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Kinetics of the reaction of 2-chloro-3-nitro- and 2-chloro-5-nitropyridines with aryloxide ions in methanol

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ABSTRACT: The kinetics of the reaction of 2-chloro-3-nitropyridine (*ortho*-like) and 2-chloro-5-nitropyridine (*para*-like) with a series of aryloxide ions were studied in methanol at different temperatures. Plots of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$ for both reactions gave good straight lines with isokinetic temperatures of 168 and 195 °C. Good linear relationships were obtained from the plots of log k_2 against σ° values with relatively large negative ρ values indicating the formation of Meisenheimer σ-complex intermediates. Plots of log k_2 against pK_a values gave good straight lines indicating that the reactions show an appreciable degree of bond formation in the transition state. An addition–elimination mechanism is suggested. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: chloronitropyridines; aryloxide ions; addition–elimination reaction

INTRODUCTION

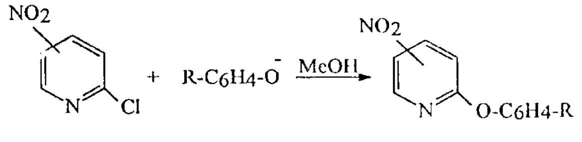
Owing to the presence of an electronegative nitrogen atom in the aromatic ring, pyridine derivatives undergo nucleophilic substitution much more easily than the corresponding benzenes, especially at the 2- and 4-positions.[1–8] The increase in liability of pyridines towards nucleophilic attack reflects the electron-withdrawing character of rings containing nitrogen.[4,9] Thus, the quantitative aspects of reactivity of heteroaromatic compounds towards different nucleophiles became of interest.[10–14]

Bunnett and Morath[15] have previously pointed out that in nucleophilic displacement reactions, *ortho*-activation of the nitro group predominates. However, others have reported that the *para*-nitro group is more effective than an *ortho*-group, depending upon the nature of the nucleophile.[16] A large number of papers have appeared which supported or argued against these proposals. Accordingly, many factors have been considered regarding the *ortho:para* ratio, namely the simple steric effect owing to the bulkiness of the *ortho*-nitro group, steric acceleration and steric exclusion of solvation in the transition states.[10,16–18]

In order to investigate the effect of the N-heteroatom on reactivity, and in continuation of previous studies on the transmission of the substituent electronic effect in the nucleophile[10,12,14] and *ortho* versus *para* activation, the reactions of 2-chloro-3-nitropyridine (**1**) (*ortho*-like) and 2-chloro-5-nitropyridine (**2**) (*para*-like) with aryloxide ions **3a–h** in methanol were examined. The results reported in this paper will help to clarify the following points: (a) the effect of substituents and the applicability of linear free energy relationships; (b) the nature of the transition state during the nucleophilic displacement; and (c) the effect of changes in the reactivity of the chloronitropyridines on the structure of this transition state as indicated by the *ortho:para* ratio.

RESULTS AND DISCUSSION

The reaction of **1** and **2** with aryloxide ions **3a–h** gave the corresponding 2-aryloxy derivatives [Eqn. 1]. Elemental analysis and UV, IR and ^{1}H NMR spectra indicated aryloxy dechlorination processes with the formation of 2-aryloxy-3-nitropyridines (**4a–h**) and 2-aryloxy-5-nitropyridines (**5a–h**) (Tables 1 and 2, respectively).



1 or 2 3a - h 4a - h , 5a - h (1)

a,R = H b,R = 4 - CH_3 c,R = 4 - OCH_3
d,R = 4-Cl e,R = 4 - Br f,R = 4 - NO_2
g,R = 3-CH_3 h,R = 3 - CF_3

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Table 1. Properties, UV, IR and ^1H NMR spectral data and elemental analyses of 2-aryloxy-3-nitropyridines (4a–h)

