Aromatic Nucleophilic Substitutions with *o*- and *p*-Fluoronitrobenzenes in Aprotic Solvents. Steric Effects on the Base-catalysed Step

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The kinetics of the reaction between *o*- and *p*-fluoronitrobenzene with n- and iso-propylamine were studied in toluene and DMSO at several amine concentrations and temperatures in the range 30—100 °C. The results show that, contrary to the previous assumption, primary steric effects due to branching in the amine do not produce a large decrease in the reaction rate when the first step is rate determining. However, reactions with bulky amines can be extremely slow because of the reduced power of the amine as a hydrogen-bond acceptor catalyst, when the second step is rate determining. The reaction rate may be increased by the addition of a non-nucleophilic base or another hydrogen-bond acceptor catalyst such as dimethyl sulphoxide.

After Bunnett and Morath [1] discussed the factors governing the *ortho*:*para* ratio in the activation of aromatic nucleophilic substitution by the nitro group, a large number of papers appeared which supported or argued against their proposals.[2] Studies on *ortho*-effects and *ortho versus para* activation has again become an area of intense research at present because of fundamental [3–6] as well as applied (synthetic) interest.[7–9]

Many papers deal with the subject in terms of classical steric effects [10] regardless of which step is rate determining in the well accepted two-step mechanism for bimolecular aromatic nucleophilic substitution. Previous work in our laboratory with 4-R- and 6-R-2-nitro-X-benzene derivatives [11] showed the rate-determining step is crucial and suggested the need of a *thorough* examination of *para*-activated substrates. Since reactions with mononitrobenzene derivatives are usually very slow, studies on amine concentration rate dependence with these substrates are scarce, most of previous studies have been done with dinitro-derivatives.

In the present paper we report the reactions of *o*- and *p*-fluoronitrobenzene with n- and iso-propylamine in toluene and in DMSO. The observed results show that the very low rate of the reaction of isopropylamine with *p*-fluoronitrobenzene in toluene cannot be interpreted as a typical primary steric effect.

Results

The reactions of *o*- and *p*-fluoronitrobenzene with n- and with iso-propylamines in toluene and in DMSO proceed straightforwardly to give the expected *o*- and *p*-nitrophenylpropylamines. Complications arising from solvolyses giving the respective nitrophenol produced by traces of water in the system [12–14] were carefully avoided. A quantitative yield of the substitution product was obtained in all the present reactions.

In all cases the rate dependence on amine concentration was studied and the reactions were carried out under pseudo-first-order conditions. All runs afforded linear plots of ln $(A_\infty - A_t)$ *versus* time: k_ψ values reckoned as the slope calculated by the least-squares method ($r > 0.999$) and the specific second-order rate coefficients, k_A, were obtained by dividing k_ψ by the amine concentration.

Tables 1 and 2 gather the k_A values for the reactions of *o*-fluoronitrobenzene with n- and iso-propylamine, respectively, in toluene at 45, 60, and 80 °C for several amine concentrations; the corresponding activation parameters are also given. It can be observed that >10-fold increase in the amine concentration produces only a mild acceleration in the rate of both reactions. The activation parameters vary in a compensating way in the reactions with n-propylamine while for the reactions with iso-propylamine they are insensitive to variations in the nucleophile concentration.

Table 3 collects the specific second-order rate coefficients for the reactions of *p*-fluoronitrobenzene with n-propylamine in toluene at 45, 60, 80, and 100 °C at several amine concentrations, and the respective activation paramaters. Table 4 gathers similar data for the reaction of *p*-fluoronitrobenzene with isopropylamine in toluene: the reaction was studied at only two amine concentrations since its low rate prevents determinations at smaller nucleophile concentrations in a reasonable time. It can be observed in Table 3 that a 10-fold increase in amine concentration produces more than a 10-fold increase in the reaction rate. The enthalpy of reaction remains almost constant within experimental error, the rate increase being completely governed by a steady increase in the entropy of activation.

