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Polar and Dipolar Substituent Effects and Transition State in the Reaction between Substituted Anilines and Nitrosobenzene. An Evaluation of Ortho and Electrostatic Effects

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The rate constants of the hydronium catalyzed attack of substituted anilines on nitrosobenzene, to give azobenzene, exhibit a large dependence on the substituent constant σ^- ($\rho^-=-1.92$). The relatively high value of ρ^- compared to that obtained from the equilibrium of protonation of anilines ($\rho^-=-2.77$) and the solvent effect on the rate constants support the idea that the transition state involves a large amount of nitrogen-nitrogen bond formation and therefore a strong charge development on the nitrogen and oxygen of the amino and nitroso groups, respectively. A good correlation between basicity and nucleophilic reactivity is obtained by the Brönsted equation ($\beta=0.65$, $r=0.988$) for the para and meta dipolar substituents. Aminobenzoates show a significantly higher reactivity than that calculated from the Brönsted line and this is attributed to an electrostatic participation of the carboxylato group. Nevertheless, this effect is somewhat compensated by repulsion between the carboxylato and the negatively charged oxygen of the nitroso group.

The substituent effects of charged and dipolar groups can be used in order to obtain information about the nature of the transition state of organic reactions. Some authors[1] are of the opinion that charged groups cannot be included with the dipolar groups in one general scale of electronic substituent constant, but others[2] list values of substituent constants for charged groups using results obtained mainly by equilibria or physical properties. Rate data are prime sources of information about the substituent effects on the transition state of the reactions but, in spite of this, few studies have been made dealing with the effect of the carboxylato group on reactivity. Capon[3] studied the participation of the carboxylato group in the hydrolysis of 2-bromopropionate, Bordwell and Knipe[4] in the hydrolysis of α-bromophenylacetic acid that follows an $\mathrm{S_N1}$ mechanism with formation of a zwitterionic-like transition state and Anderson and Fife[5] in the hydrolysis of benzaldehyde disalicylacetal.

In this work we have studied the substituent effects, especially of the carboxylato group, in the reaction of substituted anilines with nitrosobenzene in order to i) obtain a better understanding of the transition state structure of the rate determining step and ii) to evaluate the electrostatic participation of the carboxylato group and the ortho effect of the substituents.

The reaction between anilines and nitrosobenzene was previously studied[6—9] and Yunes et al.[9] showed that the mechanism of this reaction is similar to that of the reaction of weakly basic amines with benzaldehydes and other carbonyl substances.[10] Therefore, attack of the amine is rate-determining under acidic conditions and dehydration of an addition intermediate becomes rate-determining in neutral or basic pH.

Experiments were carried out in MeOH 15% wt and acid pH such that the hydronium-catalyzed attack of aniline on nitrosobenzene (k_H) is the rate-determining step (Eq. 1).

$$\mathrm{PhNO} + \mathrm{PhNH_2} \overset{\text{slow}}{\xrightleftharpoons{k_\mathrm{H}}} \mathrm{PhN(OH)\overset{+}{N}H_2Ph}$$

$$\rightleftharpoons \mathrm{PhN(OH)NHPh}$$

$$\xrightarrow{k_\mathrm{d}} \mathrm{PhN{=}NPh} + \mathrm{H_2O} \qquad (1)$$

The reaction was also studied in different mixed solvents considering that the less polar media could provide better conditions for electrostatic participation of the carboxylato group and could be a simple model for the participation of charged groups in enzyme-catalyzed reactions.

Results

The first-order constant for condensation of aminobenzoic acids with nitrosobenzene in excess of amines in 15% methanol and 85% water by weight, $\mu=0.5\ \mathrm{M}$ ($1\ \mathrm{M}=1\ \mathrm{mol\ dm^{-3}}$) (KCl), at 25 °C varies linearly with total amine concentration at constant pH. This behavior implies the absence of general acid or base catalysis by the aminobenzoic acids in the concentration range studied. The same result was observed with aniline.[9,10]

The rate law for aminobenzoic acids can be written as:

$$k_\mathrm{obs} = k_\mathrm{o}^\mathrm{NC}[\mathrm{NC}] + k_\mathrm{o}^\mathrm{A}[\mathrm{A}] + k_\mathrm{H}^\mathrm{NC}[\mathrm{NC}][\mathrm{H^+}] + k_\mathrm{H}^\mathrm{A}[\mathrm{A}][\mathrm{H^+}] \qquad (2)$$

where k_o^NC is the rate constant of the pH independent reaction of NC. k_o^A is the rate constant of the pH independent reaction of A. k_H^NC is the rate constant of the hydronium ion-catalyzed reaction of NC. k_H^A is the rate constant of the hydronium ion-catalyzed reaction of A. NC and A are the uncharged and anionic species, respectively (Scheme 1).