						ν (cm^{-1})			^1H NMR [δ (ppm)] in $CDCl_3$								Calc. (%) (Found)		
Compound **4**	R	Yield (%)	M.p. (°C)	λ[a] (nm)	ε(l mol^{-1} cm^{-1})	NO_2	C=C	C–O–C	H-2′,6′ (d, 2H)		H-3′,5′ (d, 2H)		H-5 (t, 1H)	H-4 (d, 1H)	H-6 (d, 1H)	Molecular formula	C	H	N
a	H	93	75[b]	207	11110														
				303	5970														
b	4-CH_3[c]	78	112	227	11340	1507	1587	1260	7.22		7.06		7.13	8.31	8.36	$C_{12}H_{10}N_2O_3$	62.60	4.34	12.17
				304	4850	1350		1065									(62.57	4.31	12.14)
c	4-OCH_3[d]	88	122	219.5	14610	1502	1578	1250	7.09		6.94		7.11	8.31	8.35	$C_{12}H_{10}N_2O_4$	58.53	4.06	11.38
				292	2370	1347		1030									(58.22	4.00	11.12)
d	4-Cl	91	91	228	14520	1510	1581	1271	7.13		7.38		7.18	8.31	8.37	$C_{11}H_7ClN_2O_3$	52.80	2.80	11.20
				301	5180	1352		1020									(52.80	2.79	11.18)
e	4-Br	94	95	228.5	14750	1508	1587	1270	7.07		7.55		7.15	8.31	8.38	$C_{11}H_7BrN_2O_3$	44.74	2.37	9.49
				303	4400	1360		1080									(44.71	2.36	9.48)
f	4-NO_2	98	136	227	13750	1511	1587	1260	7.35		8.31		7.28	8.35	8.39	$C_{11}H_7N_3O_5$	50.57	2.68	16.09
				278.5	11370	1355		1060									(50.55	2.67	16.00)
				395	5660				H-2′	H-4′	H-5′	H-6′							
									(s, 1H)	(d, 1H)	(t, 1H)	(d, 1H)							
g	3-CH_3[e]	72	73	226.5	11280	1509	1587	1251	6.98	7.26	7.07	7.33	7.11	8.31	8.35	$C_{12}H_{10}N_2O_3$	62.60	4.34	12.17
				304	4820	1348		1040									(62.58	4.34	12.09)
h	3-CF_3	68	65	228	14520	1510	1589	1245	7.46	7.57	7.40	7.52	7.22	8.33	8.40	$C_{12}H_7F_3N_2O_3$	50.70	2.46	9.81
				303	4400	1340		1052									(50.65	2.45	9.76)

[a] In methanol.
[b] Lit.[28] 75 °C.
[c] 4-CH_3 appear at δ 2.35 (s, 3H).
[d] 4-OCH_3 appear at δ 3.80 (s, 3H).
[e] 3-CH_3 appear at δ 2.38 (s, 3H).

Table 2. Properties, UV, IR and ^{1}H NMR spectral data and elemental analyses of 2-aryloxy-5-nitropyridines (5a–h)

