Kinetics of the reaction of 2-chloro-3,5-dinitropyridine with *meta*- and *para*-substituted anilines in methanol

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ABSTRACT: The kinetics of the reaction of 2-chloro-3,5-dinitropyridine (**1**) with *meta*- and *para*-substituted anilines (**2a–j**) to give 2-anilino-3,5-dinitropyridine derivatives (**3a–j**) were studied in methanol at different temperatures. IR studies of the products (**3a–j**) indicated the presence of hydrogen bonding between N—H and an *o*-nitro group, and UV spectra showed a red shift resulting from the interaction between an amino group and aza and nitro groups. A plot of $\Delta H\ddagger$ versus $\Delta S\ddagger$ gave a good straight line with a 324 °C isokinetic temperature. Good linear relationships were obtained from plots of $\log k_2$ against σ values at all temperatures with relatively large negative ρ values (-3.75 to -3.16) indicating the formation of a Meisenheimer σ-complex intermediate. Plots of $\log k_2$ against pK_a values ($\beta = 0.85$) gave good straight lines at 25 °C, except for **2f** (4-COCH₃), indicating that the reactions involve a significant bond formation in the transition state. An S_NAr mechanism is suggested to proceed via two stages, with the first being rate determining. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: 2-chloro-3,5-dinitropyridine; *m*- and *p*-substituted anilines; kinetics

INTRODUCTION

Most aromatic nucleophilic substitutions occur by an S_NAr bimolecular mechanism. The reaction rates are greatly enhanced by strong nucleophilic reagents and electron-withdrawing substituents in the substrate.[1] It was found that two or three nitro groups exert a very powerful effect so that 2,4,6-trinitrochlorobenzene and acyl chloride are comparable in hydrolytic reactivity whereas chlorobenzene requires a higher temperature for hydrolysis.[2–7]
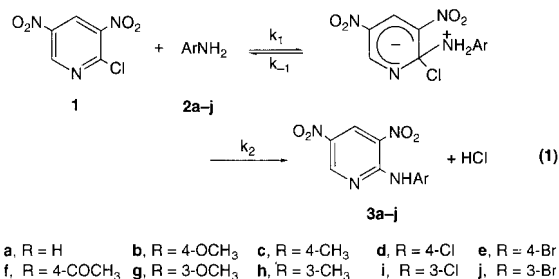
It has been found that in organic bases, such as pyridine and quinoline, the heteronitrogen atom is an activating group almost as strong as a nitro group.[8–10] Pyridine derivatives undergo nucleophilic substitution much more easily than the corresponding benzenes, owing to the presence of an electronegative nitrogen atom in the aromatic ring, specially at both 2- and 4-positions.[4,11–17] This increase in liability of pyridines to nucleophilic attack is a further reflection for the electron-attracting character of the ring nitrogen.[14,15]

In continuation to our previous studies in the field of nucleophilic aromatic substitutions,[8,9,18–21] this work involved the study of the kinetics of the reaction between 2-chloro-3,5-dinitropyridine (**1**) and substituted anilines (**2a–j**) in methanol. We investigated the heteroaromatic reactivity and the effect of substituents in aniline on the

rate of the reaction, with an indication of the transmittance of the electronic effect of these substituents.

RESULTS AND DISCUSSION

The reaction of 2-chloro-3,5-dinitropyridine (**1**) with *meta*- and *para*-substituted anilines (**2a–j**) gave the corresponding substitution products (**3a–j**) [Eqn. (1)].

a, R = H   b, R = 4-OCH₃   c, R = 4-CH₃   d, R = 4-Cl   e, R = 4-Br
f, R = 4-COCH₃   g, R = 3-OCH₃   h, R = 3-CH₃   i, R = 3-Cl   j, R = 3-Br

Elemental analysis and mass, UV, IR and ¹H NMR spectra indicated an anilinodechlorination process with the formation of 2-anilino-3,5-dinitropyridine derivatives (Tables 1 and 2).