Rate constants of the pH-independent reaction are negligible in comparison to those for the hydronium-catalyzed reaction (2.5×10^{-4} $M^{-2}\,min^{-1}$ and 5.1×10^{3} $M^{-2}\,min^{-1}$ respectively for aniline) and therefore Eq. 1 reduces to:

$$k_{obs} = k_H^{NC}[NC][H^+] + k_H^{A}[A][H^+] \qquad (3)$$

From Eq. 3 and data at different pH the third-order rate constants k_H^{NC} and k_H^{A} were calculated.

For the other amines the second-order and the third-order rate constants were calculated following methods previously described.[10)]

The hydronium ion-catalytic rate constants are collected in Table 1.

In order to evaluate the relation between basicity and nucleophilicity, a Brönsted type relation (4) was used.

Table 1. Catalytic Rate Constants for the Hydronium Ion ($M^{-2}\,min^{-1}$) for Attack of Substituted Anilines on Nitrosobenzene[a)]

	Substituent	pK_a	k_H	$\log k_H$
1	H	4.62[b)]	5100	3.70
2	*m*-COOH	3.63[c)]	1150	3.06
3	*m*-COO⁻	4.64[c)]	12500	4.09
4	*p*-COOH	2.39[c)]	210	2.32
5	*p*-COO⁻	3.73[c)]	3900	3.59
6	*p*-CH_3	5.07[b)]	11500	4.08
7	*p*-Cl	3.81[b)]	980	2.99
8	*o*-COOH	2.40[c)]	170	2.23
9	*o*-COO⁻	4.76[c)]	12300	4.09
10	*o*-CH_3	4.38[b)]	1600	3.20
11	*o*-Cl	2.62[b)]	100	2.00

a) 15 Wt% methanol–water, at 25 °C and ionic strength 0.5 M (KCl). b) W. P. Jenks and J. Regenstein, "Handbook of Biochemistry," 3rd ed, ed by G. D. Fasman Chem. Rub. Pub., Cleveland (1976). c) Ref. 31.

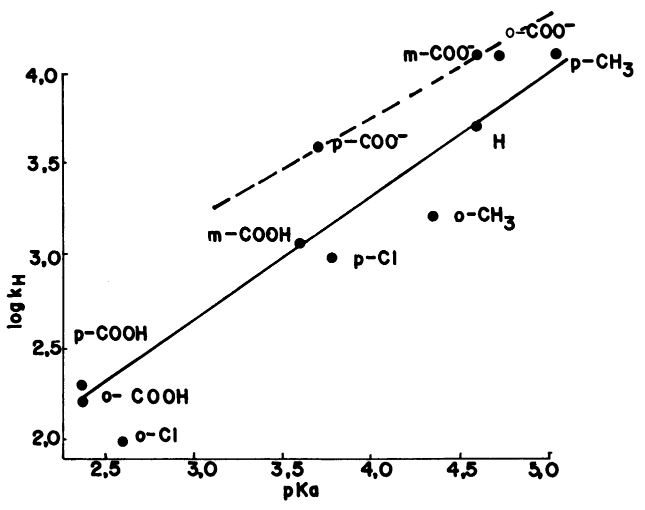


Fig. 1. Logarithms of rate constants of the hydronium ion-catalyzed reaction of nitrosobenzene with anilines in 15 wt% methanol water, 25 °C, ionic strength 0.5 M (KCl) as a function of pK_a of the anilines.

$$\log k_H = \beta pK_a + C \qquad (4)$$

The parameters determined from the data for compounds **1**, **2**, **4**, **6**, and **7** (Table 1) are $\beta=0.65$, $C=0.69$ and the correlation coefficient $r=0.988$. The plot is shown in Fig. 1. All the aminobenzoate ions give rate constants larger than those predicted by the Brönsted equation. The largest positive deviation was for the *p*-aminobenzoate ion.