Compound 5	R	Yield (%)	M.p. (°C)	λ[a] (nm)	ε (l mol^{-1} cm^{-1})	ν (cm^{-1})			^{1}H NMR [δ (ppm)] in CDCl$_3$							Molecular formula	Calc. (%) (Found)		
						NO$_2$	C=C	C–O–C	H-2′,6′ (d, 2H)		H-3′,5′ (d, 2H)		H-3 (d, 1H)	H-4 (d, 1H)	H-6 (s, 1H)		C	H	N
a	H	91	72[b]	206	11450														
				294	2770														
b	4-CH$_3$[c]	88	86	226.5	18580	1508	1587	1265	7.20		7.0		6.80	8.35	9.07	$C_{12}H_{10}N_2O_3$	62.60	4.34	12.17
				291.5	9120	1350		1038									(62.59	4.33	12.15)
c	4-OCH$_3$[d]	91	111	216.5	12620	1507	1585	1260	6.70		6.96		6.75	8.30	9.05	$C_{12}H_{10}N_2O_4$	58.53	4.06	11.38
				292	16440	1348		1030									(58.47	4.03	11.36)
d	4-Cl	95	90	226.5	7060	1511	1586	1260	7.05		7.40		6.95	8.45	9.00	$C_{11}H_7ClN_2O_3$	52.80	2.80	11.20
				292.5	8290	1349		1082									(52.79	2.80	11.17)
e	4-Br	93	63	227.5	12640	1508	1587	1292	7.02		7.55		7.06	8.45	9.03	$C_{11}H_7BrN_2O_3$	44.74	2.37	9.49
				290.5	16110	1355		1063									(44.70	2.32	9.45)
f	4-NO$_2$	92	77	227	9370	1510	1587	1262	7.33		8.33		6.81	8.44	9.04	$C_{11}H_7N_3O_5$	50.57	2.68	16.09
				290	20890	1352		1035									(50.56	2.66	16.05)
									H-2′ (s, 1H)	H-4′ (d, 1H)	H-5′ (t, 1H)	H-6′ (d, 1H)							
g	3-CH$_3$[e]	81	52	226.5	8820	1506	1582	1260	6.96	7.10	7.33	7.00	6.91	8.44	9.04	$C_{12}H_{10}N_2O_3$	62.60	4.34	12.17
				291	19390	1350		1045									(62.61	4.32	12.15)
h	3-CF$_3$	73	44	228	14520	1510	1588	1245	7.43	7.35	7.53	7.57	7.09	8.50	9.00	$C_{12}H_7F_3N_2O_3$	50.70	2.46	9.85
				303	4400	1340		1052									(50.67	2.46	9.80)

[a] In methanol.
[b] Lit.[28] 72 °C.
[c] 4-CH$_3$ appear at δ 2.35 (s, 3H).
[d] 4-CCH$_3$ appear at δ 3.85 (s, 3H).
[e] 3-CH$_3$ appear at δ 2.37 (s, 3H).

Table 3. Second-order rate constants, activation parameters and ρ for the reaction of 2-chloro-3-nitropyridine (**1**) with aryloxide ions **3a–h** in methanol

Compound **4**	R	k_2 (10^{-5} lmol^{-1} sc^{-1}) 30 °	40 °C	50 °C	$\Delta H^{\#}$ (k cal mol^{-1})	$\Delta S^{\#}$ (cal mol^{-1} K^{-1})
a	H	3.25	8.12	19.50	17.1	−23.5
b	4-CH_3	5.33	11.19	27.05	15.4	−26.9
c	4-OCH_3	6.91	14.86	32.82	15.0	−27.8
d	4-Cl	1.12	3.01	7.85	18.4	−20.8
e	4-Br	1.49	3.72	9.31	17.5	−22.3
f[a]	4-NO_2	0.24[b]	0.81	2.52	21.3	−13.7
g	3-CH_3	3.90	10.09	21.27	16.1	−25.1
h	3-CF_3	0.69	1.82	5.12	19.8	−16.7
ρ		-1.39 ± 0.03	-1.23 ± 0.02	-1.09 ± 0.02		

[a] k_2 at 60 °C = 8.92×10^{-5} l mol^{-1} s^{-1}.
[b] Extrapolated value.

The kinetics of the reactions of **1** and **2** with **3a–h** in methanol were studied spectrophotometrically under pseudo-first-order conditions at three temperatures (30, 40 and 50 °C), except for **3f** (R = 4-NO_2), which was studied electrometrically at 40, 50 and 60 °C. A second-order reaction was concluded from the straight lines passing through the origin for the plots of the reaction rate constant (k_{obs}) versus aryloxide ion concentrations (in the range of 0.1 –1 M), where the concentrations of **1** and **2** remained constant (1×10^{-3} M). Thus the overall second-order rate constants were calculated using Eqn. 2. For practical reasons an aryloxide ion concentration of 1 M for the reactions with **1** and **2** was chosen for all comparative experiments.

$$k_2 = k_{obs}/[\text{aryloxide ion}] \qquad (2)$$

In the present work, concurrent and consecutive methanolysis were avoided by adding a tenth of the original amount of the free phenol, thus shifting the equilibrium towards the aryloxide ion [Eqn. 3].

$$\bar{\mathrm{O}}\mathrm{Ar} + \mathrm{MeOH} \rightleftharpoons \mathrm{ArOH} + \bar{\mathrm{O}}\mathrm{Me} \qquad (3)$$

The absence of a methanolysis reaction was established by the substantially quantitative isolation of the pure diaryl ethers as the sole products in each reaction. Also, no change in the band spectra of both **1** and **2** (1×10^{-3} M) at 30 °C was observed when an attempt was made to react them with 1 M phenol in methanol.