Tables 5 and 6 gather the k_A values and the activation parameters for the reactions of *o*-fluoronitrobenzene with n- and iso-propylamine, respectively, in DMSO at 30, 45, and 60 °C for several amine concentrations. It can be observed that the reactions are insensitive to the nucleophile concentration within experimental error. Again the activation parameters for the reaction with n-propylamine are more affected than those for the reaction with isopropylamine which are fully insensitive to the amine concentration. These reactions were carried out in order to compare the results with the data for *p*-fluoronitrobenzene in DMSO which were previously determined by Suhr.[15]

Discussion

There is abundant experimental [2,16–18] as well as theoretical evidence [19,20] that in aromatic bimolecular nucleophilic substitutions carried out in aprotic solvents, when fluorine is the nucleofugue, the second step of the mechanism depicted in the Scheme may be rate determining and base catalysis is frequently observed. Application of the steady-state hypotheses to the Scheme gives equation (1), from which k_1k_3/k_1 and k_1k_2/k_{-1} can be obtained by standard procedures. Reaction orders even higher than two for the amine have been recently observed in certain systems.[21,22]

$$k_A = \frac{k_1(k_2 + k_3[B])}{k_{-1} + k_2 + k_3[B]} \quad (1)$$

Nevertheless the reactions of *o*-fluoronitrobenzene studied in the present work are only slightly sensitive to the nucleophile concentration. The mild acceleration observed conforms to the

Table 1. Reactions of *o*-fluoronitrobenzene with n-propylamine in toluene[a]

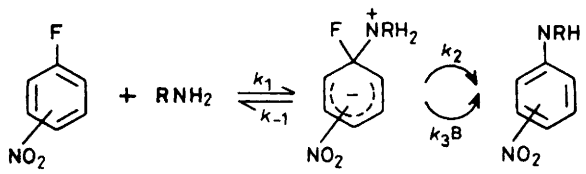
$[C_3H_7NH_2]$/M	$10^5 k_A$/l mol^{-1} s^{-1} 45 °C	60 °C	80 °C	$\Delta H^{\ddagger}$/kcal mol^{-1}	$-\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
0.034	2.27	4.92	10.80	9.68	49.5
0.067	2.40	4.95	11.65	9.81	49.0
0.168	2.46	5.23	18.09	11.47	43.7
0.337	2.69	5.27	23.82	13.76	36.3

[a] [*o*-Fluoronitrobenzene] 1.70 × 10^{-4}M.

Table 2. Reactions of *o*-fluoronitrobenzene with isopropylamine (IPA) in toluene[a]

[IPA]/M	$10^6 k_A$/l mol^{-1} s^{-1} 45 °C	60 °C	80 °C	$\Delta H^{\ddagger}$/kcal mol^{-1}	$-\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
0.034	5.12	12.51	32.37	11.54	46.6
0.069	5.09	12.83	32.71	11.28	47.7
0.172	5.80	14.35	35.97	11.41	46.8
0.221	5.90				
0.344	7.08	17.11	38.16	11.13	47.3
0.441	7.36				

[a] [*o*-Fluoronitrobenzene] 3.46 × 10^{-4}M.



Scheme.

mathematical form (2). When the effect is due to authentic base catalysis k' and k'' are the terms k_1k_2/k_{-1}, and k_1k_3/k_{-1}, respectively. Although this is not the case in the reactions of *o*-fluoronitrobenzene, k' and k'' values were calculated and gathered in Table 7 to help comparison with the reactions of *p*-fluoronitrobenzene. The very low $k'':k'$ ratio shows clearly that decomposition of the intermediate σ-complex is not a slow step.

