# Solvent and Substituent Effects on the Reaction of 2- and 4-Chloro-3,5dinitrobenzotrifluorides with Substituted Anilines

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> ABSTRACT: The solvent effect on a nucleophilic substitution reaction of 2- and 4-chloro-3,5dinitrobenzotrifluoride with substituted anilines was studied in methanol, acetonitrile, and toluene at 25°C. This reaction is of second order, except 2-chloro-3,5-dinitrobenzotrifluoride in toluene shows third order. The  $k_A$  values are found to be dependent on the substituent in aniline and give good Hammett correlations. The obtained  $\rho$  values are -4.07 and -4.62, for the reaction of anilines with 2-chloro-3,5-dinitrobenzotrifluoride in methanol and acetonitrile, respectively. The  $\rho$  values for the reaction of the anilines with 4-chloro-3,5-dinitrobenzotrifluoride are -3.38, -4.11, and -4.34 in methanol, acetonitrile, and toluene, respectively. The reaction of the former compound with anilines in toluene shows a second order in aniline. The dependence of the reaction on the external base such as DABCO suggests a proton transfer controlling step. © 2009 Wiley Periodicals, Inc. Int J Chem Kinet 41: 777-786, 2009

#### INTRODUCTION

The mechanism and reactivity for the reaction of nitroaryl derivatives with amines have interested chemists for some years and continue to attract their attention [1-11]. Many studies showed the effect of

aromatic ring substituents, amine, as well as the nature of the solvent on the reactivity and mechanism of nucleophilic aromatic substitution reactions [12–16]. The solvent effect includes the interaction of the substrate and/or the intermediate(s) with the solvent molecules, which may be extensive and complex [17–19], whereas electronic and hydrogen bonding effects have been identified as important factors that influenced reactivity [7–11,16–23]. Different mechanisms have been shown to apply for the nucleophilic aromatic substitution reaction [12–16] of several rings activated aryl halides, alkyl aryl ethers, and thio-ethers with primary or secondary amines in various solvents as given in

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Values of the first-order rate constant,  $k_{\psi}$  (in Tables S1 and S2) are available as Supporting Information in the online issue at www.interscience.wiley.com.

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pathways (a)–(c) in Scheme 1. Pathway (a) represents the uncatalyzed reaction, first order in amine and its attack is rate limiting [13–16,20–23]. However, this does not exclude the case where the reaction undergoes catalysis either by (i) specific base-general acid (SB-GA) when the  $k_3$  step, i.e., departure of the leaving group, is the rate limiting [24–30] or (ii) general base catalysis (SB) is likely to involve the rate-limiting deprotonation of the initially formed zwitterion intermediate I,  $k_{Am} > k_{-1}$ , followed by rapid loss of the leaving group [31–38].

When the rate constants show a parabolic dependence on the amine concentration, it can be explained by a dimer mechanism [39–42], pathway (b). In this mechanism, the amine dimer acts as a nucleophile forming an intermediate complex III while the third molecule of amine assists in the decomposition. Pathway (c) represents the substitution of leaving group L as a slow step followed by rapid equilibration of the substrate with adducts IV–V formed by reaction at the unsubstituted position [38].

Here we report the effect of the solvents, such as methanol (MeOH), acetonitrile (AN), and toluene (Tol), the electronic and steric effects of the trifluoromethyl group, as well as the substituent in the nucleophile on the reactivity and mechanism for the reaction 2- and 4-chloro-3,5-dinitrobenzotrifluorides (1 and 2, respectively) with aniline derivatives **3a–g**.