Examination of the data in Tables 3 and 4 shows that **2** (*para*-like) reacts with **3a–h** *ca* 4–13 times faster than **1** (*ortho*-like). This ratio is similar to that found for the reaction of *p*-chloronitrobenzene ($k_2 = 1.33 \times 10^{-4}$ l mol^{-1} s^{-1}) and its *ortho* analogue ($k_2 = 1.46 \times 10^{-5}$ l mol^{-1} s^{-1}) these reactions were studied electrometrically in methanol at 30 °C using 0.01 M substrate and 0.1 M sodium phenoxide ($k_2 = k_{obs}$/[phenoxide ion]). This is consistent with the following: (a) steric hindrance may be a factor inhibiting *ortho*-substitution; this originates from the retardation of the attack of the nucleophile in the

Table 4. Second-order rate constants, activation parameters and ρ for the reaction of 2-chloro-5-nitropyridine (**2**) with aryloxide ions **3a–h** in methanol

Compound 5	R	k_2 (10^{-4} l mol^{-1} s^{-1}) 30 °C	40 °C	50 °C	$\Delta H^{\#}$ (kcal mol^{-1})	$\Delta S^{\#}$ (cal mol^{-1} K^{-1})
a	H	2.69	4.91	10.98	13.2	−31.1
b	4-CH_3	4.94	8.57	17.50	11.9	−34.4
c	4-OCH_3	7.88	14.02	25.02	10.8	−36.9
d	4-Cl	0.62	1.45	3.31	15.7	−25.8
e	4-Br	0.84	1.82	4.66	14.7	−28.7
f[a]	4-NO_2	0.10[b]	0.24	0.66	19.1	−18.8
g	3-CH_3	4.12	7.71	15.12	12.6	−32.1
h	3-CF_3	0.35	0.84	2.21	17.4	−21.5
ρ		-1.84 ± 0.02	-1.68 ± 0.03	-1.50 ± 0.01		

[a] k_2 at 60 °C = 1.59×10^{-4} l mol^{-1} s^{-1}.
[b] Extrapolated value.

transition state; (b) for any σ-adduct-forming reactions a *para*-nitro group in **2** is more stable than an *ortho*-nitro group in **1** by *ca* 6 kJ.[19] This largely satisfies the tendency of the charged atoms in the transition state of **2** to attract polar solvent molecules.[11] The higher reactivity of **1** and **2** compared with the corresponding *o*-and *p*-nitrochlorobenzenes towards phenoxide ions is due to the presence of an aza group in the former compounds, which stabilizes the negative charge developed in the intermediate.[10,11] On the other hand, these ratios (*ca* 4–13 times) are lower than those found for the reactions of the same substrates with arenethiolates in methanol (*ca* 10–31 times).[12] This is due to the nucleophilicity or arenethiolate ions, which is known to be greater than that of aryloxide ions containing the same substituents.[20]

The presence of an aza group instead of a nitro group in the 5-nitro derivative **2** ($k_2 = 2.69 \times 10^{-4}$ l mol^{-1} s^{-1}) (Table 4), causes a decrease in the reaction rate with phenoxide ion relative to 1-chloro-2,4-dinitrobenzene ($k_2 = 15.1 \times 10^{-4}$ l mol^{-1} s^{-1})[20] [the reaction between 2,4-dinitrochlorobenzene (0.01 M) and phenoxide ion (0.1 M) was re-examined in methanol at 30 °C and gave a consistent value of the rate ($k_2 = 15.6 \times 10^{-4}$ l mol^{-1} s^{-1}) with that reported earlier[20]]. Hence an *ortho*-nitro group is more effective than an *ortho*-aza function. This may be due to (a) more efficient delocalization of the negative charge by a nitro group than by an aza group in the transition state[3,4b] and (b) release of steric strain in the transition state derived from 1-chloro-24-dinitrobenzene leading to steric acceleration of the rate.[18]

