$  for those of substituted anilines with nitrosobenzene (see Fig. 2). The point for *p*-aminobenzoic acid deviated remarkably from the line; hence it was eliminated. But if it were included in the calculation, the  $\rho$  value for the reaction of substituted anilines would become  $-2.04$ .

The rate data for *o*-chloro- and *o*-methylanilines show that the reactions are slower than those of the corresponding *p*-isomers. But *o*-aminobenzoic acid reacts more easily than its *p*-isomer.

### Discussion

**The Reaction Mechanism.**—As stated previously, a linear relation exists between the concentration of acetic acid and the apparent second-order rate constant in buffered solutions. Since the activity of proton is proportional to the acid concentration in buffered solutions with constant concentration of sodium acetate, it will be presumed that proton or undissociated acetic acid is involved in the transition state. In view of these results, a probable mechanism is expressed as A or B alone or a combination of A and B, although the

TABLE II  
SECOND-ORDER RATE CONSTANTS, ENERGIES OF ACTIVATION  
AND ENTROPIES OF ACTIVATION FOR THE CONDENSATIONS OF  
ANILINE WITH SUBSTITUTED NITROBENZENES IN BUF-  
FERED 94% ETHANOL SOLUTIONS

[AcOH] = 0.88 M; [AcONa] = 0.25 M

Substituent	Temp., °C.	$k \times 10^4$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>	$E_a$ , kcal. mole <sup>-1</sup>	$\Delta S^\ddagger$ , cal. deg. <sup>-1</sup> mole <sup>-1</sup>
<i>p</i> -CH <sub>3</sub>	72.5	12.8	6.90	-53.9
	56.0	8.36		
	40.0	4.60		
<i>m</i> -CH <sub>3</sub>	72.5	25.0	6.35	-54.2
	56.0	15.8		
	40.0	9.80		
H	72.5	26.8	5.83	-55.6
	56.0	17.1		
	40.0	11.0		
<i>p</i> -Cl	72.5	44.0	4.82	-57.5
	56.0	30.7		
	40.0	21.3		
<i>m</i> -Cl	72.5	76.0	4.0	-58.9
	56.0	56.8		

TABLE III  
SECOND-ORDER RATE CONSTANTS, ENERGIES OF ACTIVATION  
AND ENTROPIES OF ACTIVATION FOR THE CONDENSATIONS OF  
SUBSTITUTED ANILINES WITH NITROBENZENE IN BUF-  
FERED 94% ETHANOL SOLUTIONS

[AcOH] = 0.88 M; [AcONa] = 0.25 M

Substituent <sup>a</sup>	Temp., °C.	$k \times 10^4$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>	$E_a$ , kcal. mole <sup>-1</sup>	$\Delta S^\ddagger$ , cal. deg. <sup>-1</sup> mole <sup>-1</sup>
<i>p</i> -CH <sub>3</sub>	72.5	73.4	4.95	-56.2
	56.0	50.0		
	40.0	34.9		
H	72.5	26.8	5.83	-55.6
	56.0	17.1		
	40.0	11.0		
<i>p</i> -Cl	72.5	9.35	6.98	-54.3
	56.0	5.55		
	40.0	3.32		
<i>m</i> -Cl	72.5	3.45	8.0	-53.4
	56.0	1.86		
	40.0	1.1		
<i>m</i> -NO <sub>2</sub>	72.5	0.74	11.2	-47.2
	56.0	0.33		
	40.0	0.366		
<i>p</i> -COOH	72.5	1.82	10.8	-46.5
	56.0	0.84		
	40.0	0.366		
<i>p</i> -NO <sub>2</sub>	72.5	0.06	...	...
	72.5	7.41		
	56.0	4.17	7.61	-48.5
<i>o</i> -CH <sub>3</sub>	72.5	0.51	11.5	-46.9
	56.0	0.23		
	72.5	2.71		
<i>o</i> -COOH	56.0	1.25	10.3	-47.4
	72.5	0.57		
	40.0	0.57		

<sup>a</sup> With substituents *m*-CH<sub>3</sub> and *m*-OCH<sub>3</sub> the attempted measurements cannot be accomplished spectrophotometrically because of interference by side reactions.

small contribution of the reaction between neutral molecules may be conceivable from the relation 1 between  $k$  and acidity.