The IR spectra of all products (**3a–j**) showed medium to weak bands for NH stretching vibrations at low absorption values in the range 3270–3300 cm⁻¹, presumably attributable to the hydrogen bonding between N—H and the *o*-nitro group in the pyridyl moiety[22,23] (Fig. 1). This agrees with the relatively large δ value (ca 10.6) of the amino proton in the NMR spectra of products

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Table 1. Properties and analysis of 2-substituted anilino-3,5-dinitropyridines (**3a–i**)

Compound	R	Yield (%)	M.P. (°C)	Molecular formula	Found (%) (calc.)				λ^a (nm)	ε (l^{-1} mol^{-1} cm^{-1})
					C	H	N	X		
1	—	—	—	—	—	—	—		230.0	12730
3a	H	94	132	$C_{11}H_8N_4O_4$	51.90 (50.77)	2.91 (3.08)	21.55 (21.54)		230.5 347.0	2100 22700
3b	4-OCH$_3$	50	178	$C_{12}H_{10}N_4O_5$	50.05 (49.66)	3.02 (3.45)	19.19 (19.31)		232.5 361.5	16640 14040
3c	4-CH$_3$	96	149	$C_{12}H_{10}N_4O_4$	52.49 (52.55)	3.38 (3.65)	20.39 (20.44)		231.5 348.5	15900 15180
3d	4-Cl	96	189	$C_{11}H_7N_4O_4Cl$	45.01 (44.82)	2.20 (2.38)	19.01 (19.05)	Cl 12.36 (12.04)	234.5 348.5	12600 13280
3e	4-Br	96	200	$C_{11}H_7N_4O_4Br$	39.26 (38.94)	1.70 (2.06)	16.20 (16.52)	Br 24.00 (23.57)	234 346	13680 14600
3f	4-COCH$_3$	96	175	$C_{13}H_{10}N_4O_5$	52.05 (51.66)	2.94 (3.31)	18.48 (18.54)		227.5 348.5	10780 15260
3g	3-OCH$_3$	90	148	$C_{12}H_{10}N_4O_5$	50.02 (49.66)	3.69 (3.45)	19.81 (19.31)		234.0 346.0	16560 17300
3h	3-CH$_3$	96	146	$C_{12}H_{10}N_4O_4$	52.19 (52.55)	3.56 (3.65)	20.48 (20.44)		231.5 346.0	13920 14440
3i	3-Cl	96	151	$C_{11}H_7N_4O_4Cl$	45.09 (44.82)	1.93 (2.38)	18.81 (19.05)	Cl 12.40 (12.04)	232.5 346.0	15380 17180
3j	3-Br	93	156	$C_{11}H_7N_4O_4Br$	39.37 (38.94)	1.82 (2.06)	16.35 (16.52)	Br 23.87 (23.57)	228.5 346.0	15680 16240

^{a} In methanol.

(**3a–j**). However, the strong absorptions at 1491–1518 and 1327–1362 cm^{-1} indicated that hydrogen bonding has a very small effect on the NO$_2$ asymmetric and symmetric stretching vibrations.[24]

The electronic spectra (UV–visible region) of products (**3a–j**) showed two main bands at 227.5–234.5 and 346–361.5 nm (Table 1). A pronounced red shift was observed in the main absorption band in comparison with each substrate band. This shift presumably arises from the conjugative interaction between the lone pair of the amino group and the two nitro groups of the pyridyl moiety.

The reaction of compound (**1**) with various substituted anilines (**2a–j**) in methanol at five different temperatures (20, 25, 30, 35 and 40 °C) were studied spectrophotometrically under pseudo-first-order conditions and after complete reactions the measured optical densities of the solutions agreed with the calculated values. The reaction
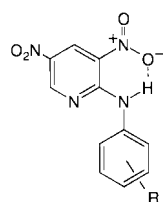
indicated (a) a second-order overall reaction where the slopes gave k_2 values (k_ψ/[aniline]) ($1\ mol^{-1}\ s^{-1}$) and (b) the rate-determining formation of a σ-complex intermediate.[8]

Under the above-mentioned experimental conditions, no methanolysis reaction was observed, as shown from the slight change in the band decay of (**1**) (1×10^{-4} M) in methanol in the absence of aniline at 25 °C within 3 days.[8]