The activation parameters show that in each reaction series the entropy of activation values is negative, as expected for bimolecular reactions (Table 3 and 4). In both series the entropy of activation $\Delta S^{\neq}$ is substituent dependent. Since all the substituents are located in *para* or *meta* positions, direct steric interaction is unlikely, so that resonance and/or inductive effects are the operating factor. The differences in the $\Delta S^{\neq}$ values between the two series are consistent with greater solvent participation in the transition state of the reaction of the 5-nitro (**2**) than the 3-nitro (**1**) isomer.[21] In the 3-nitro (**1**) and 5-nitro (**2**) reactions, the transition states involve much greater charge separation than those existing in their reactants. Moreover, the charge separation in the transition state derived from the 5-nitro reaction exceeds that of the 3-nitro reaction. Therefore, the more polar nature of the transition states derived from the 5-nitro compound is accompanied by a considerable decrease in entropy relative to those of the 3-nitro derivative.

Within the same series, electron-donating substituents in arlyoxide ions, through their resonance and/or inductive effects, localize the formal charge on the oxygen atom. This favours the formation of more ordered transition states reflecting high and negative entropies of activation. On the other hand, the presence of electron-withdrawing substituents in the aryloxide ions alters their nature, leading to much more delocalization of the change on the oxygen atom, and hence reflecting low and negative entropies of activation.

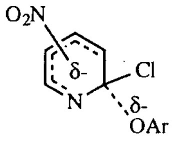
Plots of $\Delta H^{\neq}$ against $\Delta S^{\neq}$ reactions of both **1** and **2** with aryloxide ions **3a–h** gave good straight lines with slopes 168 and 195 °C, which are the values of the isokinetic temperatures, respectively (the temperature at which the substituent effect is supposed to be reversed). These values are not the real temperatures used in the kinetic runs.

The mechanism for the title reactions is common for all members in each series as indicated by (a) the good straight-line plots of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$, (b) the linear plots of $\log k_2$ at 50 °C against $\log k_2$ at 30 °C (gradient, 1.27 ± 0.03, $r = 0.99$ for the reaction of **1** and 1.22 ± 0.03, $r = 0.99$ for the reaction of **2**).

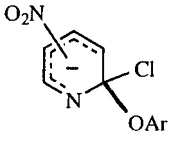
At the studied temperatures, an electron-releasing or-donating substituent in the *meta* or *para* position of the aryloxide ions increases the reaction rates while a similarly positioned electron-withdrawing substituent decreases it. This behaviour could be explained by the observation that the ratio $k4\text{-OCH}_3/k_{4\text{-NO}_2}$ for the 3-nitro reaction was 28.79, 18.30 and 13.02 and that for the 5-nitro reaction was 77.25, 58.41 and 37.45 at 30, 40 and 50 °C, respectively (Tables 3 and 4). Consequently, the variation of the rate constant depends on the nature and position of the substituent in the aryloxide ion. The order of decreasing reactivity of substituted phenoxide ions towards **1** and **2** in methanol is 4-OCH_3, 4-CH_3, 3-CH_3, H, 4-Br, 4-Cl, 3-CF_3, 4-NO_2. This order of decrease in magnitude of the substituent effect is expected on the basis of both inductive and resonance effects.