$$k_A = k' + k''[B] \qquad (2)$$

The reactions mentioned above[2,16–18] were carried out with 2,4-dinitrofluorobenzene, for which the activation is mainly due to the mesomeric effect of the *p*-nitro group. In those reactions the *o*-nitro group in the intermediate complex may be out of the plane[1] the degree of the deviation depending on the steric requirements at the sp^3 carbon.[23,24] But when the *p*-nitro group is absent, efficient activation requires coplanarity of the *o*-nitro group (the nitro-oxygen atoms support strong negative charge as is shown by theoretical calculations).[20] The hydrogen-bond formed between the ammonium hydrogen and those oxygen atoms loosens the N–H bond (calculations show that a real hydrogen-transfer occurs in the vacuum),[20] which decreases the energy of the intermediate and helps it decompose to products. The entropy of activation must be relatively high for this intramolecular process. In agreement with this thought is the early observation that the reaction of *o*-fluoronitrobenzene with piperidine in benzene is not base catalysed while the reaction of *p*-fluoronitrobenzene is second order in amine.[25] The difficulties of comparing *o*:*p* ratio from measurements done with 1,2,4-trisubstituted compounds was previously shown by Hirst *et al.*[26] in the reactions with anionic nucleophiles. For reactions with amines the inconsistency may be even higher because of the already mentioned hydrogen-bond effect.

Table 3. Reactions of *p*-fluoronitrobenzene with n-propylamine in toluene[a]

$[C_3H_7NH_2]$/M	$10^6 k_A$/l mol^{-1} s^{-1} 45 °C	60 °C	80 °C	100 °C	$\Delta H^{\ddagger}$/kcal mol^{-1}	$-\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
0.102		0.09[b]	0.21[b]	0.34	7.39	68.7
0.285		0.24	0.54	0.86	7.24	67.2
0.481		0.45	0.96	1.60	7.22	66.5
0.677		0.71	1.46	2.34	6.78	66.1
1.190	0.86	1.51	3.08		7.51	62.8
1.420	1.08	1.92	3.93		7.61	62.1

[a] [*p*-Fluoronitrobenzene] 2.37 × 10^{-4}M. [b] Point excluded from the correlation of k_A *versus* [B].

Table 4. Reactions of *p*-fluoronitrobenzene with isopropylamine (IPA) in toluene[a]

[IPA]/M	$10^7 k_A$/l mol^{-1} s^{-1} 45 °C	60 °C	80 °C	$\Delta H^{\ddagger}$/kcal mol^{-1}	$-\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
1.00	0.54	1.05	2.33	8.69	64.6
1.35	0.85	1.50	3.38	8.19	65.3

[a] [*p*-Fluoronitrobenzene] 2.37 × 10^{-4}M.

Table 5. Reactions of *p*-fluoronitrobenzene with n-propylamine in DMSO[a]

$[C_3H_7NH_2]$/M	$10^4 k_A$/l mol^{-1} s^{-1} 20 °C	30 °C	45 °C	60 °C	$\Delta H^{\ddagger}$/kcal mol^{-1}	$-\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
0.037		17.90	30.00	66.54	8.12	59.7
0.073		15.27	32.39	62.29	8.77	57.3
0.110	7.88	15.07	31.29		9.54	55.1

[a] [*o*-Fluoronitrobenzene] 3.65 × 10^{-4}M.

Table 6. Reactions of *o*-fluoronitrobenzene with isopropylamine (IPA) in DMSO[a]

[IPA]/M	$10^4 k_A$/l mol^{-1} s^{-1} 30 °C	45 °C	60 °C	$\Delta H^{\ddagger}$/kcal mol^{-1}	$-\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
0.025	2.92	6.38	14.63	10.15	41.4
0.050	3.09	6.58	15.84	10.28	40.9
0.101	2.95	6.43	13.89	10.05	41.7
0.126	3.12	6.83	14.14	9.91	42.0

[a] [*o*-Fluoronitrobenzene] 2.74 × 10^{-4}M.

The classical works of Brady and Cropper[27] and those by Suhr[28] have shown that branching in the amine produces important decreases in reactivity. The near five-times decrease in the reaction rate on passing from n- to iso-propylamine in the reaction of *o*-fluoronitrobenzene (Table 7) is a measure of the highest primary steric effect expected in this system. The reactions in DMSO show a similar trend, providing a further support to the amine branching *F* effect hypothesis.