Mechanism A

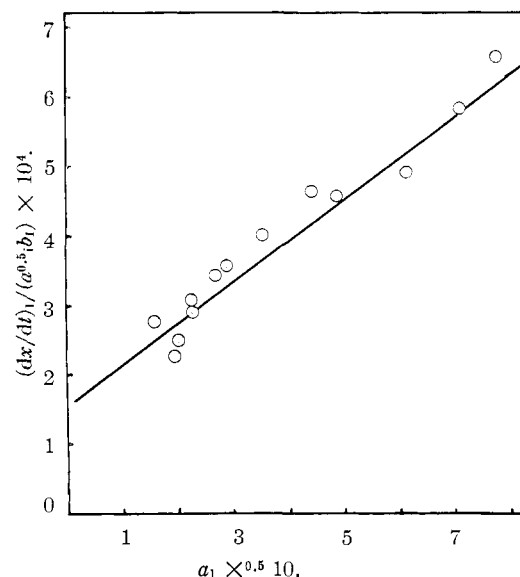
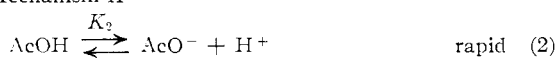


Fig. 3.—Plot of  $(dx/dt)_1 / (a_1^{0.5} b_1)$  vs.  $a_1^{0.5}$  in eq. 16; [AcOH] = 0.25 M; temp., 72.5°; solvent, 94 vol. % ethanol.

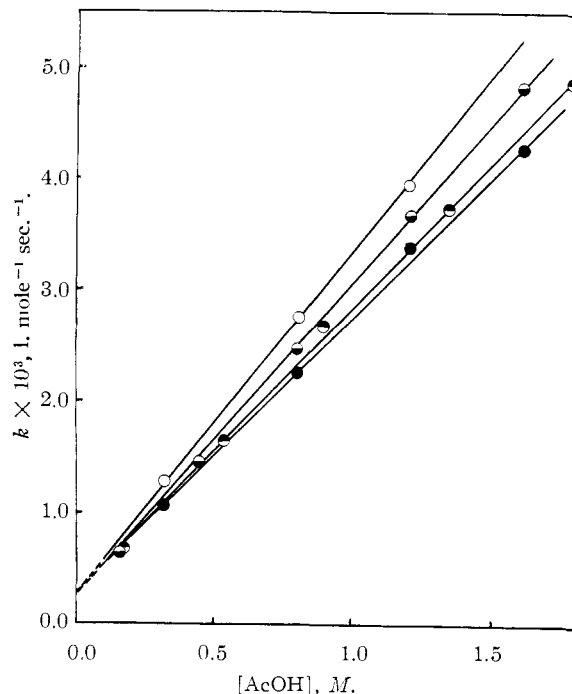
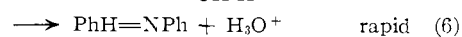
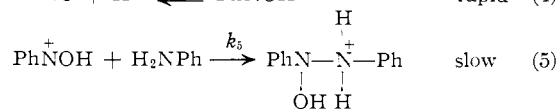
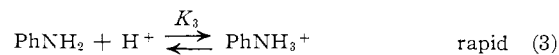


Fig. 4.—Variation of dependence of  $k$  on acidity with concentrations of acetate buffers, 94% ethanol at 72.5°: O, [AcONa] = 0.03 M; ◐, [AcONa] = 0.125 M; ●, [AcONa] = 0.25 M; ●, [AcONa] = 0.50 M.



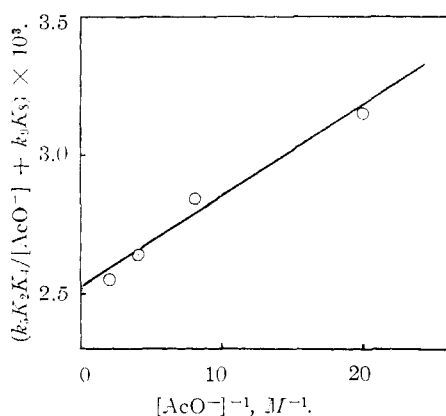


Fig. 5.—Plot of  $(k_3K_2K_4/[\text{AcO}^-] + k_3K_5)$  vs.  $1/[\text{AcO}^-]$  in eq. 17.

Here, the proton is probably in the form of lyonium ions  $\text{C}_2\text{H}_5\text{OH}_2^+$  and  $\text{H}_3\text{O}^+$ . The product azobenzene is so weak a base ( $pK_a = 2.48$  in water at  $25^\circ$ )<sup>7</sup> that it will be unable to attach an appreciable amount of proton; this was verified<sup>7</sup> by spectrophotometry in our hands.