It is useful to correlate the effect of *meta* and *para* substituents in the substrate or the nucleophile with reactivity, to investigate the properties of the activated complex and also the reaction mechanism. A modified set of substituent constants, known as $\sigma°$, which better express a universal substituent character[22,] will subsequently be employed rather than Hammett σ-values. Plots of log k_2 values versus the $\sigma°$ constants for the various substituents in the aryloxide ions gave good straight lines for **1** and **2** at different temperatures. The ρ values for the reaction of aryloxide ions **3a–h** with **1** varied between -1.09 ± 0.02 ($r = 0.99$) and -1.39 ± 0.03 ($r = 0.99$), whereas those for the same reaction with **2** ranged between -1.50 ± 0.01 ($r = 0.99$) and -1.84 ± 0.02 ($r = 0.99$) (Tables 3 and 4, respectively). This shows that when the substituents are on the nucleophile, negative ρ values are obtained.[12] The ρ values are relatively large compared with those obtained from the aryloxy dechlorination of 1-chloro-2,4-dinitrobenzene in 80% dioxane–water at 65 °C ($\rho = -1.8$)[23] and those from the protonation of the aryloxide ions in 95% ethanol at 25 °C ($\rho = -2.36$).[24] Since in the latter process the aryloxide ion loses its negative charge completely,[24] a large proportion of the charge on the aryloxide ion has been transfered to chloronitropyridine in the transition state. In other words, the approach of the aryloxide ion to C-2 leads to a cases where the pyridyl ring and the nitro group attain a negative charge, while C-2 itself exhibits a positive charge.

These facts are consistent with the concept that the transition state **I**, in which the aryloxide ions have become appreciably bonded to chloronitropyridine, closely resembles the Meisenheimer σ-complex intermediate II.



I



II

A significant feature of the results is that a plot of log (k/k_o) for the reactions of **1** against log (k/k_o) for the reactions of **2** exhibits a linear relationship with a slope very close to unity (gradient 1.27 ± 0.03, $r = 0.99$). This indicates that the structure of the transition state does not alter significantly with change in the substituent on the electrophilic species, despite the difference in reactivity caused by this change.

Good linear correlations are obtained from the plots of log k_2 for the reactions of aryloxide ions **3a–h** with **1** and **2** at 30 °C against the pK_a values of the corresponding substituted phenols,[24] with β values of 0.86 ± 0.01 ($r = 0.98$) and 1.22 ± 0.02 ($r = 0.99$), respectively. This indicates a similar sensitivity of the two reactions to the change in the nucleophilicity (polarizability) of the oxygen atom as a function of substituent in the nucleophile. Since β values are generally associated with bond formation in the transition state, the reactions of **1** and **2** with aryloxide ions in methanol show an appreciable degree of bond formation in the transition state.[25,26]

On the basis of experimental observations and kinetic data, it is evident that the reactions of **1** and **2** with **3a–h** follow second-order kinetics. The activation parameters and ρ values suggest an addition–elimination mechanism (S_NAr) similar to the commonly accepted aromatic bimolecular two-stage process in which the formation of the intermediate **II** is the rate-determining step with rapid decomposition of this intermediate into product[20,26,27] (k_2 k_1, k_1), Eqn. 4.

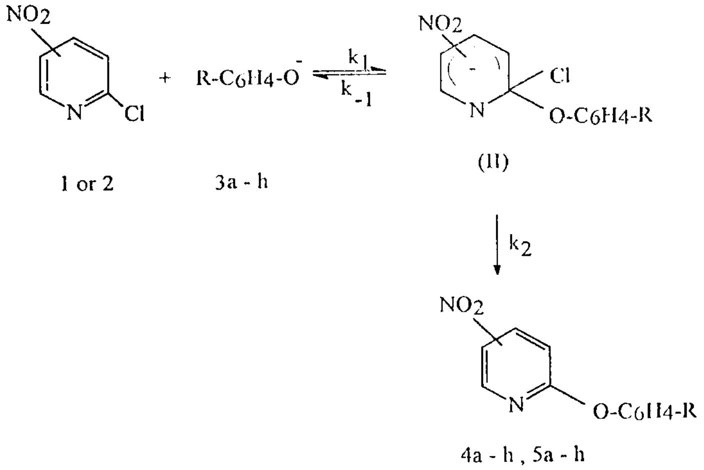
The derived rate expression explains the observed second-order kinetics, Eqn. 5. Hence the measured second-order rate constants will represent values for k_1.

$$\text{rate} = \frac{-\mathrm{d}[\mathbf{1}\text{ or }\mathbf{2}]}{\mathrm{d}t} = k_1[\mathbf{1}\text{ or }\mathbf{2}]\,[\mathbf{3}] \qquad (5)$$

