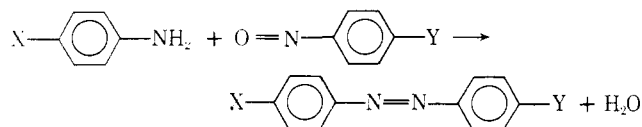


Kinetics and Mechanism for Azobenzene Formation¹R. A. Yunes,² A. J. Terenzani,² and Luciano do Amaral**Contribution from the Instituto de Química, Universidade de São Paulo, São Paulo, Brazil. Received May 5, 1973*

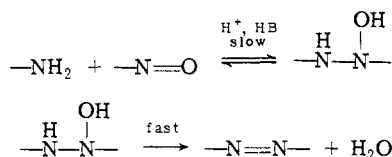
Abstract: The condensation of anilines with nitrosobenzenes to yield azobenzenes in 50% aqueous ethanol occurs with rate-determining attack of the nucleophilic reagent under neutral and acidic conditions. This reaction is subject to both hydronium ion and general acid catalysis, $\alpha \approx 0.35$, and exhibits a water reaction as well. Rate constants for the attack reaction are increased by electron-withdrawing substituents in the nitrosobenzene moiety and by electron-donating substituents in the aniline moiety. In the case of *p*-nitroazobenzene formation, there is evidence for a transition in rate-determining step from amine attack to intermediate dehydration under basic conditions.

The kinetics and mechanism for the addition of amines to the carbonyl function, to yield imines, have been extensively studied.^{3,4} In consequence, these reactions are quite well understood in terms of such basic considerations as nature of the rate-determining step, structure-reactivity correlations, susceptibility to general acid-base catalysis, and the like. A formally closely related series of reactions, addition of amines to the nitroso function, has, in contrast, received very little mechanistic study despite the fact that the reaction has been known since 1893.⁵

Ogata and Takagi,⁶ following the earlier efforts of others,⁷ have demonstrated that condensation of anilines with nitrosobenzenes to yield azobenzenes is subject to acid ca-



talysis in acetate-buffered 94% ethanol-6% water solutions. Rate constants were found to increase with increasing electron-withdrawing power of polar substituents in the nitrosobenzene moiety and to decrease with increasing electron-withdrawing power of polar substituents in the aniline moiety.⁶ These results were interpreted in terms of rate-determining acid-catalyzed addition of amine to the nitroso group, followed by rapid dehydration of the resulting intermediate:



A counterpart to these studies was subsequently undertaken under basic conditions, employing an 80% pyridine-20% water solution containing tetramethylammonium hydroxide, for the same substrates.⁸ Results of effects of polar substituents were also interpreted in terms of rate-determining attack of amine, although the data are much better accounted for in terms of rate-determining dehydration of the intermediate (see Discussion).

It would clearly be advantageous to carry out a study of the various features of azobenzene formation under a variety of conditions but employing a single solvent, preferably one which would permit careful study of general acid-base catalysis. The details of such a study are reported herein.

Experimental Section

Materials. Nitrosobenzenes were synthesized according to published procedures.^{9,10} Other reagents were obtained commercially and, with the exception of reagent grade salts, were recrystallized or redistilled prior to use. Solutions of anilines were prepared just

prior to use as were those of carboxylic acids in 50% alcohol. Distilled water was employed throughout.

Kinetic measurements were carried out spectrophotometrically with the aid of a Zeiss PMQ II spectrophotometer equipped with a cell holder through which was circulated water from a bath maintained at 25°. All kinetic studies were performed in a solvent of 50% ethanol-50% water (wt/wt) at an ionic strength of 0.50, maintained with LiCl, NaBr, NaNO₃, or NaClO₄ and containing 2×10^{-4} M EDTA to retard decomposition of the anilines. The condensation of anilines and nitrosobenzenes to yield azobenzenes was followed by monitoring the appearance of product as a function of time at 340 nm with the exception of *m*-nitroazobenzene whose formation was followed at 335 nm. An initial concentration of the various nitrosobenzenes of 6.6×10^{-5} M was employed. In all cases, a sufficient excess of aniline was employed so that good pseudo-first-order kinetics were obtained. First-order rate constants were calculated from semilogarithmic plots of $(\text{OD}_\infty - \text{OD}_t)$ against time. Second-order rate constants were calculated by dividing first-order rate constants by the concentration of aniline as the free base, calculated from the Handerson-Hasselbalch equation and the $\text{p}K_a$ for aniline in 50% ethanol, 3.92.¹¹ Values of apparent pH were recorded with a Radiometer Model PHM 4d pH meter.

Basicity of Nitrosobenzenes. Infrared shifts of the O-D band of deuterioethanol were determined in carbon tetrachloride in accordance with the procedure of Gordy,¹² employing a Perkin-Elmer 457 spectrometer. Infrared shifts of the O-H band of phenol were determined in carbon tetrachloride in accordance with the procedure of Engberts,¹³ employing a Perkin-Elmer 221 spectrometer.

