Monatsh Chem (2013) 144:301–306
DOI 10.1007/s00706-012-0860-z

ORIGINAL PAPER

Kinetic and equilibrium studies of σ-adduct formation and nucleophilic substitution in the reactions of 2-chloro-3,5-dinitropyridine and 2-ethoxy-3,5-dinitropyridine with *p*-substituted anilines in DMSO

Basim H. Asghar

Received: 23 March 2012 / Accepted: 1 September 2012 / Published online: 18 October 2012

Abstract Rate and equilibrium results for the reactions of 2-chloro-3,5-dinitropyridine and 2-ethoxy-3,5-dinitropyridine with a series of *p*-substituted anilines in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) were studied in DMSO. The reactions yielded 2-anilino-3,5-dinitropyridine derivatives, and no accumulation of intermediates could be detected spectrophotometrically. The rates were compatible with a two-step mechanism involving initial nucleophilic attack followed by either base-catalysed or uncatalysed conversion to the product. The base-catalysed pathway was likely to involve rate-limiting proton transfer from the zwitterionic intermediate to the base to yield the anionic σ-adduct. Plots of log K_1k_{DABCO} against pK_a values gave good straight lines at 25 °C, with slopes of 0.42 for 2-chloro- and 0.45 for 2-ethoxy-3,5-dinitropyridine. The results were compared with those for the reactions of 2-phenoxy-3,5-dinitropyridine with substituted anilines.

Keywords Rate and equilibrium · 2-Chloro-3,5-dinitropyridine · 2-Ethoxy-3,5-dinitropyridine · *p*-Substituted anilines