The catalytic rate constants for the hydronium ion-catalyzed reactions of substituted anilines **1**, **2**, **6**, and **7** were plotted logarithmically against the σ substituent constant,[11)] yielding a ρ value of -2.08 ($r=0.955$). If compound **4** is included in the plot a better correlation is obtained with σ^{-}[12] and ρ^{-} is -1.92 ($r=0.978$).

The ratios of the rate constants of the hydronium ion-catalyzed reactions for formation of azobenzene from *o*- and *p*-substituted anilines are collected in Table 2. With the uncharged substituents chloro, methyl, and carboxyl groups the ratio is less than unity, whereas for the carboxylato group the ratio is greater than unity. It is interesting to note that the corresponding ratios for similar reactions of substituted benzaldehydes with a variety of nitrogen nucleophiles, including hydroxylamine, semicarbazide, *p*-toluidine, and phenylhydrazine are considerably greater than unity.[13–17)] This result has been attributed to greater electronic delocalization in benzaldehydes brought about by para substituents, as

Table 2. Ortho/Para Ratios for the Hydronium-Catalyzed Reaction of Anilines with Nitrosobenzene[a)]

Substituent	k_H^{ortho}/k_H^{para}
-CH_3	0.17
-Cl	0.10
-COOH	0.80
-COO⁻	3.1

a) In 15 wt% methanol, at 25 °C and ionic strength 0.5 M (KCl).

Table 3. Rate Constants ($M^{-2}\,min^{-1}$) of Hydronium Ion-Catalyzed Reactions of Nitrosobenzene with Anilines[a),b)]

	EtOH wt%			
	20	35	50[c)]	65
k_H	4100	1540	410	250
$k_H^{o\text{-}CH_3}$	1400	600	190	125
$k_H^{p\text{-}CH_3}$	9000	3600	960	550
$k_H/k_H^{p\text{-}CH_3}$	0.45	0.44	0.43	0.45
$k_H/k_H^{o\text{-}CH_3}$	2.93	2.56	2.15	2.00
$k_H^{o\text{-}CH_3}/k_H^{p\text{-}CH_3}$	0.16	0.17	0.19	0.22

a) At 25 °C, in different mixtures of EtOH–H_2O. b) pK_a of anilines from B. Gutbenzahl and E. Grunwald, *J. Am. Chem. Soc.*, **75**, 559 (1953). c) Ref. 7.

Table 4. Rate Constants ($M^{-2}\,min^{-1}$) of Hydronium Ion-Catalyzed Reactions and Charge Effects in Condensation between Aminobenzoic Acids, Aminobenzoates, and Nitrosobenzene[a)]

	CH_3OH wt%	
	15	53
k_H	5100	520
$k_H^{o\text{-}COOH}$	170	35
$k_H^{m\text{-}COOH}$	1150	190
$k_H^{p\text{-}COOH}$	210	40
$k_H^{o\text{-}COO^-}$	12300	70000
$k_H^{m\text{-}COO^-}$	12500	72000
$k_H^{p\text{-}COO^-}$	3900	31500
$k_H^{o\text{-}COO^-}/k_H^{o\text{-}COOH}$	72	2285
$k_H^{m\text{-}COO^-}/k_H^{m\text{-}COOH}$	11	379
$k_H^{p\text{-}COO^-}/k_H^{p\text{-}COOH}$	18	787

a) 15 wt% and 53 wt% methanol, at 25 °C.

compared with ortho substituents.[15,17)]

The reaction between *o*-methyl-, *p*-methyl-, and unsubstituted aniline with nitrosobenzene was studied in different mixtures of ethanol–water (Table 3). Increasing the proportion of ethanol decreases the ratio $k_H/k_H^{o\text{-}CH_3}$, but the ratio $k_H/k_H^{p\text{-}CH_3}$ stays practically constant.