Steric effects on the reaction centre were also assumed to be responsible for the observed *o*:*p* ratio in numerous aromatic bimolecular substitutions.[2b,5,26,28–30] Nevertheless, we have previously observed that piperidine dechlorination[31] or demethoxylation[6,11] in 6-R-2-nitro-X-benzenes are not strongly influenced by steric effects. Examination of the literature

Table 7. Calculated values for reactions of *o*- and *p*-fluoronitrobenzene[a]

	n-$C_3H_7NH_2$		iso-$C_3H_7NH_2$	
	Toluene	DMSO	Toluene	DMSO
o-Fluoronitrobenzene				
$10^6\ k_A$/l mol^{-1} s^{-1}	24	3 130	5.4	643
$10^6\ k''$	12.9		6.04	
$10^6\ k'$	22.6		4.77	
k''/k'	0.57		1.27	
$\Delta H^{\ddagger}$/kcal mol^{-1}	10.6	9.5	11.1	10
$-\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	46	55	48	42
p-Fluoronitrobenzene				
$10^6\ k_A$/l mol^{-1} s^{-1}	0.054	205[b]	0.0005	400[b]
$10^6\ k_3k_1/k_{-1}$	0.75		0.06[c]	
$10^6\ k_2k_1/k_{-1}$			0.01[c]	
k_3/k_2	∞		5[c]	
$\Delta H^{\ddagger}$/kcal mol^{-1}	7.4		9	
$-\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	69		65	

[a] At 45 °C, [Amine] 0.1M. [b] Data at 50 °C from ref. 28. [c] Only the order of magnitude is accurate. See text.

indicates that Cl, Br, and I exhibit similar rate reactivities even in cases where steric effects are assumed to be important.[26,28a] Zollinger observed that the rate of reaction of 6-R-aniline *increases* with the size of the 6-R-substituent.[5] Taking into account the preceding observations, it is difficult to accept that reactions where fluorine is the nucleofugue may be strongly influenced by primary steric factors.

The date of Table 7 show an *o*:*p* ratio of 444 for the reactions in toluene which demonstrates that the high stabilization of the intermediate σ complex in the *ortho*-isomer supersedes the small steric effect. But an interesting fact is that the reaction of *p*-fluoronitrobenzene goes exclusively by the base-catalysed pathway. Fluorine is known to be a poor nucleofugue in aprotic solvents and, in the absence of an intramolecular hydrogen-bond, decomposition of the intermediate can only take place by the assistance of a second molecule of amine. In some cases a salt effect has also been observed.[32] The low values of the entropy of activation are consistent with a transition state involving three molecules.

The reactions of *p*-fluoronitrobenzene with isopropylamine exhibit a >100-times decrease in rate when compared with the reaction with n-propylamine in toluene. It is obvious that primary steric effects cannot be greater than those in *o*-fluoronitrobenzene. The large diminution in rate is due to a great slowness in the base-catalysed step. It is known that tertiary amines[33] or highly hindered secondary amines[34] are not good catalysts. The present data (Table 7) show that the low rate of reaction with isopropylamine is due to a large decrease in the base-catalysed pathway with this branched primary amine. Although the k_3/k_2 value for this reaction has not the precision of the others, it is certainly much lower than infinity. Therefore, when comparing reactivities in reactions with fluorine substrates, steric effects must be examined at different amine concentrations: it is almost certain that primary steric effects should be low, but steric effects on the hydrogen abstraction in the intermediate complex are expected to be important. The *o*:*p* ratio for isopropylamine in toluene is *ca.* 10^4. This has an important consequence in synthetic applications: since the steric effect affects the rate of the second step the overall reaction rate may be increased by the addition of a non-nucleophilic amine, such as has been observed in other systems[21,22] or by the addition of another hydrogen-bond acceptor catalyst.[35]

Although it may be argued that branching in the amine reduces the k_3/k_{-1} values not only by reducing the rate of proton transfer (k_3) but also by increasing the rate of decomposition of the intermediate to reactants (k_{-1}) because of the steric congestion, this effect was shown to be not very important. (Tables 1 and 2).