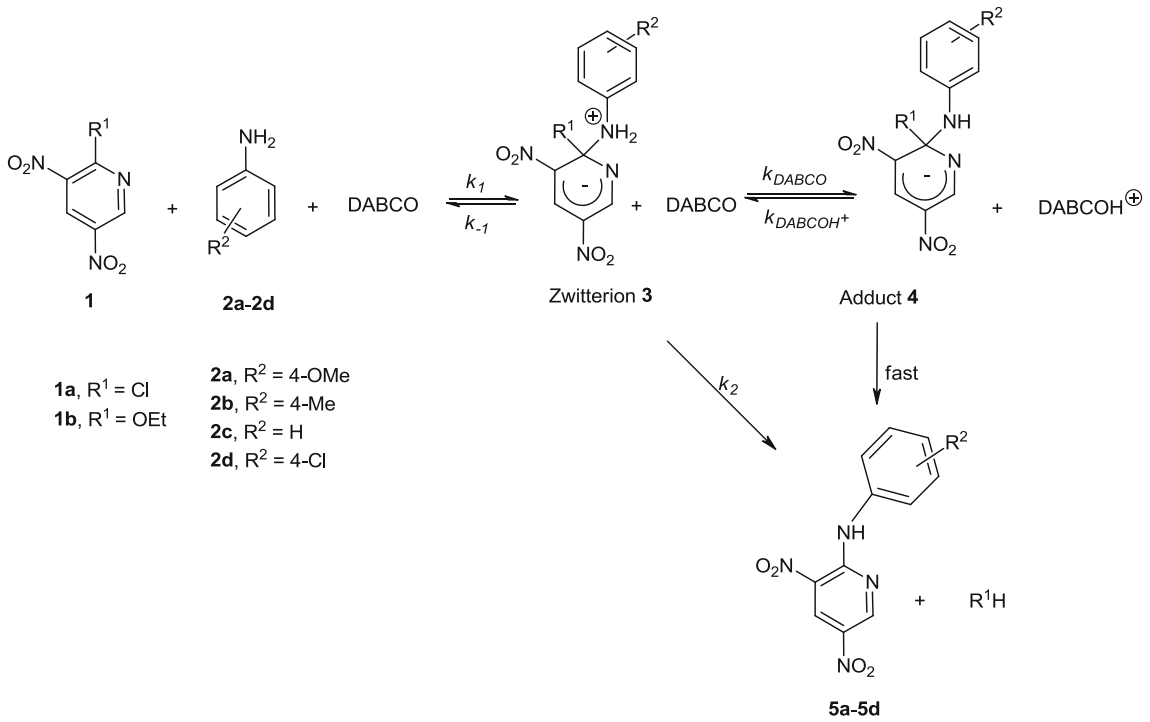
Introduction

Rate studies for nucleophilic substitution reactions of aromatic substrates have been the subject of several excellent reviews and books [1–4] and remain an active research area [5–9]. The presence of electron-withdrawing ring substituents, such as the nitro group, strongly accelerates substitution, and ring nitrogen atoms have also been found to exert a powerful activating effect [7]. However, a ring nitrogen *ortho* to the substitution position has generally been found to be less effective than a corresponding nitro group [8–12]. It was found that two or three nitro groups exert a very powerful effect, such that 2,4,6-trinitrochlorobenzene and an acyl chloride were comparable in hydrolytic reactivity, whereas chlorobenzene requires a higher temperature for hydrolysis [13–18].

In organic bases such as pyridine and quinoline, the nitrogen heteroatom is an activating group which is almost as strong as a nitro group [19, 20]. Pyridine derivatives undergo nucleophilic substitution much more easily than the corresponding benzenes, especially at both the 2- and 4-positions, owing to the presence of the electronegative nitrogen atom in the aromatic ring [15, 21–25]. This increase in the susceptibility of pyridines to nucleophilic attack is a further reflection of the electron-attracting character of the ring nitrogen [23, 24].

In agreement with the classic work of Orvik and Bunnett [26] the results for ethyl 2,4,6-trinitrophenyl ether indicated that substitution involves the specific base–general acid catalysis mechanism (SB-GA) in which leaving group expulsion is the overall rate-limiting step. However, the phenoxy group is a considerably better leaving group than the ethoxy group, and the observation of base catalysis in reactions of phenyl aryl ethers was best explained in terms of rate-limiting proton transfer from a zwitterionic intermediate to the base [27, 28]. El-Zahraa et al. [29] have previously examined the kinetics of the reaction of 2-chloro-3,5-dinitropyridine with *meta*- and *para*-substituted anilines in methanol at different temperatures to give 2-anilino-3,5-dinitropyridine derivatives. The kinetics of

B. H. Asghar (✉)
Department of Chemistry, Faculty of Applied Sciences, Umm Al-Qura University, P.O. Box: 9569, Makkah, Saudi Arabia
e-mail: basim15@yahoo.com



Scheme 1

the displacement of chloride and phenoxide from the strongly activated compounds 1-chloro-2,4-dinitrobenzene and 1-phenoxy-2,4-dinitrobenzene by aliphatic amines have also been investigated [30]. This study identified the following major factors affecting values of k_1, the rate constant for nucleophilic attack: (a) steric effects at the reaction centre; rate constant values decrease with steric congestion at the reaction centre; steric effects increase in the order Cl < OPh; (b) ground-state stabilization, involving resonance interactions between the phenoxy group and the ring, may decrease reactivity.

In continuation of our previous studies in the field of nucleophilic aromatic substitution [19, 31–35], this work involved the study of the kinetics of the reactions between 2-chloro-3,5-dinitropyridine (**1a**) or 2-ethoxy-3,5-dinitropyridine (**1b**) with a series of substituted anilines (4-OMe, 4-Me, H and 4-Cl, **2a**–**2d**), in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) in DMSO (Scheme 1). The results were compared with those reported in earlier studies for the reaction of 2-phenoxy-3,5-dinitropyridine with anilines [33]. The pK_a values for the substituted anilinium ions in DMSO were available from previous work using the proton-transfer equilibrium with 2,4-dinitrophenol [36]. We investigated the heteroaromatic reactivity and the effect of the aniline substituents on the rate of the reaction.