Results

In Figure 1, first-order rate constants for condensation of aniline with nitrosobenzene in 50% aqueous ethanol at 25° are plotted as a function of aniline concentration at three values of pH. In each case, the reaction is observed to be accurately first order in aniline concentration.

Consequently, over the concentration range employed, there is no detectable general acid or base catalysis of the reaction by either aniline or anilinium ion. Note that the slopes of these plots increase with decreasing pH indicating that azobenzene formation is subject to hydronium ion catalysis. This point is shown more clearly in Figure 2, in which first-order constants for this reaction at a constant total concentration of aniline of 0.15 M are plotted as a function of pH. Note that the values of the rate constants attain constant levels at both the acid and basic ends of the pH range employed, indicating the existence of both acid-catalyzed and pH-independent reactions. The line in this figure is a theoretical one based on the following rate law:

$$k_{\text{obsd}} = [\text{aniline}]_{\text{free base}} (k_{\text{H}}[\text{H}^+] + k_0)$$

in which $k_{\text{H}} = 4.1 \times 10^2 \text{ M}^{-2} \text{ min}^{-1}$, and $k_0 = 0.0009 \text{ M}^{-1} \text{ min}^{-1}$.

With the background information just presented in hand,

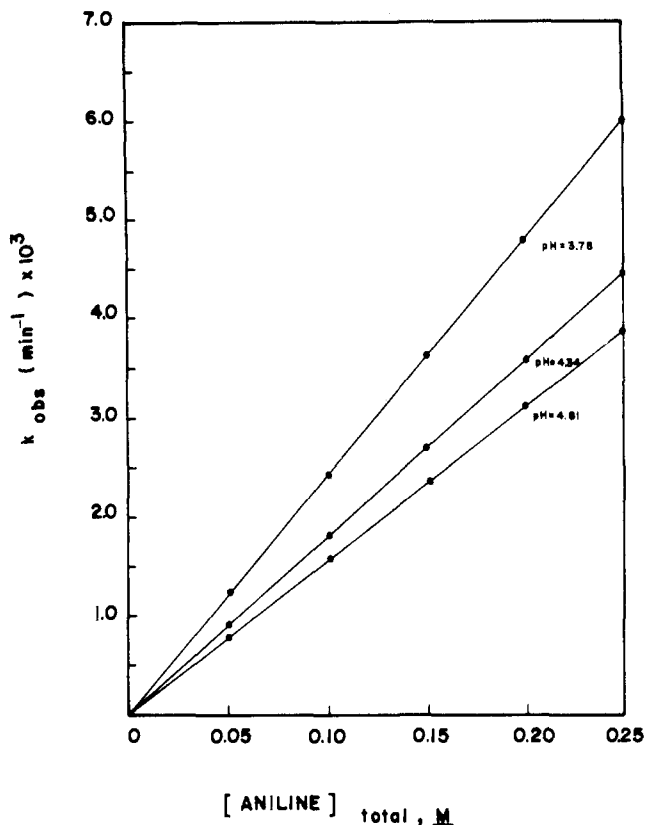


Figure 1. Pseudo-first-order rate constants for condensation of aniline with nitrosobenzene in 50% aqueous ethanol at 25° and ionic strength 0.50 plotted against total aniline concentration at three values of pH.

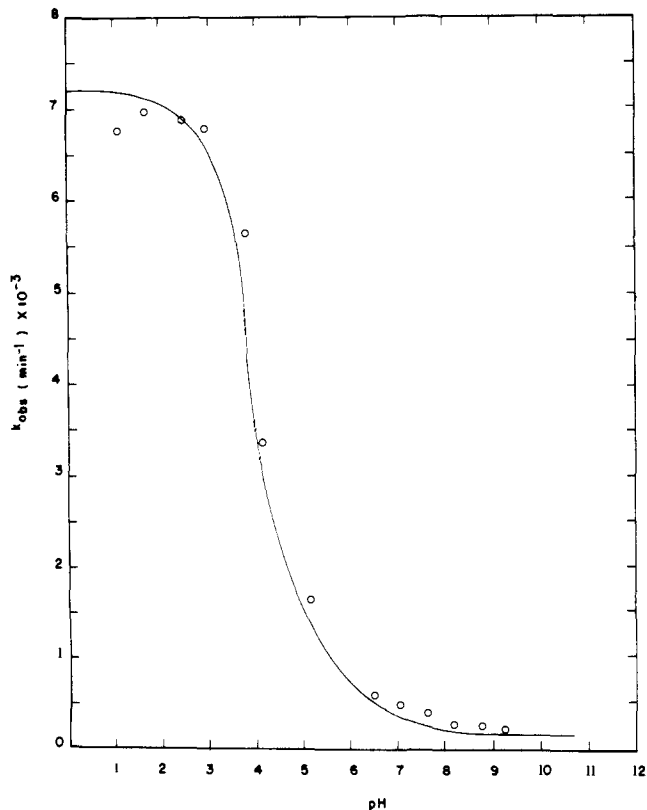


Figure 2. Pseudo-first-order rate constants for the condensation of nitrosobenzene with 0.15 M total aniline in 50% aqueous ethanol at 25° plotted as a function of pH. The line is a theoretical one calculated as described in the text. Where necessary, all rate constants have been extrapolated to zero buffer concentration.