EXPERIMENTAL

Melting-points were determined on a Thomas–Hoover capillary apparatus and are uncorrected. ^{1}H NMR spectra were obtained in $CDCl_3$ using a JEOL EX-270 spectrometer with Me_4Si as internal standard. IR spectra (KBr pellets) were measured on a Perkin-Elmer Paragon 1000 instrument. Electronic spectra were measured on a Shimadzu 160-A UV–visible spectrophotometer. Elemental analyses of the reaction products were carried out at the Faculty of Science, Cairo University, Egypt. Analytical thin-layer chromatography (TLC) was carried out on silica gel using light petroleum–ethyl acetate (9.5:0.5).

Starting Material. 2-Chloro-3-nitropyridine (**1**), m.p. 102 °C, and 2-chloro-5-nitropyridine (**2**), m.p. 107 °C, were commercially available (Aldrich) and were purified by crystallization twice from methanol as yellow crystals. It was found that the two compounds are unaffected by boiling methanol, as indicated from their m.p.s and UV spectra. The phenols **3a–h** used were phenol, 4-methylphenol, 4-methoxyphenol, 4-chlorophenol, 4-bromophenol, 4-nitrophenol, 3-methylphenol and 3-trifluoromethylphenol. These compounds were commercial products (Aldrich) and were purified by crystallization or vacuum distillation.



(4)

*Synthesis of 2-aryloxy-3-nitropyridines (**4a–h**) and 2-aryloxy-5-nitropyridines (**5a–h**).* 2-Chloro-3-nitropyridine (**1**) and 2-chloro-5-nitropyridine (**2**) (1 g, 6.31 mmol) were dissolved in absolute methanol (5 ml) and a methanolic solution of sodium phenolate (6.33 mmol) (prepared by dissolving 0.59–1.09 g of phenol in 5 ml of methanol containing 6.3 mmol of sodium metal) was added. The reaction mixture was refluxed for 1–2 h, cooled and then poured into 5% cold aqueous sodium hydroxide. The precipitated solid was filtered, washed well with cold water, dried and crystallized from benzene–light petroleum. The physical properties, spectral and elemental analyses are given in Tables 1 and 2.

Kinetic Measurements. The reactions of 2-chloro-3-nitropyridine (**1**) and 2-chloro-5-nitropyridine (**2**) with aryloxide ions **3a–h** in absolute methanol were followed spectrophotometrically at 30, 40 and 50 °C In all the reactions studied, the recorded spectra at the end of the reaction were identical with the spectra of the corresponding authentic sample of the substitution product in the same solvent.

A 1.0×10^{-2} M stock solution of **1** or **2** in absolute methanol was prepared and diluted before use to 1.0×10^{-3} M). Solutions of various sodium phenoxides (1 M) were prepared just before use by dissolving a weighted amount of phenol in a known volume of methanol and the required quantity (equal molarity) of standardized sodium methoxide in methanol. A sufficient excess of phenol over base was used to ensure virtually complete conversion of methoxide ion into phenoxide.

Solutions of **1** or **2** and sodium aryloxide ions were allowed separately to attain the desired temperature ±0.5 °C in a thermostated bath before being mixed. The change in absorbance with time was recorded on a Shimadzu 160-A UV–visible spectrophotometer at 350 nm.

Owing to the interference from absorption by 4-nitrophenoxide (**3f**) with the wavelength of maximum absorption of the 4-nitrophenoxy derivatives **4f** and **5f**, aryloxy dechlorination rate constants were determined by measuring the liberated chloride ion electrometrically[14] using a GVM 22c spot galvanometer. The first-order rate constants were calculated using Eqn. 6, where A_0, A_t and A_∞ are the values of the absorbance at zero time, time t and at the end of reaction, respectively.

$$\ln(A_\infty - A_t) = -k_{\text{obs}}t + \ln(A_\infty - A_0) \qquad (6)$$

For each system studied, the values of k_{obs} measured with different aryloxides were determined and the second-order rate constants $k_2 = k_{\text{obs}}$/[aryloxide ion] were calculated.

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