Results and discussion

Spectroscopic characterisation of 2-anilino-3,5-dinitropyridines

The reactions of 0.2 g 2-chloro-3,5-dinitropyridine (**1a**) (1.3×10^{-3} mol) with 1 cm^3 *para*-substituted anilines **2a**–**2d** (0.01 mol) in the presence of 0.1 g DABCO (1×10^{-3} mol) dissolved in ethanol gave the corresponding substitution products **5a**–**5d**. ^{1}H NMR spectra recorded in DMSO-d_6 indicated an anilinodechlorination process with the formation of 2-anilino-3,5-dinitropyridine derivatives (Table 1).

Rate and equilibrium studies

Rate measurements of the reactions of **1a** and **1b** with substituted anilines **2a**–**2d** were generally made in the presence of DABCO and DABCO hydrochloride, 0.01 mol dm^{-3} in DMSO at 25 °C. The products exhibited absorption maxima at ca. 375 or 395 nm. The concentration of **1a** or **1b** was kept at 5×10^{-5} mol dm^{-3}, and was very much lower than that of the other components (one of the substituted anilines **2a**–**2d** and DABCO). Under these conditions, accurate first-order rates were observed and the variation in value of the rate constant with aniline and

Table 1 Properties and ^{1}H NMR data for 2-substituted anilino-3,5-dinitropyridines **5a**–**5d**

Comp.	R	Yield/%	M.p./°C	Pyridyl protons			Aryl protons	
				–NH	H_4	H_6	$H_{2',6'}$	$H_{3',5'}$
1a	–	–	–	–	8.99 (d)	9.45 (d)	–	–
					$J_{4,6} = 2.2$	$J_{6,4} = 1.8$		
5a[a]	4-OMe	51	176	10.46 (s)	9.31 (d)	9.38 (d)	7.56 (d)	7.05 (d)
					$J_{4,6} = 2.2$	$J_{6,4} = 2.2$	$J = 8.8$	$J = 8.8$
5b[b]	4-Me	95	148	10.53 (s)	9.34 (d)	9.38 (d)	7.56 (d)	7.33 (d)
					$J_{4,6} = 2.3$	$J_{6,4} = 2.3$	$J = 8.3$	$J = 8.2$
5c[c]	H	94	130	10.59 (s)	9.37 (d)	9.39 (d)	7.69 (d)	7.54 (t)
					$J_{4,6} = 2.3$	$J_{6,4} = 2.3$	$J = 7.8$	$J = 7.3$
5d	4-Cl	95	187	10.55 (s)	9.36 (d)	9.40 (d)	7.49 (d)	7.49 (d)
					$J_{4,6} = 2.4$	$J_{6,4} = 2.3$	$J = 8.8$	$J = 8.8$

δ/ppm, *J*/Hz

[a] 4-OCH_3 protons appear at 3.92 ppm (s, 3H)

[b] 4-CH_3 protons appear at 2.49 ppm (s, 3H)

[c] H-4′ proton appears at 7.38 ppm (t, 1H)

DABCO concentrations was examined. Measurements were also made in the absence of DABCO, and plots of the second-order rate constant, k_{obs}/[aniline], versus aniline concentration were linear with positive intercepts.

These results are interpreted in terms of the processes shown in Scheme 1. It is known that phenoxide is a considerably better leaving group than ethoxide, by a factor of ca. 10^6 [27, 28, 37, 38]. Values of the rate constant [30] for nucleophilic attack at the 1-position increase with increasing ring activation, but may be reduced by steric repulsion at the reaction centre, which increases in the order Cl < OPh.