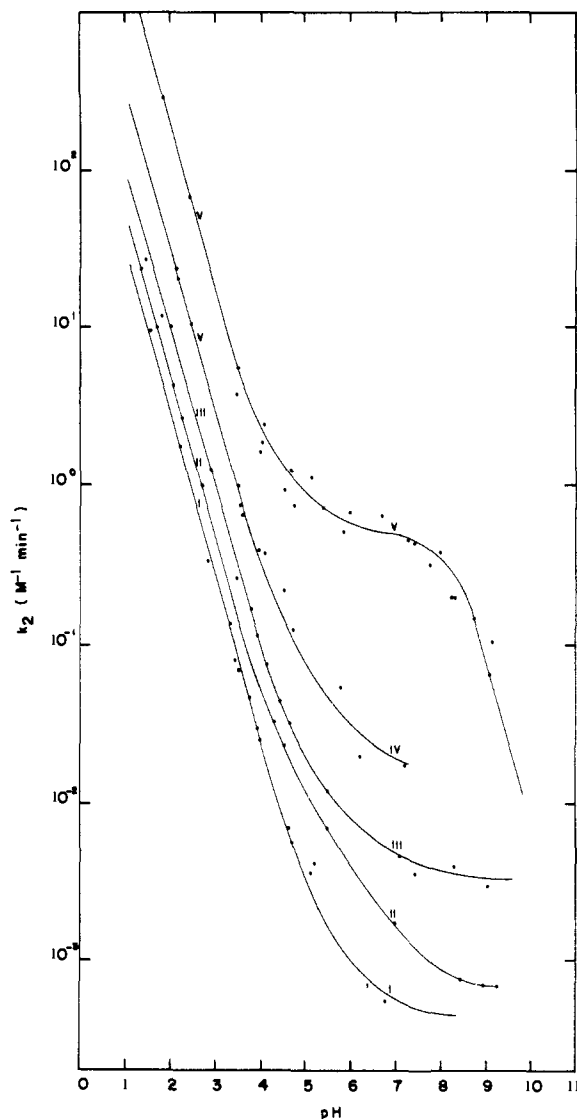


Figure 3. Logarithms of second-order rate constants for condensation of aniline with a series of substituted nitrosobenzenes in 50% aqueous ethanol at 25°. All points have been extrapolated to zero buffer concentration: (I) *p*-methyl; (II) unsubstituted; (III) *p*-chloro; (IV) *m*-nitro; (V) *p*-nitro.

the kinetic studies were extended to include a series of substituted nitrosobenzenes; the pH range from 1 to 9 was investigated. Use of more basic conditions tended to yield unreliable results reflecting either substrate or product decomposition or the incursion of a side reaction. The data collected are shown graphically in Figure 3 in which logarithms of second-order rate constants for substituted azobenzene formation are plotted as a function of pH. As before, all measurements were made in 50% aqueous ethanol at 25°, ionic strength of 0.50, and all rate constants have been extrapolated to zero buffer concentration. In each case, there exist both acid-catalyzed and pH-independent reactions. Third-order rate constants have been calculated from these data and are collected in Table II. Note that the pH-rate profile for formation of *p*-nitroazobenzene shows a break in the pH range 7–8. With increasing base, the rate constants decrease and eventually become again linear with respect to concentration of the hydrated proton.

Second-order rate constants for azobenzene formation are sensitive to the nature and concentration of carboxylic acid-carboxylate buffers employed to maintain constant

Table I. Catalytic Constants Calculated for Acetic Acid for the Reaction of Aniline with Nitrosobenzene^a

Catalyst	% base	pK _a	pH	Concn range, M	Compensating electrolyte	k _{cat} , M ⁻² min ⁻¹
AcOH	80	5.84	6.44	0.1-0.5	LiCl	0.19
AcOH	50	5.84	5.96	0.1-0.5	LiCl	0.18
AcOH	20	5.84	5.20	0.1-0.5	LiCl	0.18
AcOH	50	5.84	5.88	0.1-0.5	NaNO ₃	0.17
AcOH	50	5.84	5.85	0.1-0.5	NaClO ₄	0.18

^a In the presence of acetic acid-acetate buffers in 50% ethanol, 25°, and ionic strength 0.50 maintained with several compensating electrolytes.