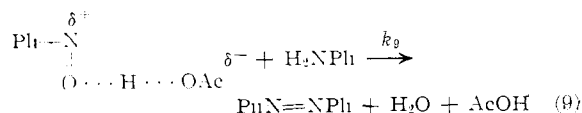
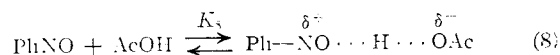
The over-all rate, *i. e.*, the rate of step 5, is expressed similar to the case of azoxybenzene formation.<sup>5</sup>

$$\frac{dx}{dt} = v_3 = \frac{k_3K_4[\text{H}^+]}{(1 + K_3[\text{H}^+])(1 + K_4[\text{H}^+])} (a - x)(b - x) \quad (6a)$$

where  $k$  and  $K$  represent rate and equilibrium constants of the subscripted steps. The above expression is simplified by the fact that both  $K_3[\text{H}^+]$  (or  $[\text{PhNH}_3^+]/[\text{PhNH}_2]$ ) and  $K_4[\text{H}^+]$  (or  $[\text{PhNOH}^+]/[\text{PhNO}]$ ) are much smaller than unity, since the ultraviolet absorption of aniline or nitrosobenzene in ethanol solution showed no appreciable change on addition of acetic acid. Hence

$$v_3 = k_3K_4[\text{H}^+](a - x)(b - x) \quad (7)$$

Mechanism B



This mechanism leads to a rate equation 10.

$$v_3 = k_3K_3[\text{AcOH}](a - x)(b - x) \quad (10)$$

These two mechanisms agree with the experimental data in buffers of constant acetate concentration and are indistinguishable. However, the rate behavior in unbuffered solutions as well as the effect of buffer concentrations on the rate implies the possibility that these two mechanisms are simultaneously operating as described below.

In mechanism A, from equations 1 and 2 together with the equations  $[\text{PhNH}_3^+] + [\text{H}^+] = [\text{AcO}^-]$ ,  $[\text{PhNH}_2] + [\text{PhNH}_3^+] = (a - x)$  and  $[\text{AcOH}] + [\text{AcO}^-] = s$ , equation (11) for the concentration of proton may be obtained

$$[\text{H}^+] = \frac{K_2K_3\{s - (a - x)\}}{2K_3(a - x)} + \frac{\sqrt{K_3^2K_3^2\{s - (a - x)\}^2 + 4K_2K_3s(a - x)}}{2K_3(a - x)} \quad (11)$$

As the approximate values of  $K_2$  and  $K_3$  in aqueous ethanol at  $25^\circ$  are  $10^{-8}$  and  $10^4$ , respectively, the terms except  $\sqrt{4K_2K_3s(a - x)}$  are negligible. Therefore

$$[\text{H}^+] = \sqrt{\frac{K_2s}{K_3(a - x)}} \quad (12)$$

Introduction of this expression into equation 7 leads to the rate expression

$$v_3 = k_3K_4 \sqrt{\frac{K_2s}{K_3}} (a - x)^{0.5} (b - x) \quad (13)$$

But the order of 0.5 with respect to aniline is not in accord with the experimental results.

In mechanism B, where undissociated acetic acid activates nitrosobenzene, the rate expression does not agree with our results either, since a second-order rate equation would be followed according to this mechanism.

The rate data are explicable, however, by assuming a combination of two mechanisms A and B. In this case the rate is expressed as

$$\frac{dx}{dt} = k_3K_4 \sqrt{\frac{K_2s}{K_3}} (a - x)^{0.5} (b - x) + k_3K_3s(a - x)(b - x) \quad (14)$$

Assuming  $k_3K_4\sqrt{K_2s/K_3} = \alpha$  and  $k_3K_3s = \beta$ , the equation is reduced to

$$\frac{dx}{dt} = \alpha(a - x)^{0.5}(b - x) + \beta(a - x)(b - x) \quad (15)$$

The curves of the percentage conversion vs. time with varying ratio of the initial concentration of aniline to nitrosobenzene were drawn and the slopes of these curves,  $dx/dt$ , at a definite percentage conversion were estimated graphically. Introduction of these values into equation 13 gives simultaneous equations 16 where  $a_i$  and  $b_i$  are concentrations of aniline and nitrosobenzene remaining, respectively, and  $\alpha$  and  $\beta$  are unknown constants.

$$(dx/dt)_i = \alpha a_i^{0.5} b_i + \beta a_i b_i \quad (i = 1, 2, \dots) \quad (16)$$

The values of  $\alpha$  and  $\beta$  were calculated from these equations to be  $1.5 \times 10^{-4}$  and  $6 \times 10^{-4}$ , respectively, using least squares. As shown in Fig. 3, a plot of  $(dx/dt)_i/(a_i^{0.5}b_i)$  vs.  $a_i^{0.5}$  gives a straight line, which indicates that  $\alpha$  and  $\beta$  are constants and justifies equation 16.