Elemental Analysis,  $\nu(cm^{-1}), -NO_2$ Calcd (Found) MP Yield (%)  $\lambda(nm)(\varepsilon)$  Asymmetric Symmetric NH С Η Ν Compound R MF 4a Η 121.0 47.72 2.46 12.84 86 360 (19369) 1595 1340 3349 C13H8F3N3O4 240 (23119) (47.50) (2.13) (12.64) 4b 4-OCH3 105.6 90 370 (18479) 1612 1343 47.07 3384 C<sub>14</sub>H<sub>10</sub>F<sub>3</sub>N<sub>3</sub>O<sub>5</sub> 2.82 11.76 240 (21897) (46.88) (2.63) (11.60) 4-CH<sub>3</sub> 122.0 95 1600 4c 370 (20023) 1338 3398 C<sub>14</sub>H<sub>10</sub>F<sub>3</sub>N<sub>3</sub>O<sub>4</sub> 49.28 2.95 13.31 240 (23975) (49.50) (2.53) (13.64) 4d 4-Cl 116.7 90 365 (18631) 1600 1338 3396 C<sub>13</sub>H<sub>7</sub>ClF<sub>3</sub>N<sub>3</sub>O<sub>4</sub> 43.17 1.95 11.62 240 (24436) (43.51) (2.03) (11.44) **4e** 3-OCH<sub>3</sub> 90.0 89 360 (17009) 1596 1338 3351 C<sub>14</sub>H<sub>10</sub>F<sub>3</sub>N<sub>3</sub>O<sub>5</sub> 47.07 2.82 11.76 240 (19520) (47.45) (2.44) (11.64) 4f  $3365\ C_{14}H_{10}F_3N_3O_4$ 3-CH<sub>3</sub> 110.0 96 360 (19525) 1601 1337 49.28 2.95 13.31 240 (22256) (49.58) (2.73) (13.74) 4g 3-C1 108.9 95 360 (17076) 1595 1337 3360 C<sub>13</sub>H<sub>7</sub>ClF<sub>3</sub>N<sub>3</sub>O<sub>4</sub> 43.17 1.95 11.62 240 (23118) (43.57) (1.93) (11.69)

**Table I**Physical Properties, IR, UV Spectra, and Elemental Analysis of N-(2,4-Dinitro-6-trifluromethylphenyl)anilineDerivatives, **4 a-g** 

#### EXPERIMENTAL

The purification of AN, MeOH, Tol, and aniline was reported previously [43]. 4-Methyl-, 4-methoxy-, 4-chloro-, 3-chloro-, 3-methyl-, and 3-methoxy-anilines used were of commercial grade and were purified by crystallization or vacuum distillation. 2- and 4-Chloro-3,5-dinitrobenzotrifluorides were the purest available materials (Sigma-Aldrich, Steinheim, Germany).

#### **Reaction Product**

*General Procedure.* A methanol solution of 1 (1.8 mmol, 5 mL methanol) was treated with the appropriate aniline derivatives 3a-g (18 mmol, 5 mL methanol). The reaction was refluxed for approximately 1 h, and the solid precipitate was filtered and crystallized from benzene-petroleum ether to give N-(2,4-dinitro-6-trifluoromethyl-phenyl)aniline derivatives 4a-g. Tables I and II show the physical properties, IR, UV, and <sup>1</sup>H NMR characteristics of compounds 4a-g,

**Table II** <sup>1</sup>HNMR<sup>*a*</sup> Spectra of *N*-(2,4-Dinitro-6-trifluromethylphenyl)aniline Derivatives, **4a–g** 

			•		• • •		0	
	R	—NH	H-4	H-2	H 2′, 6′	H3	', 5'	H-4′
4a	Н	7.63	$8.91 (J_{2,4} = 2.3 \text{ Hz})$	$8.69 (J_{2,4} = 2.3 \text{ Hz})$	7.01 (d)	7.3	5 (t)	7.24 (t)
					(J = 7.65  Hz)	(J = 7.7)	7;7.7 Hz)	(J = 7.65  Hz)
4b	$4\text{-OCH}_3^b$	7.45	$8.88 (J_{2,4} = 2.3 \text{ Hz})$	8.65 ( $J_{2,4} = 2.3 \text{ Hz}$ )	6.98 (m)	6.85	5 (m)	
					$(J^* = 8.4 \text{ Hz})$	$(J^* =$	8.4 Hz)	
4c	$4-CH_3^c$	7.59	$8.89(J_{2,4} = 2.3 \text{ Hz})$	8.67 ( $J_{2,4} = 2.3$ Hz)	7.14 (m)	6.91	(m)	
	5				$(J^* = 8.4 \text{ Hz})$	$(J^* =$	8.4 Hz)	
4d	4-Cl	7.64	$8,89 (J_{2,4} = 2.3 \text{ Hz})$	8.7 ( $J_{2,4} = 2.3$ Hz	7.31(m)	6.95	5 (m)	
					$(J^* = 6.8 \text{ Hz})$	$(J^* =$	6.8 Hz)	
					H- 2′	H4′	H-5′	H-6′
4e	$3-OCH_3^d$	7.5	$8.89 (J_{2,4} = 2.3 \text{ Hz})$	$8.69 (J_{2,4} = 2.3 \text{ Hz})$	6.51 (d)	6.56 (d)	6.75 (t)	7.24 (d)
					(J = 2.3  Hz)	(J = 7.5  Hz)	(J = 7.5  Hz)	(J = 7.3  Hz)
4f	3-CH3 <sup>e</sup>	7.53	$8.93 (J_{2,4} = 2.3 \text{ Hz})$	$8.68 (J_{2,4} = 2.3 \text{ Hz})$	6.8 (d)	7.03 (d)	7.21 (t)	7.25 (d)
					(J = 2.3  Hz)	(J = 7.65  Hz)	(J = 7.65  Hz)	(J = 7.65  Hz)
4g	3-Cl	7.59	$8.94 (J_{2,4} = 2.3 \text{ Hz})$	$8.72 (J_{2,4} = 2.3 \text{ Hz})$	7.01 (d)	7.19 (d)	7.27 (t)	6.88 (d)
_			,	,	(J = 2.3  Hz)	(J = 8.0  Hz)	(J = 8.3  Hz)	(J = 8.2  Hz)