Table II. Catalytic Constants of Several Acids for the Reaction of Aniline with a Series of Meta- or Para-Substituted Nitrosobenzenes in 50% Ethanol, 25°, and Ionic Strength 0.50

Substituent	Catalyst	pK _a	pH	Concn range, M	k _{cat} , M ⁻² min ⁻¹
<i>p</i> -NO ₂	H ₃ O ⁺ ^a	-1.74	1-3.5		14000
	CNAcOH	3.39	3.40	0.05-0.25	27.0
	ClAcOH	3.95	4.00	0.05-0.25	17.0
	HCO ₂ H	4.60	4.60	0.05-0.25	8.3
	AcOH	5.84	5.70	0.05-0.25	8.2
	H ₂ O ^b	15.74		27.8	18.0
<i>m</i> -NO ₂	H ₃ O ⁺ ^a	-1.74	1-3.5		2400
	CNAcOH	3.39	3.42	0.05-0.25	7.6
	ClAcOH	3.95	4.05	0.05-0.25	5.7
	HCO ₂ H	4.60	4.70	0.05-0.25	3.1
	AcOH	5.84	5.74	0.05-0.25	1.5
	H ₂ O ^b	15.74		27.8	7.2
<i>p</i> -Cl	H ₃ O ⁺ ^a	-1.74	1-3		940
	CNAcOH	3.39	3.40	0.05-0.25	1.6
	ClAcOH	3.95	3.97	0.05-0.25	0.93
	HCO ₂ H	4.60	4.60	0.05-0.25	0.57
	AcOH	5.84	5.70	0.05-0.25	0.23
	H ₂ O ^b	15.74		27.8	1.2
H	H ₃ O ⁺ ^a	-1.74	1.5-3		410
	CNAcOH	3.39	2.94	0.1-0.5	0.95
	ClAcOH	3.95	3.80	0.1-0.5	0.61
	HCO ₂ H	4.60	4.32	0.1-0.5	0.34
	AcOH	5.84	5.96	0.1-0.5	0.18
	H ₂ O ^b	15.74		27.8	0.33
<i>p</i> -CH ₃	H ₃ O ⁺ ^a	-1.74	1-3.5	0.05-0.25	250
	CNAcOC	3.39	3.39	0.05-0.25	0.35
	ClAcOH	3.95	3.95	0.05-0.25	0.23
	HCO ₂ H	4.60	4.57	0.05-0.25	0.11
	AcOH	5.84	5.70	0.05-0.25	0.040
	H ₂ O ^b	15.74		27.8	0.16

^a Catalytic constants for hydronium ion were based on apparent pH values. ^b Catalytic constants for water have been multiplied by 10⁴.

Table III. Catalytic Constants of Several Acids for the Reaction of Nitrosobenzene and Para-Substituted Anilines in 50% Ethanol, at 25°, and Ionic Strength 0.50

Substituent	Catalyst ^a	pK _a	pH	Concn range, M	k _{cat} , M ⁻² min ⁻¹
<i>p</i> -Cl	H ₃ O	-1.74	3-5		250
	CNAcOH	3.39	3.09	0.1-0.5	1.00
	ClAcOH	3.95	3.39	0.1-0.5	0.60
	HCO ₂ H	4.60	3.91	0.1-0.5	0.31
	AcOH	5.84	4.80	0.1-0.5	0.14
H	H ₃ O ⁺	-1.74	1.5-3		410
	CNAcOH	3.39	2.94	0.1-0.5	0.95
	ClAcOH	3.95	3.80	0.1-0.5	0.61
	HCO ₂ H	4.60	4.32	0.1-0.5	0.34
	AcOH	5.84	5.96	0.1-0.5	0.18
<i>p</i> -CH ₃	H ₃ O ⁺	-1.74	3-5		960
	CNAcOH	3.39	3.32	0.1-0.5	2.50
	ClAcOH	3.95	3.61	0.1-0.5	1.60
	HCO ₂ H	4.60	4.33	0.1-0.5	0.84
	AcOH	5.84	5.08	0.1-0.5	0.51

^a Catalytic constants for hydronium ion were based on apparent pH values.

pH (Figure 4). Buffers employed include cyanoacetate, chloroacetate, formate, and acetate. Measurement of the catalytic effect as a function of the ratio of acidic and basic forms of the acetic acid-acetate buffer established that the catalysis is of general acid type. That is, plots of second-order rate constants against the concentrations of the acid

component of buffer yield straight lines with equal slopes regardless of buffer composition. Catalytic constants were obtained directly from these slopes.