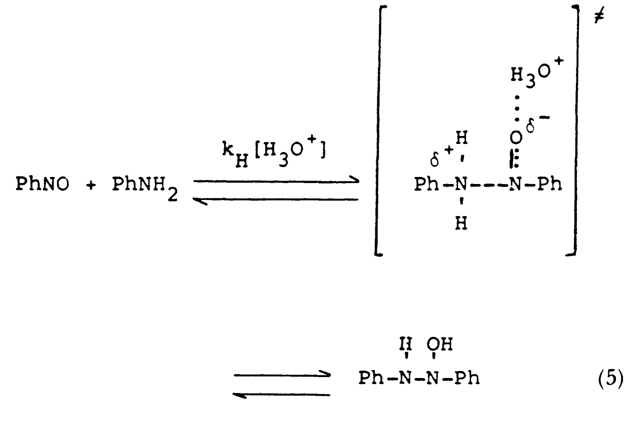
Condensation of aniline, aminobenzoic acids, and aminobenzoate ions with nitrosobenzene was studied in 53 wt% of methanol–water (Table 4). The rate constant for the hydronium ion-catalyzed reaction between aniline and nitrosobenzene decreases approximately 10 times when the proportion of methanol is changed from 15 wt% to 53 wt%. With *o*-, *m*-, and *p*-aminobenzoic acids the rate decrease is 4 to 6 fold, and with aminobenzoate ions the rates increase by factors of 6 to 8. Reaction of the *o*-aminobenzoate ion should have a rate constant of $2.5\times10^3\,M^{-2}\,min^{-1}$ in 53 wt% methanol if its response to the change of methanol proportion was similar to that for *o*-aminobenzoic acid, but it has a hydronium-catalytic rate constant of $7.0\times10^4\,M^{-2}\,min^{-1}$ and thus the reaction is 28 times faster. *m*- and *p*-Aminobenzoate ions show similar behavior. The $k_H^{COO^-}/k_H^{COOH}$ ratios are given in Table 4. Correlations of the catalytic constants of hydronium ion for compounds **1**, **2**, **3**, **4**, and **5** (Table 1) using the substituent constants of McDaniel and Brown,[11)] in Hammett plots, yield the following values: $\rho=-2.62$ ($r=0.952$) for the reaction in MeOH 15 wt% and $\rho=-4.78$ ($r=0.820$) for the reaction in MeOH 53 wt% (plots are not shown).

Discussion

For aniline protonation in water at 25 °C based on σ^- constants the ρ^- value equals −2.77.[18)] This value is considered a measure of the susceptibility of the reaction to substituent effects and is an indication of the complete charge development at the nitrogen atom adjacent to the ring in passing from reagents to products. The correlation with σ^- shows that the conjugation, existing in aniline, between the amino group and the substituents is not present between the ammonio group and the substituents in the anilinium ion. This last assumption is reasonable, theoretically, because the nitrogen on the ammonio group has no unshared electron pair and, being a first-row element, cannot expand its valence shell to accommodate more than eight electrons.

The correlation of nucleophilic reactivity towards the nitroso group, in methanol 15 wt% at 25 °C, and σ^-, gives $\rho^-=-1.92$. Even considering the solvent effect, this value is large, compared with that of aniline protonation in pure water, and is an indication of an extensive charge formation on the nitrogen of the amino group in going from the initial state to the transition state. The good correlation with σ^- shows that there is a clear difference of resonance interaction between the substituents and the reaction center (the amino group) in the initial state and in the transition state. Indeed the delocalization of the unpaired electrons of the amino group in the aniline should be very much reduced in the transition state and consequently the formation of the N–N bond must have proceeded to a considerable extent.

Other piece of evidence about the nature of the transition state is the correlation by the Brönsted equation. The β value for the addition of a proton to aniline, with complete formation of the positive charge, is by definition 1. This value should be smaller for the complete addition of the polarized nitroso group, because it is somewhat less electropositive than the proton. In consideration of this, the value of β obtained 0.65 indicates that the dependence of the reaction on basicity is large. This fact indicates that there should be a large amount of positive charge developed in the attacking nucleophile in the transition state.[10,19)] All these results suggest a probable transition state structure that is represented in Eq. 5.



(5)

Considering that the negative charge on the oxygen of the nitroso group is somewhat stabilized by the catalyst, the strong charge formation on the nitrogen of the amino group would be the main reason for the observed decrease of the catalytic rate constant of aniline and its derivatives with dipolar substituents when the solvent polarity is lowered (Tables 3, 4); under the same conditions, the delocalization of positive charge on the nitrogen of the amino group explains the increase of the rate constants of the attack of water[20] on Schiff bases.