The failure to observe **4**, the intermediate on the substitution pathway, may be attributed to its rapid decomposition through loss of chloride. The assumption that **3** may be treated as a steady-state intermediate leads to the rate expression of Eq. (1), where k_{An} and k_{DABCO} represent the respective bases [28].

$$k_{obs} = \frac{k_1[An](k_2 + k_{An}[An] + k_{DABCO}[DABCO])}{k_{-1} + k_2 + k_{An}[An] + k_{DABCO}[DABCO]} \quad (1)$$

The results, which provide evidence for base catalysis, indicate that the condition

$$k_{-1} \gg k_2 + k_{An}[An] + k_{DABCO}[DABCO]$$

applies, so that Eq. (1) reduces to Eq. (2):

$$k_{obs} = K_1[An](k_2 + k_{An}[An] + k_{DABCO}[DABCO]) \quad (2)$$

Rate measurements at 395 nm showed a single first-order process for the reaction of **1a** with **2a**. Values of the rate constant, k_{obs}/[**2a**], for the reaction with **2a** are given in Table 2. Values calculated with $K_1k_{DABCO} = 162.18$ dm^6 mol^{-2} s^{-1}, $K_1k_{An} = 1.18$ dm^6 mol^{-2} s^{-1} and $K_1k_2 = 5.5 \times 10^{-3}$ dm^3 mol^{-1} s^{-1} were in good agreement with values of k_{obs}. Rate measurements at 375 nm showed a single first-order process for the reaction of **1b** with **2a**. Values of the rate constant, k_{obs}/[**2a**], for the reaction with **2a** are given in Table 3. Values calculated with $K_1k_{DABCO} = 1.12 \times 10^{-2}$ dm^6 mol^{-2} s^{-1}, $K_1k_{An} = 6.5 \times 10^{-5}$ dm^6 mol^{-2} s^{-1} and $K_1k_2 = 3.3 \times 10^{-5}$ dm^3 mol^{-1} s^{-1} were in good agreement with values of k_{obs}.

Table 2 Rate results for the reaction of **1a** with **2a** in DMSO at 25 °C

[**2a**]/mol dm^{-3}	[DABCO][a]/mol dm^{-3}	k_{obs}/[**2a**]/mol^{-1} dm^3 s^{-1}
0.05	–	0.065
0.075	–	0.094
0.10	–	0.123
0.20	–	0.242
0.30	–	0.360
0.02	0.10	16.250
0.10	0.10	16.342
0.25	0.10	16.520
0.10	0.03	4.989
0.10	0.06	9.854

[a] Solutions containing DABCO also contain DABCO hydrochloride, 0.01 mol dm^{-3}. Measurements were made at 395 nm

It is known that reaction at unsubstituted ring positions to give anionic adducts may precede the attack at the 2-position [27, 28, 37, 38]. Previous work at lower base concentrations and in different solvents did not find evidence for base catalysis [26–28, 39]. However, the present work showed that in DMSO, such catalysis occurs, and the values of K_1k_{An} and K_1k_{DABCO} for reactions of **1a** and **1b** with anilines can be calculated. Base catalysis indicates

Table 3 Rate results for the reaction of **1b** with **2a** in DMSO at 25 °C

[**2a**]/mol dm^{-3}	[DABCO][a]/mol dm^{-3}	k_{obs}/[**2a**]/mol^{-1} dm^3 s^{-1}
0.05	–	0.000036
0.075	–	0.000037
0.10	–	0.000039
0.20	–	0.000046
0.30	–	0.000053
0.02	0.10	0.0015
0.2	0.10	0.0016
0.3	0.10	0.0017
0.10	0.03	0.00037
0.10	0.06	0.00071

[a] Solutions containing DABCO also contain DABCO hydrochloride, 0.01 mol dm^{-3}. Measurements were made at 375 nm

Table 4 Summary of results for the reactions of anilines **2a**–**2d** with **1a** in DMSO at 25 °C

Aniline	K_1k_{DABCO}/ dm^6 mol^{-2} s^{-1}	K_1k_{An}/ dm^6 mol^{-2} s^{-1}	K_1k_2/ dm^3 mol^{-1} s^{-1}	pK_a (DMSO)[a]
4-OMe	162.18	1.18	5.5×10^{-3}	5.08
4-Me	77.62	0.70	3.3×10^{-3}	4.48
H	39.81	0.30	1.4×10^{-3}	3.82
4-Cl	14.12	0.10	4.5×10^{-4}	2.86