Specifically, in the reaction of aniline with nitrosobenzene, plots of second-order rate constants against the concentration of the acid component of acetic acid-acetate

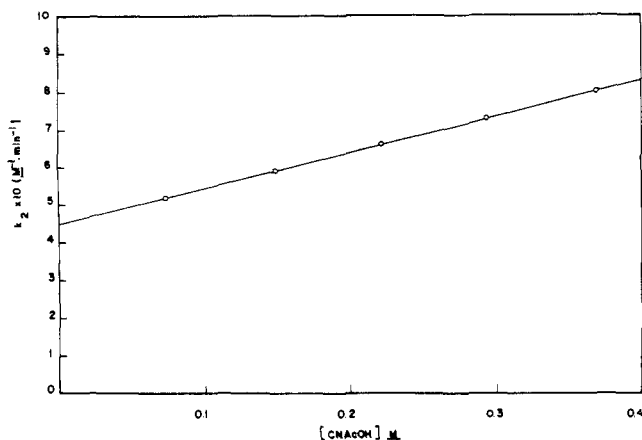


Figure 4. Second-order rate constants for azobenzene formation as a function of cyanoacetic acid concentration in 50% aqueous ethanol at 25° and pH 2.94.

buffer with 80% base (pH 6.44), 50% base (pH 5.96), and 20% base (pH 5.20) yield straight lines with equal slopes regardless of buffer composition (Table I). The observed rate acceleration by carboxylic acid-carboxylate buffers represents true catalysis and not a specific salt effect since plots of second-order rate constants against the concentration of the acid component of the buffer yield straight lines with equal slopes in the presence of different compensating electrolytes¹⁶ (Table I). For the calculations of the concentration of the acidic component of the buffers, values of pK_a which refer to 50% ethanol have been used.¹⁷ The catalytic constants derived from the studies of buffer catalysis are collected in Tables II and III. Correlations of the catalytic constants of carboxylic acids for the reaction of aniline and the substituted nitrosobenzenes, in Brønsted plots, by least-square analysis yield the following values for α : *p*-nitro, 0.38; *m*-nitro, 0.35; *p*-chloro, 0.34; and *p*-methyl, 0.39.

For the reaction of para-substituted anilines and nitrosobenzene, the values of α are as follow: *p*-chloroaniline, 0.34; aniline, 0.29; and *p*-methylaniline, 0.28; a typical example is shown in Figure 5.

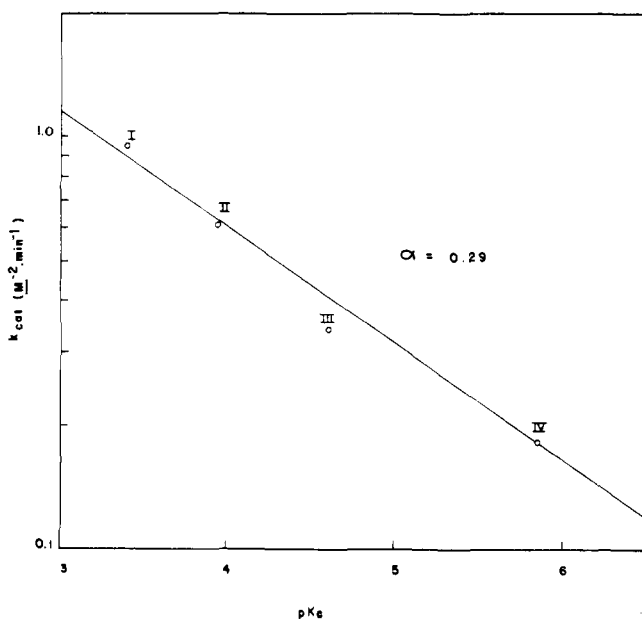


Figure 5. Logarithms of catalytic constants for cyanoacetic acid (I), chloroacetic acid (II), formic acid (III), and acetic acid (IV) for the attack of aniline on nitrosobenzene in 50% aqueous ethanol at 25° plotted against their respective pK_a values (Table I).