The pK_a of substituted anilines measures the electronic and steric effects of the substituents to protonation of the amino group, however the electron-donating methyl group and the electron-withdrawing chloro atom at the ortho position of aniline give rate constants that fall below the correlation line of the Brönsted plot (Fig. 1) and ortho/para ratios smaller than unity (Table 2). This can be explained by a greater steric effect on the reaction than on the protonation of anilines because the electronic effects of the substituents should be similar in kinetics and equilibria. Wepster[21] has suggested that steric hindrance to solvation of the protonated species is the principal cause of the low basic strength of *o*-alkyl anilines. The reactivity of anilines in different mixtures of ethanol–water (Table 3) suggests that in reaction (5) the steric hindrance to solvation of the transition state is one cause of the smaller experimental value of the catalytic rate constants for ortho-substituted anilines with respect to the value obtained from the Brönsted line. Thus, the $k_H/k_H^{o\text{-CH}_3}$ ratio decreases when the solvating power of the solvent decreases (increasing the ethanol proportion) showing the steric effect of the *o*-methyl group on the transition state solvation. For the *p*-methyl group, where the steric hindrance of transition state solvation is negligible, the $k_H/k_H^{p\text{-CH}_3}$ ratio stays constant. Other steric effects can exist as was indicated by Fujita and Nishioka,[22] in their analysis of ortho effect, but it is evident from the results that they should not be so important to explain the deviation mentioned above. The rate constant of the hydronium ion-catalyzed reaction of *o*-aminobenzoic acid falls on the correlation line of the Brönsted plot. An explanation of this behavior is that there should exist an internal association between the $-\overset{+}{N}H_2$ and the $-COOH$ groups, in the transition state, as is suggested by ^{13}C NMR spectral data[23] of protonated *o*-aminobenzoic acid.

Spectral studies, dipole moment data,[24,25] and kinetic data[15–17] indicate that, when the ortho substituents are in the electrophilic reagent as in the reaction between substituted benzaldehydes and nitrogen nucleophiles,[16,17] steric effects are unimportant. The reaction of *o*-methylnitrosobenzene and aniline gives a hydronium-catalyzed rate constant of 4.8×10^3 $M^{-2}\,min^{-1}$[26] while the rate constant for the unsubstituted compounds is $5.1 \times 10^3\,M^{-2}\,min^{-1}$; this small decrease should be attributed to electronic effects of the methyl group and indicates that in this case the ortho substituent does not affect significantly the attack of aniline and the solvation of the transition state. This last result can be explained because in the transition state the substituents are sufficiently separated from the charged atoms to affect their stabilization by solvation.

One of the most striking facts of this reaction is that the carboxylato-substituted anilines react faster than predicted by the Brönsted plot (for the anilines with uncharged meta and para substituents) giving a different line with a smaller slope (dashed line in Fig. 1 that was drawn considering the points of *m*- and *p*-aminobenzoates). Bruice and Lapinski[27] have shown that the reactivities of a series of nitrogen nucleophiles toward *p*-nitrophenyl acetate fall on lines of slopes 0.8 but with separate lines for substituted imidazols, pyridines, and anilines. It has also been shown for the reactivities of primary, secondary and tertiary amines toward different substracts.[28] Now it is reported that the reactivities toward nitrosobenzene of the same nucleophile aniline, with charged and uncharged substituents, fall in different lines.

A large number of factors may affect the nucleophilic reactivity of the carboxylato anilines and it is possible that their high reactivity should not depend on a single cause. However, the dramatic increase in the rate constant for these anilines on changing from methanol 15 wt% to methanol 53 wt% indicates an electrostatic participation of the carboxylato group which stabilizes the transition state of the reaction. The participation of electrostatic effect in reactions with charged nucleophiles was demonstrated in different systems.[29] However, in this case, the question is why the electrostatic participation of the carboxylato group is different in kinetics and in equilibria. Basicity of anilines in aqueous solution depends strongly, as the amines in general, on specific solvation of their conjugated acids by hydrogen bonding to the solvent.[21,30] In the transition state of the reaction between anilines and nitrosobenzene there is a smaller adhesion, by hydrogen-bonded structure, of solvent molecules on the charged reaction center surface of the activated complex. Thus, the less polar character of the cavity of low dielectric constant near the reaction center, according to the model of Kirwood–Westheimer,[31] make possible a greater electrostatic effect of the carboxylate group on the transition state.

Considering the arguments discussed above it seems probable that the stabilization of the anilinium positive charge by ion–dipolo interactions with the solvent molecules should be smaller than the corresponding to the positive charge of the activated complex of the reaction between anilines and nitrosobenzene. As the ortho substituents in aniline should affect more the solvent molecules that interact by ion–dipolo forces than those that interact by hydrogen bonding it is possible to interpret the greater steric effect of *o*-methyl and *o*-chloro substituents to the solvation of the transition state of the reactions than to the solvation of the products of the equilibrium.