[a] Results from Ref. [36], pK_a values listed correspond to the conjugate acids of the anilines

Table 5 Summary of results for the reactions of anilines **2a**–**2d** with **1b** in DMSO at 25 °C

Aniline	K_1k_{DABCO}/ dm^6 mol^{-2} s^{-1}	K_1k_{An}/ dm^6 mol^{-2} s^{-1}	K_1k_2/ dm^3 mol^{-1} s^{-1}	pK_a (DMSO)[a]
4-OMe	1.12×10^{-2}	6.5×10^{-5}	3.3×10^{-5}	5.08
4-Me	5.88×10^{-3}	4.2×10^{-5}	2.1×10^{-5}	4.48
H	3.16×10^{-3}	2.0×10^{-5}	1.0×10^{-5}	3.82
4-Cl	1.09×10^{-3}	7.6×10^{-6}	3.8×10^{-6}	2.86

[a] Results from Ref. [36], pK_a values listed corresponding to the conjugate acids of the anilines

that proton transfer from the zwitterion to the base is rate limiting.

The presence of chloride or ethoxy groups rather than a phenoxy group is not expected to drastically affect the value of K_1 for zwitterion formation [29, 40]. The k_2 step is likely to involve intramolecular proton transfer from nitrogen to oxygen coupled with carbon–oxygen cleavage. Leaving group expulsion is part of the rate-limiting step here.

Values obtained for K_1k_{DABCO}, K_1k_2 and K_1k_{An} are summarised in Tables 4 and 5, together with pK_a values for the conjugate acids of the anilines, measured in DMSO. The highest value for 4-OMe indicates that the higher basicity of 4-OMe is reflected in higher values of K_1k_2, K_1k_{An} and K_1k_{DABCO}. Values of K_1k_{DABCO}, K_1k_2 and K_1k_{An} decrease strongly as the substituent R is made more electron withdrawing.

The proton transfer process, k_{DABCO}, will be strongly favoured thermodynamically. This is because protons are transferred to a strong base (DABCO). In the absence of steric effects, values would be close to the diffusion limit. The reaction centre in **3** is quite hindered; hence, values will be lower than the diffusion limit. However, since the steric effects will be the same for **2a**–**2d**, the value of k_{DABCO} will be the same for each aniline. Therefore, changes in K_1k_{DABCO} in **2a**–**2d** reflect changes in values of K_1, the equilibrium constant for the formation of the zwitterions, rather than changes in k_{DABCO}.

It is customary to correlate the effect of the *para*-substituent in the 2-anilino-3,5-dinitropyridines by the Hammett relationship [41]. Hammett constants σ are applied when there is no direct mesomeric interaction between the substituent and the reaction centre. Thus, a linear plot of values of log K_1k_{DABCO} for the reactions of **1a** and **1b** versus Hammett σ values gives a slope, ρ, of −2.2 for **1a** in Fig. 1, and −1.9 for **1b** (not shown). Since values of k_{DABCO} are expected to be independent of the nature of the remote substituent, this ρ value reflects the substituent effect on values of K_1. The negative value obtained is consistent with the increase in the positive charge on nitrogen associated with the formation of **3**.

The Brønsted relationship is generally applicable to combinations of nucleophiles and electrophiles. It has been successfully applied to S_NAr reactions of nitro-activated aromatic compounds with amines [42]. The Brønsted plot of log K_1k_{DABCO} shown in Fig. 2 for the reaction of **1a** with anilines versus the pK_a values of the corresponding anilinium ions provides further evidence for the steric requirement of the anilines. Thus, the slope of the plot, β_{nuc}, has a value of 0.42 for **1a** (and 0.45 for **1b**, not shown), and this low value is compatible with a steric