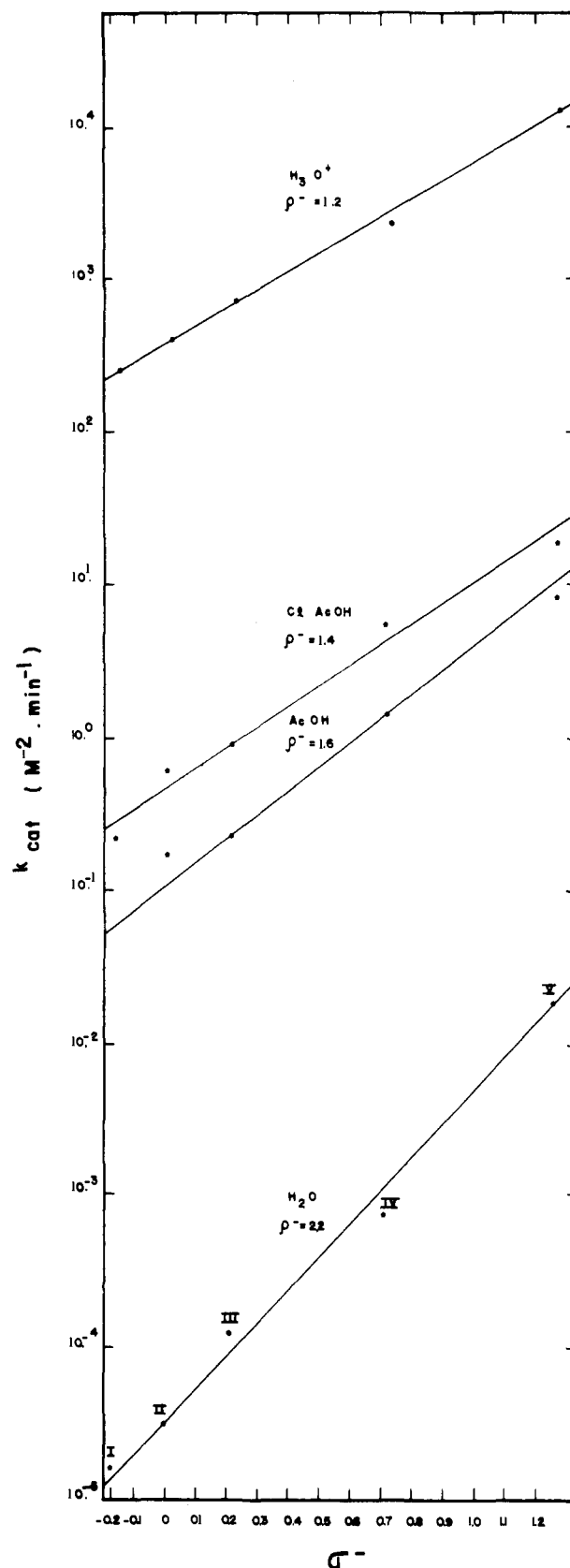


Figure 6. Logarithms of catalytic constants for the hydrated proton, chloroacetic acid, acetic acid, and water for the attack of aniline on a series of substituted nitrosobenzenes [(I) *p*-methyl; (II) unsubstituted; (III) *p*-chloro; (IV) *m*-nitro; (V) *p*-nitro] plotted against the σ^- substituent constants. Data have been taken from Table II.

In Figure 6, values of the catalytic constants for the hydrated proton, chloroacetic acid, acetic acid, and water (Table II) for the attack of aniline on a series of substituted