The reactivity of the aminobenzoates follows the order of stabilization of the zwitterionic species of aminobenzoic acids: meta>ortho>para, but the order of positive deviation of the values of the experimental catalytic rate constants with respect to the values calculated from the Brönsted lines is: para>meta> ortho (2.9; 2.4; and 1.9 times respectively). In the zwitterions there is a positive charge on the ammonio group but in the proposed structure of the transition state, in addition to the positive charge on the nitrogen of the amino group, there is a negative charge on the oxygen of the nitroso group that, although somewhat stabilized by the catalyst, should cause some repulsive interaction with the carboxylato group. The order of positive deviation corresponds to the distance between the carboxylato and the nitroso groups since the electrostatic repulsion decreases with distance. The strong deviation of the *o*-aminobenzoate, considering the small distance between the two negative groups, can be explained by an intramolecular hydrogen bond between the ortho carboxylato and the positive amino group in the transition state.[23]

The application of the Hammett equation to the hydronium-catalytic rate constants of compounds with polar and dipolar groups (**1**, **2**, **3**, **4**, and **5** of Table 1) using the substituent constants of McDaniel and Brown[11] gives a good correlation for the reaction in MeOH 15 wt% and a bad correlation for the reaction in MeOH 53 wt%. This result can be attributed to the significant increase of the electrostatic effect of pole (carboxylato group) with the change of the solvent and support the observation of Wepster et al.[32] that the variation of σ values of poles is so large, considering the conditions of the reactions, that it probably makes no sense to average σ values of poles.

The principal conclusions drawn from this work are the following:

i) The transition state of the reaction of formation of azobenzenes from nitrosobenzene and aniline when the rate-determining step is the attack of aniline on nitrosobenzene involves a large amount of nitrogen–nitrogen bond formation and consequently a strong charge formation on the nitrogen and on the oxygen of the amino and nitroso group, respectively.

ii) There exists a clear ortho effect, due principally to inhibition of the transition state solvation, in the reaction between nitrosobenzene and *o*-substituted anilines whereas there is none when the reaction is between aniline and *o*-substituted nitrosobenzene.

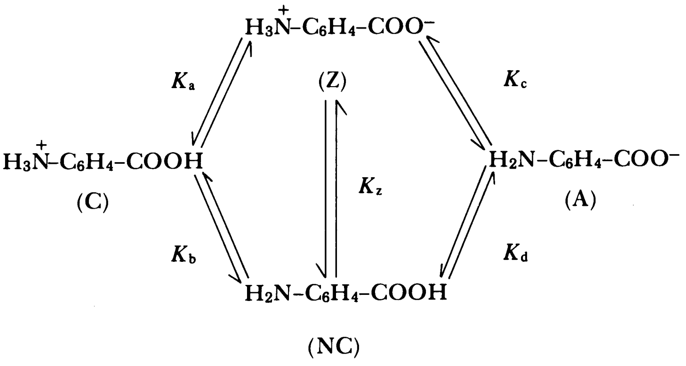
iii) The substituents and ortho effects, specially of poles, depend significantly on the transition state structure and on the reaction media.

Experimental

Materials: Nitrosobenzene was synthesized according to standard procedures[33] and purified by sublimation. Anilines were redistilled or recrystallized and their solutions were prepared just prior to use.

Kinetic measurements were carried out spectrophotometrically at 25 °C with a Shimadzu 210 A ultraviolet spectrophotometer. Reactions were monitored by observing the appearance of the bands of azobenzene at 435 and 350 nm in solutions containing initial concentrations of 3.33×10^{-4} M and 10^{-1} to 10^{-2} M, or 10^{-2} to 10^{-3} M and 1.6×10^{-5} M, for nitrosobenzene and the anilines respectively. The kinetic studies were performed with nitrogen-degassed solutions. The pH range was between 1 to 5. The error of the obtained rate constants was never higher than 3%, for *p*-carboxylato substituted anilines agreement was within 5%.

Calculations of Concentrations of Anilines: The concentrations of all the aminobenzoic acids and aminobenzoates were calculated considering the equilibria of Scheme 1 and Eqs. 6, 7, and 8 that give the relation between the microscopic constants K_a, K_b, K_c, and K_d and the macroscopic constant K_1 and K_2 given in the literature as acidity constants of the aminobenzoic acids.