It was observed from the analytical data used to obtain the k_ψ values that the extrapolation of the absorbance to zero time was not increased on increasing the aniline concentration. This indicated that no molecular complex exists between the reactants and the activated complex in the reaction under investigation.[25] In principle, 2-halo-nitropyridines were considered as halogen-substituted aromatic derivatives in which the aza substituent has an activating effect similar to a =C—NO$_2$ group.[8,20,26] To evaluate this aza activation, the kinetic data for the
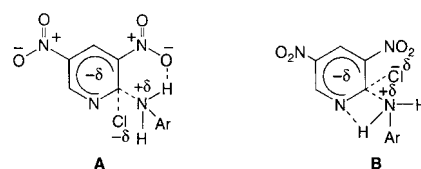

Figure 1

Figure 2

Table 2. IR, ^{1}H NMR and mass spectral data for 2-substituted anilino-3,5-dinitropyridines (**3a–j**)

| Compound | R | $\tilde{\nu}$(cm^{-1}) in methanol | | | | ^{1}H NMR [δ (ppm)] in CDCl$_3$ ^{g} | | | | | | | M$^+$ |
| | | NO$_2$ unsym. | NO$_2$ sym. | N—H | C—H pyridyl | Pyridyl protons | | | Aryl protons | | | | |
						—NH	H$_4$	H$_6$	H$_{2',6'}$ / H$_{2'}$	H$_{4'}$	H$_{3',5'}$ / H$_{5'}$	H$_{6'}$	
1	—	1589	1344		3077		8.98(d), $J_{4,6}=2.2$	9.42(d), $J_{6,4}=1.8$					
3a	H^a	1500	1335	3300	3080	10.56(s)	9.34(d), $J_{4,6}=2.3$	9.36(d), $J_{6,4}=2.3$	7.67(d), $J=7.8$		7.51(t), $J=7.3$		259.1
3b	4-OCH$_3$^{b}	1508	1339	3270	3069	10.44(s)	9.29(s)	9.35(s)	7.53(d), $J=8.8$		7.02(d), $J=8.8$		289.9
3c	4-CH$_3$^{c}	1508	1362	3287	3083	10.50(s)	9.31(d), $J_{4,6}=2.2$	9.35(d), $J_{6,4}=2.2$	7.53(d), $J=8.3$		7.30(d), $J=8.2$		273.7
3d	4-Cl	1498	1357	3291	3085	10.53(s)	9.33(s)	9.37(s)	7.46(d), $J=8.8$		7.46(d), $J=8.8$		293.7
3e	4-Br	1500	1329	3285	3083	10.52(s)	9.33(s)	9.37(s)	7.60(m)		7.60(m)		337.6
3f	4-COCH$_3$^{d}	1491	1331	3285	3053	10.73(s)	9.40(s)	9.40(s)	7.86(d), $J=8.6$		8.09(d), $J=8.6$		301.9
3g	3-OCH$_3$^{e}	1505	1327	3295	3072	10.54(s)	9.34(d), $J_{4,6}=2.5$	9.37(d), $J_{6,4}=2.5$	7.33(s), $J_{2,5}=2.2$	6.89(d), $J_{4,5'}=2.4$	7.40(t), $J_{5,4}=8.8$, $J_{5,6'}=8.2$	7.21(d), $J_{6,5'}=7.8$	290.0
3h	3-CH$_3$^{f}	1518	1300	3291	3094	10.51(s)	9.33(d), $J_{4,6}=2.3$	9.36(d), $J_{6,4}=2.3$	7.34(s)	7.16(d), $J_{4,5'}=7.2$	7.40(t), $J_{5,6'}=7.6$	7.48(d), $J_{6,5'}=9.2$	274.1
3i	3-Cl	1498	1330	3301	3086	10.55(s)	9.37(s)	9.38(s)	7.85(s), $J_{2',4'}=1.2$, $J_{2',6'}=1.2$	7.51(d), $J_{4,5'}=8.0$, $J_{4,6'}=1.3$	7.33(t), $J_{5,4'}=9.1$, $J_{5,6'}=7.6$	7.43(d), $J_{6,5'}=7.7$	293.0
3j	3-Br	1500	1356	3293	3078	10.53(s)	9.37(s)	9.37(s)	7.98(s)	7.58(d), $J_{4,5'}=7.8$	7.35(t), $J_{5,4'}=7.9$, $J_{5,6'}=8.0$	7.47(d), $J_{6,5'}=8.0$	338.1