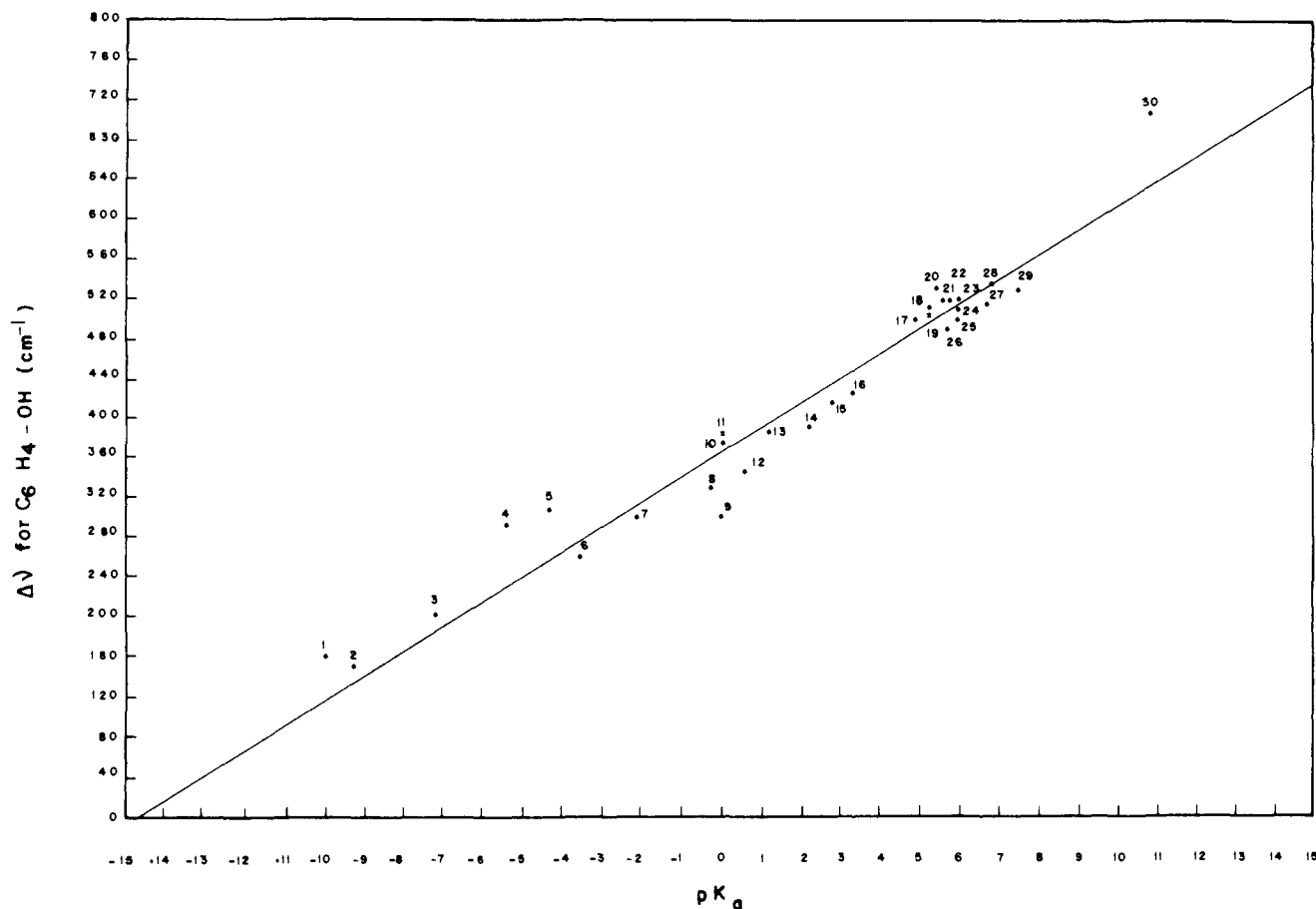


Figure 7. Values for infrared shifts of phenol caused by various bases vs. their pK_a 's: (1) acetonitrile; (2) ethyl acetate; (3) acetone; (4) di-*n*-butyl ether; (5) diisopropyl ether; (6) diethyl ether; (7) tetrahydrofuran; (8) *N,N*-dimethylacetamide; (9) *N,N*-dimethylformamide; (10) dimethyl sulfoxide; (11) diethyl sulfoxide; (12) 2-chloropyridine; (13) pyrimidine; (14) pyridazine; (15) 3-chloropyridine; (16) 2-methoxypyridine; (17) quinoline; (18) 3-5-dimethylpyridine; (19) pyridine; (20) isoquinoline; (21) acridine; (22) 2-methylquinoline; (23) 4-methylpyridine; (24) 4-ethylpyridine; (25) 2-methylpyridine; (26) 3-methylpyridine; (27) 2,4-dimethylpyridine; (28) 2,6-dimethylpyridine; (29) 2,4,6-trimethylpyridine; (30) triethylamine.

nitrosobenzenes are plotted as a function of the σ^- substituent constants.¹⁸ In each case, a satisfactory straight line relationship is obtained; values of ρ^- are: hydrated proton, 1.2; chloroacetic acid, 1.4; acetic acid, 1.5; and water, 2.2.

Quantitative data on the basicity of the nitroso group are scarce. Arnett found a good linear correlation of pK_a vs. infrared shift of the O-D band of deuteriomethanol for a series of compounds, but not including nitroso compounds.¹⁹

We measured the infrared shift of the O-D band of deuteriomethanol (2–10 mg/ml) caused by nitrosobenzene (0.2–0.5 *M* in carbon tetrachloride) as 57 cm^{-1} . This value, applied to the Arnett plot, gives a pK_a for nitrosobenzene of -8.9 ± 2 , which differs substantially from that previously determined by Ogata.⁶

Recently Engberts, *et al.*,¹³ have studied by infrared spectroscopy the intermolecular hydrogen bonding between phenol and a series of para-substituted nitrosobenzenes. They found that the infrared shifts of the O-H band of phenol correlates with σ^+ substituent constants.

With the literature data,^{13,20–22} we find a good linear correlation of pK_a vs. infrared shifts for many compounds of entirely different functional type. A plot of the phenol shift values vs. pK_a for 30 compounds, with a coefficient of correlation of 0.98, is presented in Figure 7.

Plotting in Figure 7 the shift measured by Engberts for nitrosobenzene¹³ (130 cm^{-1}), we find a pK_a of -9.5 ± 2 , that is, close to the value that we have determined with deuteriomethanol.

We have determined the infrared shift of the O-H bond

of phenol (2 mg/ml) caused by *m*-nitro- and *p*-nitronitrosobenzene in carbon tetrachloride. The shifts are respectively 67 and 45 cm^{-1} . Those values are close to those determined with the Engberts plot and the σ^+ value for the *m*- and *p*-nitro group. The shifts applied to the plot of Figure 7 give a pK_a for *m*-nitronitrosobenzene of -12.1 ± 2 and for *p*-nitronitrosobenzene of -13.0 ± 2 .

Discussion

The most striking aspect of the kinetics of azobenzene formation is the similarity to that for addition of weakly basic amines to benzaldehydes and other carbonyl substrates.^{3,4} The following parallels in the behavior of the two systems exist.

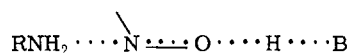
First, the shape of the pH-rate profile is strongly reminiscent of those for addition of weakly basic amines to benzaldehyde^{3,4,14,15} and is suggestive of a transition to rate-determining dehydration of the intermediate.