Scheme 1.

$$K_1 = K_a + K_b \tag{6}$$

$$1/K_2 = 1/K_c + 1/K_d \tag{7}$$

$$K_z = K_a/K_b = K_d/K_c \tag{8}$$

The total concentration of aminobenzoic acid is

$$[\mathrm{AMT}] = [\mathrm{C}] + [\mathrm{NC}] + [\mathrm{A}] + [\mathrm{Z}] \tag{9}$$

and considering the equilibria of Scheme 1, it is possible to obtain Eqs. 10 and 11 that permit calculation of the concentrations of the reactives species NC and A:

$$[\mathrm{NC}] = \frac{1}{(1+K_z)(1+[\mathrm{H}^+]/K_1+K_2/[\mathrm{H}^+])}\cdot[\mathrm{AMT}] \tag{10}$$

$$[\mathrm{A}] = \frac{1}{1+[\mathrm{H}^+]^2/K_1\cdot K_2+[\mathrm{H}^+]/K_2}\cdot[\mathrm{AMT}] \tag{11}$$

The pK_a values of anilines under the experimental conditions: MeOH 15 wt%, μ=0.5 M [KCl], [anilines] 10^{-1}—10^{-2} M, [nitrosobenzene] 3.33×10^{-4} M were assumed to be the same as in water at zero ionic strength because the opposing effects of a higher ion strength and a change in polarity of the solvent tend to cancel.[34] The values of K_1 and K_2 for aminobenzoic acids[35] given at 20 °C were corrected to 25 °C using the method of Perrin[36] for the values of K_b and K_c.[35] The value of K_z was calculated from Eq. 8.

Reactions of nitrosobenzene (10^{-2} to 10^{-3} M) with *p*-chloro- and *p*-methylaniline (1.66×10^{-5}) were run in MeOH 15 wt%, μ=0.5 M (KCl) using the apparent pK_a's of anilines (see pK_a determinations) to calculate the third-order rate constant. As anilines react in the form of free base the kinetic expression is:

$$v = k_H(\text{PhNO})(\text{An})_l(\text{H}^+) \tag{12}$$

where $(\text{An})_l$: aniline as free base concentration. $(\text{An})_l$ can be written as a function of total aniline concentration: $(\text{An})_t$

$$(\text{An})_l = \frac{(\text{An})_t \cdot K_a'}{K_a' + (\text{H}^+)} \tag{13}$$

K_a': acid dissociation constant of anilinium ion determined in the same conditions of the reactions.

Combinations of Eqs. 12 and 13 leads to

$$v = k_H \frac{(\text{PhNO})(\text{An})_t(\text{H}^+)K_a'}{K_a' + (\text{H}^+)} \tag{14}$$

and as the reaction is carried out with a large excess of nitrosobenzene Eq. 14 takes the form that permit us to determine the third-order rate constant: k_H

$$k_{obs} = v/(\text{An})_t = k_H \frac{(\text{PhNO})(\text{H}^+)K_a'}{K_a' + (\text{H}^+)} \tag{15}$$

The values obtained with this method agree with corresponding values of the first method. The second method was also used in the determination of third-order rate constant in MeOH 53 wt% according to Eq. 16 for aminobenzoic acids. The values of the apparent constant K_1 and K_2 of the aminobenzoic acids were from Mentré[37] and corrected to 25 °C using the above mentioned method (the error introduced is negligible).

$$k_{obs} = k_H^{NC} \frac{[\text{PhNO}][\text{H}^+]}{(1+K_z)(1+[\text{H}^+]/K_1 + K_2/[\text{H}^+])} + k_H^{A} \frac{[\text{PhNO}][\text{H}^+]}{1+[\text{H}^+]^2/K_1K_2 + [\text{H}^+]/K_2} \tag{16}$$

The K_z value for *m*-aminobenzoic acid was considered to be 0.1 (calculated from thermodynamic values[35]) and to be negligible for ortho and para aminobenzoic acids.

pK_a Determination: The apparent values of pK_a were determined following the spectrophotometric method of Albert and Serjeant.[36] The apparent pK_a of *p*-chloro- and *p*-methylaniline in methanol 15 wt%, μ=0.5 M, (KCl) 25 °C were 3.71 and 4.99 respectively. The apparent pK_a of aniline in methanol 53 wt% was 3.18.

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