The idea that the undissociated acetic acid as well as proton catalyzes the reaction explains the unique catalytic action of acetic acid and the unsatisfactory results with strong acids. The reaction is, therefore, a sort of general acid catalysis, although strong acids are not suitable catalysts. Thus on the basis of equations 1, 7 and 10 the apparent rate constants in buffer solutions are expressed as the equation 17, where  $0.20 \times 10^{-3}$  corresponds to the reaction between neutral molecules or a solvent term.

$$k = 0.20 \times 10^{-3} + \left( \frac{k_3K_2K_4}{[\text{AcO}^-]} + k_3K_3 \right) s \quad (17)$$

(7) I. M. Koltz, H. A. Fless, J. Y. Chen Ho and M. Melody, *This Journal*, **76**, 5136 (1954).

(8) (a) E. Grunwald and B. J. Berkwitz, *ibid.*, **73**, 4939 (1951); (b) E. Gutbezahl and E. Grunwald, *ibid.*, **75**, 559 (1953).

From the experiments following rate-acidity relationships in various concentrations of sodium acetate ( $[\text{AcO}^-] = 0.05, 0.125$  and  $0.50 M$ ), the slopes of the lines of  $k$  vs.  $s$  were estimated (Fig. 4). Thence the values of  $k_5K_2K_4$  and  $k_9K_8$  were calculated from the slope to be  $3.28 \times 10^{-5}$  and  $2.53 \times 10^{-3}$ , respectively, by means of simultaneous equations and least squares. Figure 5 shows a plot of  $\{(k_5K_2K_4/[\text{AcO}^-]) + k_9K_8\}$  vs.  $(1/[\text{AcO}^-])$ , which justifies the constancy of  $k_5K_2K_4$  and  $k_9K_8$  and thus proves equation 17. In these cases no salt effect (ionic strength effect) was observed on addition of lithium chloride.

The same idea of general acid catalysis seems applicable to another condensation carried out in alcoholic solution; *e. g.*, the esterification of methanol with acetic acid alone which has been reported<sup>9</sup> to proceed according to the rate equation

$$v = [\text{CH}_3\text{OH}](k_0[\text{AcOH}][\text{H}^+] + k_1[\text{AcOH}]^2 + k_2) \quad (18)$$

The condensation using benzoic acid as the catalyst gave azobenzene, but was not studied in detail. In alkaline solution, the reaction could not be studied because of the decomposition of nitrosobenzene.

**The Effect of Substituents.**—The facts that the substituent effect on nitrosobenzene affords a positive  $\rho$  value (+1.22) and the effect on aniline a negative  $\rho$  value (-2.14) agree with the above mechanism of an electrophilic attack of nitrogen atom of activated nitrosobenzene on nitrogen atom of aniline. However, it should be noted that  $k$  is an apparent rate constant which includes the equilibrium constant for steps 4 or 8; hence the  $\rho$  value for the reactions of substituted nitrosobenzenes is the sum of the  $\rho$  value for the protonation equilibrium of nitrosobenzene and that for the rate-determining step, in which the substituent effect should be reversed. On the other hand, this cancellation seems very small with reactions of substituted anilines because these reactions occur with free anilines, and the amount of protonated anilines under these conditions is negligible even with *p*-toluidine which is the most basic among the anilines used. The absolute value of  $\rho$  for the reaction of substituted nitrosobenzenes is much smaller than that of substituted anilines. The fact may be ascribed partly to this cancellation of the substituent effect.

An approximate linear relationship exists between the energy of activation  $E_a$  and the substituent constant  $\sigma$  with both types of reactions (Fig. 6). An approximately linear but cancelling relationship was observed between the energy of activation and entropy of activation in both of these reactions (Fig. 7). The latter phenomenon is explicable by the parallelism between the higher polarization of the reactant (*e. g.*,  $^-\text{O}_2\text{N}=\text{C}_6\text{H}_4=\text{NH}_2^+$  or  $^+\text{H}_3\text{C}=\text{C}_6\text{H}_4=\text{NO}^-$ ) and the larger decrease of solvation in the activated complex, the polarization relating to  $E_a$  and the solvation to  $\Delta S^\ddagger$ . It is interesting to note that the same linearity exists also with *o*-substituted anilines.