Second, under mildly acidic conditions, rate-determining formation of the intermediate has been demonstrated for imine formation, and the analogous assignment of the rate-determining step is most consistent with the observed structure-reactivity correlations for azobenzene formation. Specifically, the enhancement of the rate of azobenzene formation by electron-withdrawing polar substituents in the nitroso substrate and by electron-donating ones in the aniline substrate and the existence of specific and general acid catalysis strongly support this suggestion. Note that the rate constants are better correlated by the σ^- than by σ substitu-

ent constants. For those substituents employed in this study, these differ significantly only for the *p*-nitro group, which is more reactive than expected on the basis of σ constants. This suggests that the transition state is stabilized more than the ground state by those substituents capable of accepting electrons by resonance. Of particular importance is the observation of the break in the pH-rate profile for *p*-nitroazobenzene formation (Figure 3). This finding is most readily interpreted as a change in rate-determining step from attack to dehydration as the pH becomes more basic. It follows that attack of the amine is likely to be rate determining under acidic conditions. This conclusion cannot be regarded as being as firmly established as the comparable one for carbonyl addition reactions since it is based on observations with a single compound. One possible alternative, the addition of hydroxide ion to the nitroso group of the *p*-nitro substrate to yield an unreactive form of the substrate at high pH has been excluded on the basis that the ultraviolet spectrum of *p*-nitronitrosobenzene does not change detectably between pH 5 and 9. The suggested change in rate-determining step is the most reasonable and attractive possibility to explain the experimental observations.

Third, attack of weakly basic amines on both the nitroso function and the carbonyl function exhibits hydronium ion, general acid, and water reactions. The ratio of rate constants for the specific acid and water reactions is larger for attack on the nitroso group than for attack on the carbonyl function.¹⁵ Similarly, values of the Brønsted α for general acid catalysis are somewhat larger for azobenzene formation than for imine formation.¹⁵ In neither case do the α values vary significantly with reactivity of the substrate.¹⁵

The mechanism of both hydronium ion and general acid catalysis for attack of aniline on nitrosobenzenes is very likely true general acid catalysis in which substrate protonation and covalent bond formation are in some sense concerted:²³



The strongest evidence against the involvement of protonated nitrosobenzene in azobenzene formation comes from a consideration of the proton-catalyzed reaction.²⁴ Second-order constants were calculated from the determined basicities of *p*-nitronitrosobenzene and the observed third-order rate constants for a hypothetical mechanism involving attack of aniline on the protonated *p*-nitronitrosobenzene. The calculated second-order rate constant for the attack of aniline on the conjugate acid of *p*-nitronitrosobenzene, taking the value for the $\text{p}K_a$ of this compound as -11 , is $1.4 \times 10^{15} \text{ M}^{-1} \text{ min}^{-1}$ ($1.4 \times 10^4/10^{-11}$), or $2.3 \times 10^{13} \text{ M}^{-1} \text{ sec}^{-1}$. This value is larger than the diffusion-controlled limit,²⁴ indicating that protonated nitrosobenzenes are not intermediates along the reaction pathway.

Fourth, for amine attack on both the nitroso and carbonyl functions, the reactions become more sensitive to polar substituents as the strength of the catalyzing acid is decreased.¹⁵ This accords with behavior expected on the basis of the Hammond postulate.²⁵

Finally, both reactions exhibit a transition to rate-determining dehydration of an intermediate with increasing

values of pH. In the case of nitrosobenzene formation, this conclusion rests on the single observation of the break in pH-rate profile for the *p*-nitro substrate. However, there is no other evident explanation for the observed break. This conclusion is contrary to one reached earlier by Brown and Kipp, who have suggested rate-determining attack of amine under basic conditions.⁸ However, the substituent effect observed by these workers, decreasing reactivity with increasing electron withdrawal in the nitrosobenzene substrate, cannot be accommodated by this mechanism but is consistent with rate-determining dehydration.

It has been observed that the rate of formation of azobenzene in 80% pyridine–20% water in the presence of strong base is accelerated by electron-donating polar substituents in the nitrosobenzene moiety.⁸ Surprisingly these workers interpret this result in terms of rate-determining attack of an anilide ion on the nitrosobenzene, accounting for the negative value of ρ in terms of a preequilibrium addition of hydroxide ion to the nitrosobenzene to yield an unreactive adduct. That is, substrates possessing electron-withdrawing polar substituents are more fully converted to the unreactive hydroxide adduct than those possessing electron-donating groups, more than off-setting their inherently greater reactivity toward nucleophilic attack. However, this explanation cannot be correct since the reaction was observed to be first order in hydroxide ion, and the suggested mechanism would yield a pH-independent reaction. These results are nicely interpreted in terms of rate-determining dehydration of a tetrahedral intermediate, in accord with results presented herein.

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