^{a} H-4' proton appears at δ 7.35 ppm (t, 1H).
^{b} 4-OCH$_3$ protons appear at δ 3.89 ppm (s, 3H).
^{c} 4-CH$_3$ protons appear at δ 2.46 ppm (s, 3H).
^{d} 4-COCH$_3$ protons appear at δ 2.67 ppm (s, 3H).
^{e} 3-OCH$_3$ protons appear at δ 3.9 ppm (s, 3H).
^{f} 3-CH$_3$ protons appear at δ 2.46 ppm (s, 3H).
^{g} J in Hz.

Table 3. Second-order rate constants, activation parameters and ρ values for the reaction of 2-chloro-3,5-dinitropyridine (**1**) with substituted anilines (**2a–j**) in methanol

Compound	R	$k_2 \times 10$ (1 mol^{-1} s^{-1})					$\Delta H^{\ddagger}$ (kcal mol^{-1})	$-\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1})	pK_a [37]
		20°C	25°C	30°C	35°C	40°C			
2a	H	3.14 (± .03)	3.23 (± .04)	4.10 (± .11)	5.85 (± .03)	6.12 (± .07)	5.58 (± .27)	41.89 (± .88)	4.60
2b	4-OCH$_3$	30.10 (± .36)	33.41 (± .90)	41.30 (± .77)	44.80 (± .41)	49.70 (± .90)	2.59 (± .09)	47.09 (± .30)	5.36
2c	4-CH$_3$	12.40 (± .32)	13.40 (± .15)	14.00 (± .16)	15.50 (± .33)	16.30 (± .67)	2.66 (± .04)	49.00 (± .14)	5.08
2d	4-Cl	0.42 (± .01)	0.51 (± .02)	0.78 (± .01)	0.83 (± .03)	1.05 (± .04)	6.87 (± .19)	40.89 (± .64)	3.98
2e	4-Br	0.49 (± .02)	0.60 (± .04)	0.72 (± .02)	0.80 (± .01)	1.09 (± .01)	6.42 (± .16)	42.49 (± .53)	3.89
2f	4-COCH$_3$	0.08 (± .002)	0.11 (± .001)	0.13 (± .001)	0.17 (± .001)	0.22 (± .001)	8.89 (± .13)	37.79 (± .44)	2.19
2g	3-OCH$_3$	2.75 (± .06)	3.07 (± .08)	3.55 (± .05)	4.98 (± .21)	5.41 (± .16)	5.49 (± .19)	42.39 (± .65)	—
2h	3-CH$_3$	3.55 (± .08)	4.85 (± .06)	5.12 (± .14)	5.69 (± .15)	6.83 (± .29)	5.19 (± .21)	42.69 (± .68)	4.71
2i	3-Cl	0.18 (± .004)	0.23 (± .006)	0.30 (± .004)	0.35 (± .014)	0.47 (± .007)	7.29 (± .10)	41.39 (± .33)	3.52
2j	3-Br	0.22 (± .01)	0.28 (± .01)	0.38 (± .01)	0.42 (± .01)	0.56 (± .01)	7.69 (± .14)	39.59 (± .46)	3.53
ρ		−3.75 (±0.18), $r = 0.99$	−3.50 (±0.18), $r = 0.99$	−3.35 (±0.18), $r = 0.99$	−3.25 (±0.18), $r = 0.99$	−3.16 (±0.18), $r = 0.99$			
β		0.85 (±0.09), $r = 0.95$							

anilinodechlorination of 1-chloro-2,4-dinitrobenzene in methanol ($k_2 = 4.2 \times 10^{-4}$ 1 mol^{-1} s^{-1} at 30 °C)[8] and 2-chloro-1,3,5-trinitrobenzene (picryl chloride) ($k_2 = 1.16 \times 1$ mol^{-1} s^{-1} at 30 °C)[33] were compared with that of 2-chloro-3,5-dinitropyridine (**1**). These values showed that the presence of either an aza group in (**1**) or a nitro group in picryl chloride, in comparison with 1-chloro-2,4-dinitrobenzene, enhanced the rate by *ca.* 970- and 2720-fold, respectively. This was presumably attributable to the efficient delocalization of the developed charge with the aza or the nitro group in their transition state. The comparable rate constant values of (**1**) and picryl chloride indicated that both the aza and nitro groups exhibit almost the same kinetic effect on the rate, in contrast to that reported earlier.[8]