There is evidence[36,37] for unfavourable stereoelectronic–conformational effects when the transition step contains the piperidine group and it has been recently shown[38] that a change from primary amines to piperidine results in a reduction in the rate of proton transfer. But as far as we know, this is the first observation that steric crowding in a primary amine results in a *ca.* 20-times increase in the *o*:*p* ratio due to a reduction in the rate of proton transfer from zwitterionic intermediates to amine catalyst, which is rate determining for the reactions of *p*-fluoronitrobenzene but not for the *ortho*-isomer.

Reactions with DMSO are also very indicative. In reactions of *p*-fluoro- and -chloro-nitrobenzene with anions it was previously shown that catalysis by DMSO is almost the same for fluorine as for chlorine substrates, concluding that differential solvation effects of the leaving group are of little importance whether or not the detachment of fluoride is rate determining.[39] The effect was studied in methanol–DMSO mixed solvents. Nevertheless, it was then proved that reactions where the second step is rate determining[40] shift to first-step rate-determining when performed in methanol.[41] It was recently shown that additions of DMSO to toluene diminishes by an order of magnitude the amine rate-dependence for DMSO content >2%.[35] The present work shows that reactions in DMSO are not sensitive to base catalysis since solvation by DMSO assists fluorine detachment and the first step is now rate determining. Supporting again the idea that primary steric effects are not very important, $k_{\text{n-propylamine}}/k_{\text{isopropylamine}}$ changes from 100 in toluene (second-step rate-determining) to almost 1 in DMSO (first-step rate-determining), in the reactions with *p*-fluoronitrobenzene.

Conclusion.—The present work confirms that primary steric effects at the reaction centre are not very important in lowering the rate of reaction of bimolecular aromatic nucleophilic substitution. Nevertheless, reactions with bulk amines can be extremely slow when the second step is rate determining because of the reduced power of the amine as a hydrogen-bond acceptor catalyst. The reaction rate may be increased by the addition of a non-nucleophilic base or by performing the reaction in the presence of another hydrogen-bond acceptor catalyst such as DMSO.*

Experimental

Reagents and Solvents.—*o*- and *p*-fluoronitrobenzene were distilled at reduced pressure, b.p. 89—91 °C at 8 mmHg (lit.,[42] 214.8 and 89—90 °C at 5 mmHg; lit.,[43] 205.3 °C). n-Propylamine was kept over sodium wire, refluxed, and then fractionated over sodium; the fraction of b.p. 47—48 °C was used. Isopropylamine was purified in a similar way (b.p. 31—32 °C).

* One referee inquired about the application of the 'dimer mechanism' (ref. 35 and references therein) to these reactions. Several conditions must be met for this mechanism to be observed. One is that the second step must be slow, and a quadratic dependence of k_A on [B] is evident at low [B]. Among the systems studied in the present paper only the reaction of *p*-fluoronitrobenzene with n-propylamine in toluene has a rate-determining second step.

The plots of k_A *versus* [B] at 60 and 80 °C (Table 3) show deviation from the line at lower [B] (<0.481M), exhibit a 'negative intercept', and the plot of k_A/[B] *versus* [B] gives a straight line, in which only the point at [B] 0.102M (80 °C) departs from the line. Although the experimental conditions prevent a more detailed study it is reasonable to expect that at [B] < 0.1M the dimer mechanism could be clearly observable in this system.