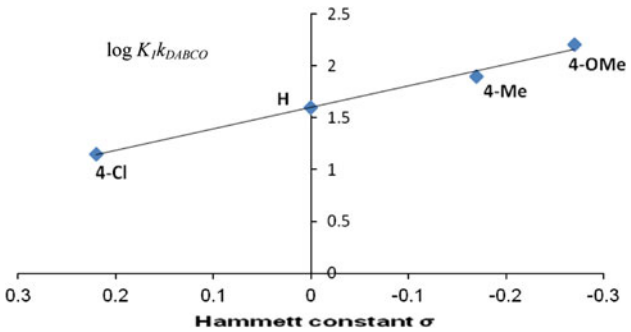


Fig. 1 Plot of log K_1k_{DABCO} for the reaction of **1a** with anilines **2a**–**2d** against the Hammett constant

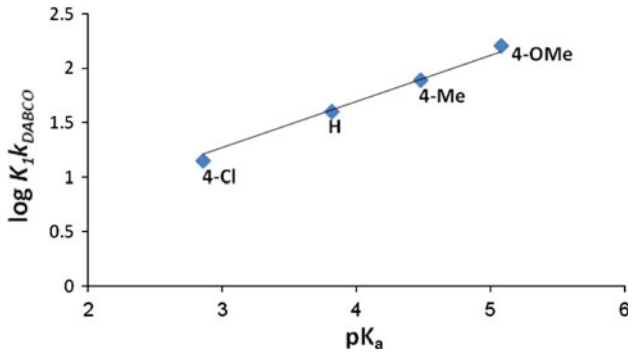


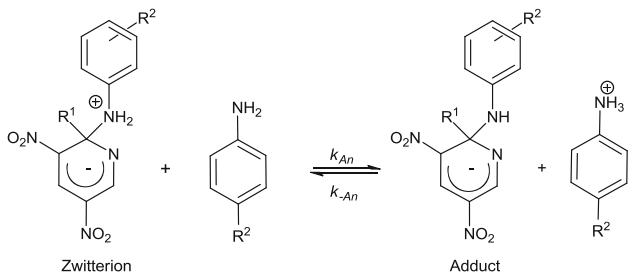
Fig. 2 Brønsted plot of log K_1k_{DABCO} versus pK_a values of the anilines **2a**–**2d** has a slope, β, of 0.42 for **1a**

effect involving a large separation of reactants in the transition state. As the transition state of a nucleophile implies (partial) donation of an electron pair from the nucleophile to the reaction centre, the Brønsted coefficient, β_{nuc}, is related to the extent of bond formation between the nucleophile and the reaction centre. However, the moderate values of ρ and β_{nuc} for the title reaction indicate that the bond-making process lags behind the π-bond breaking of the pyridine ring in the transition state to give the zwitterionic intermediate **3**.

Values of K_1k_2 show similar changes with the nature of the substituent as seen for the values of K_1k_{DABCO}. This implies that values of k_2 vary only slightly with the nature of the substituent R.

Values of K_1k_{An} decrease much more dramatically on going from **2a** to **2d**. This indicates that the k_{An} process is far more favourable with 4-methoxyaniline than with 4-chloroaniline. A possible explanation is that the proton-transfer equilibrium in Scheme 2 is not strongly thermodynamically favoured. Hence, as the basicity of the aniline decreases, the rate constant for the process is reduced.

The results in Tables 4 and 5 allow comparison of the reactions of **1a** and **1b** with the anilines **2a**–**2d**. They show that values of both K_1k_{DABCO} and K_1k_{An} were considerably higher for **1a** than for **1b**. Both electronic (leaving group) and steric factors will be important in determining the relative reactivities. Proton transfer from the zwitterions to DABCO will be strongly favoured thermodynamically, so



Scheme 2

that steric effects will be dominant in determining values of k_{DABCO}.

The ratio of the K_1k_{An} values for **1a/1b** is ca. 16,000, and is higher than the corresponding ratio of K_1k_{DABCO} values. This is likely a result of the reduction in the value of k_{An} in the reaction of **1b**, because the proton transfer process involved (Scheme 2) is less thermodynamically favourable than in the corresponding reaction involving **1a**.