The reactivity of the substituted anilines was found to decrease in the order 4-OCH$_3$, 4-CH$_3$, 3-CH$_3$, H, 3-OCH$_3$, 4-Cl ≈ 4-Br, 4-COCH$_3$ (Table 3). This order is expected on the basis of the inductive and resonance effets of the substituents and their position in the aniline molecule. The activation parameter values indicated that the reaction is moderately entropic and the difference in reactivity is enthalpy dependent. The $\Delta S\ddagger$ values are negative, as expected for bimolecular nucleophilic substitution,[27] and are explained on the following basis: (a) the transition state involves much greater charge separation than that existing in the reactants, and therefore the change from reactants to a more polar transition state is accompanied by a considerable loss of solvent freedom, causing a consequent decrease in entropy; (b) some degree of hydrogen bonding, involving the amino hydrogens and *o*-nitro group or amino hydrogens and aza group[8] may occur with further entropy decrease (Fig. 2).

A plot of $\Delta H\ddagger$ against $\Delta S\ddagger$ gave a straight line of slope 324 ± 57 ($r = 0.96$), which is the value of the isokinetic temperature for this reaction (the temperature at which the substituent effect is supposed to be reversed). This value was far from the temperature used in the kinetic runs. Furthermore, the mechanism for the reaction series was common for all members, as indicated by the excellent linearity of the plot[28] of $\log k_{40\,°C}$ against $\log k_{20\,°C}$ (slope 0.89; $r = 0.99$).

The correlations between $\log k_2$ for the reaction of (**1**) with *para*- and *meta*-substituted anilines and the appropriate Hammett σ values,[29] but not σ^+ values, at all temperatures gave good straight lines. The values of the reaction constants (ρ) were calculated at 20, 25, 30, 35 and 40 °C (Table 3). The sign and magnitude of ρ (-3.16 to -3.75 (± 0.18, $r = 0.99$) depending on temperature) indicated that (a) the negative ρ values are in agreement with the donor ability of aniline derivatives,[25] (b) a positive charge is developed on the anilino nitrogen atom when the transition state is formed[30] and (c) the reaction is facilitated by electron-releasing groups of the substituted anilines.

The ρ values for the reaction under investigation were

in full agreement with that of Chapman *et al.*[12b] hypothesis of ρ values, (between -3.1 and -3.5), which are characteristic of displacement of the chlorine atom from an aromatic carbon by aromatic amines. On the other hand, our ρ values were similar to the value given by Wepster *et al.*[31] ($\rho = -3.19$) for the ionization of substituted anilinium ions in 30% aqueous ethanol at 25 °C. The similarity of these ρ values is explained by the formation of a Meisenheimer complex-type intermediate in which the conjugation of the amino group with benzene ring is destroyed.

The dissociation of anilinium ions and the reaction rate constants of (**1**) with substituted anilines gave good Hammett plots. However, the latter reaction also gave a good straight line for Brønsted-like plot at 25 °C, except for **2f** (R = 4-COCH$_3$); the Brønsted coefficient (β) value was 0.85 ± 0.09 ($r = 0.95$). Similar correlations were observed for the reactions of picryl chloride[32] ($\beta = 1.08$), 2-bromo-3,5-dinitrothiophene[33] ($\beta = 1.05$) and 2-chloro-quinoxaline[34] ($\beta = 0.45$) with substituted anilines in methanol. Hirst and Ur-Rahman[32] attributed the large difference in their β value (1.08) compared with that reported by Biggi and Pietra[35] ($\beta = 0.63$) to the various types of amines used. Meanwhile, the comparison of our β value with those mentioned above is presumably due to the difference in the substrates used, as suggested by Bevan *et al.*[36]