The energy of activation  $5.83 \text{ kcal.mole}^{-1}$  for the aniline-nitrosobenzene reaction is rather small if

(9) A. C. Rolfe and C. N. Hinshelwood, *Trans. Faraday Soc.*, **30**, 935 (1934).

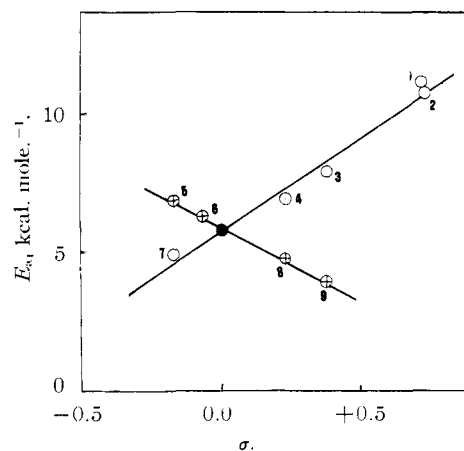


Fig. 6.—Relationship between  $\sigma$  values and energies of activation for the reactions of anilines with nitrosobenzenes;  $[\text{AcOH}] = 0.88 M$ ;  $[\text{AcONa}] = 0.25 M$ ; 94% ethanol at  $72.5^\circ$ : ●, unsubstituted; ⊕, aniline with substituted nitrosobenzenes; ○, substituted anilines with nitrosobenzene; 1, *m*-NO<sub>2</sub>; 2, *p*-COOH; 3, *m*-Cl; 4, *p*-Cl; 5, *p*-CH<sub>3</sub>; 6, *m*-CH<sub>3</sub>; 7, *p*-CH<sub>3</sub>; 8, *p*-Cl; 9, *m*-Cl.

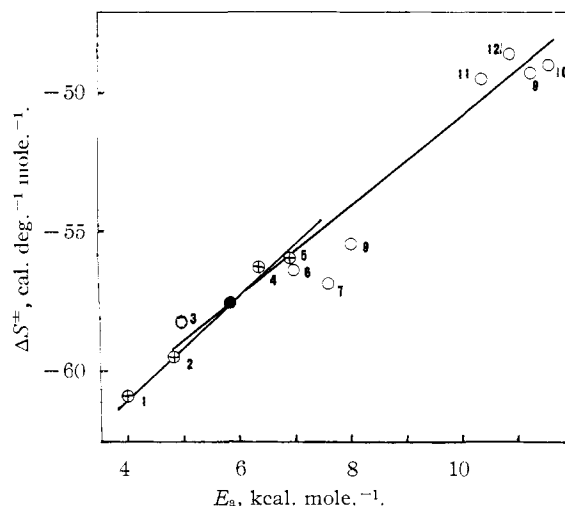


Fig. 7.—Plot of entropies of activation vs. energies of activation for the reactions of anilines with nitrosobenzenes;  $[\text{AcOH}] = 0.88 M$ ;  $[\text{AcONa}] = 0.25 M$ ; 94% ethanol at  $72.5^\circ$ : ●, unsubstituted; ⊕, aniline with substituted nitrosobenzene; 1, *m*-Cl; 2, *p*-Cl; 3, *p*-CH<sub>3</sub>; 4, *m*-CH<sub>3</sub>; 5, *p*-CH<sub>3</sub>; 6, *p*-Cl; 7, *o*-CH<sub>3</sub>; 8, *m*-Cl; 9, *m*-NO<sub>2</sub>; 10, *o*-Cl; 11, *o*-COOH; 12, *p*-COOH.

compared with that of the related condensation of phenylhydroxylamine with nitrosobenzene ( $E_a = 10.8 \text{ kcal.mole}^{-1}$ ). The higher basicity of phenylhydroxylamine ( $pK_a$  for protonated aniline<sup>10</sup> and phenylhydroxylamine<sup>5</sup> in methanol at  $25^\circ$  are 5.804 and 3.462, respectively) will contribute partly to the higher reactivity of phenylhydroxylamine toward nitrosobenzene. Also the entropy of activation is small in comparison with the phenylhydroxylamine-nitrosobenzene condensation, where  $\Delta S^\ddagger$  has been estimated to be  $-32.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ .<sup>5</sup>

(10) A. L. Bacarella, E. Grunwald, H. P. Marshall and E. L. Purlee, *J. Org. Chem.*, **20**, 747 (1955).