Toluene was kept over sodium wire for several days, refluxed, and then fractionated over sodium; the fraction of b.p. 110—111 °C was stored in a special vessel which allowed delivery without air contamination. DMSO was purified as previously described[44] and distilled immediately prior to use. *N*-4-Nitrophenylpropylamine was prepared by mixing *p*-nitrofluorobenzene (0.250 g, 1.77 mmol) in anhydrous toluene (10 ml) with propylamine (2 ml, 24.3 mmol). After a few hours at room temperature crystals of the amine fluorohydrate appeared which were filtered off and the filtrate distilled at reduced pressure. The yellow crystalline residue was crystallized from ethanol to constant m.p. 63.5—64 °C (lit.,[45] 64—65 °C), δ_H($CDCl_3$; 100 MHz) 6.73 (2 H, dd, H-3 and -5), 5.42 (2 H, dd, H-2 and -6), 3.75 (1 H, br s, HN<), 2.65 (2 H, m, $HNCH_2$), 1.40 (2 H, m, $CH_2CH_2CH_3$), and 0.85 (3 H, t, CH_3); *m/z* 180 (M^+, 43%), 151 (100), 105 (82), and 43 (4). *N*-4-Nitrophenylisopropylamine was prepared in a similar way but the mixture was heated at 60 °C in a sealed bulb for 13 days. The yellow residue was crystallized from methanol until constant m.p. 84—85 °C (lit.,[45] 85.5—86.5 °C), δ_H ($CDCl_3$; 100 MHz) 8.16 (2 H, dd, H-3 and -5), 6.47 (2 H, dd, H-2 and -6), 4.35 (1 H, br s, HN<), 3.71 (1 H, m, HNC*H*<), and 1.24 [6 H, d, $-CH(CH_3)_2$]; *m/z* 180 (M^+, 25%), 165 (100), and 119 (54). *N*-2-Nitrophenylpropylamine was prepared analogously to the 4-nitro isomer. The residue is an orange oil which was distilled at reduced pressure and characterized spectroscopically, δ_H ($CDCl_3$; 100 MHz) 6.80 (1 H, dd, H-3), 6.70 (1 H, br s, HN<), 6.17 (1 H, m, H-5), 5.7 (1 H, dd, H-6), 5.52 (1 H, m, H-4), 2.73 (2 H, m, $HNCH_2$), 1.47 (2 H, m, $HNCH_2CH_3$), and 0.87 (3 H, t, CH_3); *m/z* 180 (M^+, 42%), 151 (100), 134 (3), 121 (10), 105 (19), and 43 (3). *N*-2-Nitrophenylisopropylamine was prepared in a similar way but by heating the reaction mixture at 60 °C in a sealed bulb for 40 h. The orange oil[46] has the following spectral characteristics, δ_H ($CDCl_3$; 100 MHz) 8.11 (H-3), 8.0 (HN<), 7.39 (H-5), 6.82 (H-6), 6.57 (H-5), 3.78 [1 H, m, $>NCH(CH_3)_2$], and 1.32 [6 H, $>NCH(CH_3)_2$]; *m/z* 180 (M^+, 45%), 165 (100), 163 (4), 162 (7), 135 (8), 119 (29), 118 (21), and 43 (11).

Kinetic Procedure.—The kinetics of the reaction were studied spectrophotometrically[47] using a Gilford model 260 spectrophotometer. Standard solutions of each substrate and each amine were prepared in the desired solvent at room temperature. The reactions in toluene and in DMSO were run by mixing known amounts of each solution in the reaction flask and making up to volume. Portions of the reaction mixtures in sealed bulbs were put at once in the thermostat and the optical densities measured at appropriate intervals. The pseudo-first-order, k_ψ, and second-order, k_A, rate coefficients and the activation parameters were obtained as previously described.[48]

Several kinetic runs were carried out in duplicate and the error in k_A is ≤2—3%. Values of $\Delta H^\ddagger$ are accurate to *ca.* ±0.1 kcal mol^{-1} and values of $\Delta S^\ddagger$ to ±2 cal mol^{-1} K^{-1}. The present units for the activation parameters have been used instead of the recommended SI units since they are still found more frequently in this type of study.

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