Since β values are generally associated with bond formation in the transition state, the reaction of 2-chloro-3,5-dinitropyridine (**1**) with anilines in methanol shows an appreciable degree of bond formation in the transition state. The positive sign of $\beta = 0.85$ is a criterion for nucleophilic substitution reactions.[16,27]

On the basis of our kinetic data, it is evident that the reaction between 2-chloro-3,5-dinitropyridine (**1**) and substituted anilines (**2a–j**) (ArNH$_2$) is a second-order reaction, and the activation parameters and ρ values suggest an aromatic nucleophilic substitution S_NAr via two stages with the first being rate determining.[30]

EXPERIMENTAL

Melting-points were uncorrected. ^{1}H NMR spectroscopy was performed in CDCl$_3$ using a Bruker 200 MHz spectrophotometer with Me$_4$Si as internal standard. IR spectra (KBr pellets) were measured on a Perkin-Elmer Model 1430 instrument. Electronic spectra were measured on Shimadzu Model 160-A UV–visible spectrophotometer. Elemental analyses of the reaction products were carried out at the Faculty of Science, Ain Shams University, Egypt. Mass spectra were carried out on a Finnigam Mat TSQ 700 triple-quadrupole tandem mass spectrometer at the Université Catholique de Louvain, Belgium. Analytical thin-layer chromatography (TLC) was carried out on silica gel using ethyl acetate–hexane (1:9).

Starting material. 2-Chloro-3,5-dinitropyridine (**1**), m.p. 64 °C, was obtained from Aldrich and was purified by crystallization twice from methanol – light petroleum as yellow needles. The anilines (**2a–j**) were aniline, 4-methoxyaniline, 4-methylaniline, 4-chloroaniline, 4-bromoaniline, 4-acetylaniline, 3-methoxyaniline, 3-methylaniline, 3-chloroaniline and 3-bromoaniline, respectively, supplied by Aldrich. They were purified by crystallization or vacuum distillation.

General procedure. 2-Chloro-3,5-dinitropyridine (**1**) (0.25 g; 12 mmol) was dissolved in absolute methanol (10 ml) and a methanolic solution of substituted aniline (13.2 mmol) (prepared by dissolving 0.14 –0.239 of the substituted aniline in 10 ml of methanol). The reaction mixture was stirred for 30–45 min at room temperature. The precipitated solid was filtered and crystallized from benzene–light petroleum. The physical properties, spectral data and elemental analyses are given in Tables 1 and 2.

Kinetic measurements. The reactions of 2-chloro-3,5-dinitropyridine (**1**) with different anilines (**2a–j**) in absolute methanol were followed spectrophotometrically at 20, 25, 30, 35 and 40 °C. The recorded spectrum at the end of each reaction was identical with that of an authentic sample of the substitution product in the same solvent. A stock solution of 2-chloro-3,5-dinitropyridine in absolute methanol was prepared (1.0×10^{-3} M) and diluted before use to 5.0×10^{-5} M. Solutions of various substituted anilines (0.1 M) were prepared just before use by dissolving a weighed amount of the required aniline in a known volume of methanol. A sufficient excess of aniline over substrate concentration was used (1:20 to 1:600). Solutions of 2-chloro-3,5-dinitropyridine (**1**) and an appropriate aniline were allowed separately to attain the desired temperature ±0.5 °C in a thermostated bath before being mixed. The resulting change in absorbance with time was recorded on a Shimadzu 160-A UV–visible spectrophotometer at $\lambda = 350$ nm.

The pseudo-first-order rate constants k_Ψ at $\lambda = 350$ nm for the reactions of the substrate (**1**) with anilines at different concentrations at 20, 25, 30, 35 and 40 °C were calculated using the equation

$$\ln(A_\infty - A_1) = -k_\Psi t + \ln(A_\infty - A_0) \qquad (2)$$

where A_0, A_1 and A_∞ are the values of the absorbance at zero time, time t and the end of the reaction, respectively.

Plots of k_Ψ versus aniline concentration gave straight lines passing through the origin with slopes equal to the second-order rate constants (k_2).

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