In **1a**, 2-phenoxy-3,5-dinitropyridine, and **1b**, the rate constants for nucleophilic attack at the 2-position increased with increasing ring activation, which correlates with the electronegativities of the respective substituents. Table 6 compares the product K_1k_{DABCO} for the reactions of the anilines **2a**–**2d** with **1a**, **1b**, and 2-phenoxy-3,5-dinitropyridine [33]. The product had a higher value for the reaction of **1a** than for **1b** or the phenoxy compound (**1a/1b** was ca. 15,000; **1a**/2-phenoxy-3,5-dinitropyridine was ca. 1,300). As previously discussed [37], the dominant factor was the higher value of k_{DABCO} associated with the lower steric hindrance to proton transfer when the reaction occurred at an unsubstituted ring position. The value of K_1 must also be considerably higher for **1a** than for **1b**. Despite the fact that the bulky phenoxy group is a good leaving group and also benefits from greater steric strain relief in the transition state compared to the chloride, the large difference in Brønsted acidities for the conjugate acids of these groups would appear to dominate their leaving group abilities in this reaction, as reflected by the rate constants. The order of reactivities was found to be **1a** > 2-phenoxy-3,5-dinitropyridine > **1b**, which illustrates the difficulty in quantifying these factors. It should be noted that because proton transfer is rate determining in all these reactions, it is not possible to obtain values for the rate constants k_1 and k_{-1} relating to formation of the zwitterionic intermediates.

Table 6 Comparison of the reactions of 2-phenoxy-3,5-dinitropyridine, **1a**, and **1b** with anilines **2a**–**2d** in DMSO

Anilines	$K_1k^a_{DABCO}$/ dm^6 mol^{-2} s^{-1}	$K_1k^b_{DABCO}$/ dm^6 mol^{-2} s^{-1}	$K_1k^c_{DABCO}$/ dm^6 mol^{-2} s^{-1}
4-MeO	0.120	162.18	1.12×10^{-2}
4-Me	0.052	77.620	5.88×10^{-3}
H	0.028	39.810	3.16×10^{-3}
4-Cl	0.012	14.120	1.09×10^{-3}

[a] Results from Ref. [33]: reaction of 2-phenoxy-3,5-dinitropyridine with anilines

[b] Results from the present work: reaction of 2-chloro-3,5-dinitropyridine (**1a**) with anilines

[c] Results from the present work: reaction of 2-ethoxy-3,5-dinitropyridine (**1b**) with anilines

Conclusions

Activation parameters and ρ values were determined for the nucleophilic aromatic substitution reactions of various anilines with 2-substituted 3,5-dinitropyridines in the presence of DABCO in DMSO. The kinetic data suggested that the S_NAr reaction occurred through a two-step mechanism involving initial nucleophilic attack followed by either base-catalysed or uncatalysed conversion (direct elimination of the leaving group) to the product. The base-catalysed pathway was likely to involve rate-limiting proton transfer from the zwitterionic intermediate to DABCO to yield the anionic σ-adduct. The trends in reactivity and leaving group ability were consistent with established substituent effects.

Experimental

2-Chloro-3,5-dinitropyridine (**1a**) was obtained from Aldrich and purified by crystallization twice from methanol/light petroleum as yellow needles. 2-Ethoxy-3,5-dinitropyridine (**1b**) was prepared by the reaction of **1a** with one equivalent sodium ethoxide in ethanol [43]. 4-Methoxyaniline (**2a**), 4-methylaniline (**2b**), aniline (**2c**) and 4-chloroaniline (**2d**) were supplied by Aldrich and were purified by crystallization or vacuum distillation. DABCO and DMSO were the purest commercially available grades. Amine salts were prepared in solution by the accurate neutralization of amines with concentrated hydrochloric acid.

^{1}H NMR spectra were recorded in DMSO-d_6 at 24 °C using a Bruker Avance-400 instrument. UV–Vis spectra and rate measurements were conducted with a Shimadzu UV-2101 PC. All measurements were made at 25 °C. First-order rate constants, precise to ±3 %, were evaluated using standard methods.

References

1. Miller J (1969) Aromatic nucleophilic substitution. Elsevier, New York, p 18
2. Strauss M (1970) Chem Rev 70:667
3. Terrier F (1991) Nucleophilic aromatic displacement. VCH, New York
4. Terrier F (1982) Chem Rev 82:77
5. Asghar BHM, Crampton MR (2007) J Phys Org Chem 20:702
6. Asghar BHM, Crampton MR (2007) Org Biomol Chem 5:1646
7. Asghar BHM, Crampton MR, Isanbor C (2008) Can J Chem 86:225
8. Asghar BHM (2010) J Saudi Chem Soc 14:261
9. Crampton MR, Emokpae TA, Howard JAK, Isanbor C, Mondal R (2003) Org Biomol Chem 1:1004
10. Emokpae TA, Uwakwe PU, Hirst J (1993) J Chem Soc Perkin Trans 2:125
11. Emokpae TA, Uwakwe PU, Hirst J (1991) J Chem Soc Perkin Trans 2:509
12. Emokpae TA, Hirst J, Uwakwe PU (1990) J Chem Soc Perkin Trans 2:2191
13. Loudon JD, Smith DM (1964) J Chem Soc 2806
14. Etsinger RIL, Ramsay OB, McCian JH (1965) J Am Chem Soc 87:2945
15. Bunnett JF, Zahler RE (1951) Chem Rev 49:273
16. Ross SD (1963) Prog Phys Org Chem 1:31
17. Beckwith AL, Leahy GD, Miller J (1952) J Chem Soc 3552
18. Bunnett JF, Nudelman NS (1969) J Org Chem 34:2038
19. Hamed EA (1997) Int J Chem Kinet 29:599
20. Chapman NB, Russell-Hill DQ (1956) J Chem Soc 1563
21. Pietra FQ (1969) Rev Chem Soc 23:504
22. Eggiman W, Schmid P, Zollinger H (1975) Helv Chim Acta 58:257
23. Brenelli ECS, Moran PJS (1989) J Chem Soc Perkin Trans 2:1219
24. Brenelli ECS, Moran PJS, Rodrigue JAR (1989) J Chem Res (S) 389
25. Chupakhin ON, Charushin VN (1988) Tetrahedron 44:1
26. Orvik JA, Bunnett JF (1970) J Am Chem Soc 92:2417
27. Chamberlin R, Crampton MR (1995) J Chem Soc Perkin Trans 2:1831
28. Crampton MR, Robotham IA (1998) Can J Chem 76:627
29. El-Zahraa F, El Hegazy M, Abdel Fattah SZ, Hamed EA, Sharaf SM (2000) J Phys Org Chem 13:549
30. Crampton MR, Emokpae TA, Isanbor C, Batsanov AS, Howard JAK, Mondal R (2006) Eur J Org Chem 1222
31. Hamed EA, El-Bardan AA, Saad EF, Gohar GM, Hassan GM (1997) J Chem Soc Perkin Trans 2:2415
32. El-Bardan AA (1999) J Phys Org Chem 12:347
33. Asghar BH (2008) Int J Chem Kinet 41:198
34. Asghar BH (2010) E J Chem 7:253
35. Asghar BH, Fathalla FM, Hamed EA (2009) Int J Chem Kinet 41:777
36. Asghar BHM, Crampton MR (2005) Org Biomol Chem 3:3971
37. Crampton MR, Robotham AI (1997) J Chem Res (S) 22
38. Bernasconi CF, Muller MC (1978) J Am Chem Soc 100:5530
39. Hirst J, Hussain G, Onyido I (1986) J Chem Soc Perkin Trans 2:397
40. Chamberlin R, Crampton MR, Knight RL (1993) J Chem Res (S) 444
41. Hammett LP (1954) Physical organic chemistry. McGraw-Hill, New York
42. Dixon JE, Bruice TC (1974) J Am Chem Soc 94:2052
43. Barycki J, Plazek E (1963) Roczniki Chem 37:1443