<sup>a</sup>In CDCl<sub>3</sub>/TMS.

<sup>*b*</sup>4-OCH<sub>3</sub> proton appears at  $\delta$  3.80 (s) ppm.

<sup>*c*</sup>4-CH<sub>3</sub> protons appear at  $\delta$  2.33 (s) ppm.

<sup>*e*</sup> 3-CH<sub>3</sub> protons appear at δ 2.41(s); (e)AA' XX' system ( $J^* = 2.3 = J = 2.5$ ).

H-2', 4',5',6' aromatic hydrogens of the phenylamino moiety.

<sup>&</sup>lt;sup>*d*</sup> 3-OCH<sub>3</sub> appears at  $\delta$  3.77(s) ppm.

whereas compounds **5a–g** were prepared and identified earlier by us [13]. IR spectra were recorded on a Perkin–Elmer 1430 ratio, recording IR spectrophotometer using potassium bromide pellets. The <sup>1</sup>H NMR spectra were measured in CDCl<sub>3</sub> and recorded on a JEOL 500 MHz spectrometer. Elemental analyses were performed at the microanalytical laboratory in the Faculty of Science, Cairo University, Egypt.

#### **Kinetic Measurements**

The kinetics of 1 and 2 with substituted anilines 3(a-g) was measured spectrophotometrically using Shimadzu UV-160A spectrophotometer in conjunction with Shimadzu thermo bath (TB-85) temperature control ( $\pm 0.1$ ). The kinetic runs were carried out at different concentrations of substituted anilines ranging from  $2 \times 10^{-3}$  to 1.6 mol dm<sup>-3</sup> at  $\lambda$  ranging from 360 to 370 nm for compound 1 and from 400 to 410 nm for compound 2, depending on the nature and position of the substituent in aniline. All reactions were carried out under pseudo-first-order kinetic conditions, utilizing  $4 \times 10^{-4}$  mol dm<sup>-3</sup> for both **1** and **2**. The observed rate constants  $k_{\Psi}$  were calculated from the slope of the plot of  $\ln(A_{\infty} - A_t)$  versus time. The second-order rate constants  $k_A$  were calculated from the slope of the plot of  $k_{\Psi}$  versus amine concentrations.

#### **RESULTS AND DISCUSSION**

Attack by substituted anilines on **1** and **2** results in displacement of a chlorine substituent in quantitative yield (Eq. (1)). Elemental analyses, IR, UV, and <sup>1</sup>H NMR spectra indicated the formation of N-(2,4-dinitro-6-trifluoromethyl-phenyl)aniline derivatives **4a–g** via an anilino-dechlorination process (see the Experimental section), whereas N-(2,6-dinitro-4-trifluoromethyl-phenyl) aniline derivatives **5a–g** were prepared previously [13].





Table I shows a remarkable shift for the N–H and  $-NO_2$  stretching vibration of compounds **4a–g**. It is observed that the frequency of NH for **4a–g** is shifted by about 2–49 cm<sup>-1</sup> compared to that of the unsubstituted aniline moiety and depending on the nature and position of the substituent in the aniline moiety. Table II indicates that H-3 and H-5 appear as highly deshielded doublets because of their location between two nitro groups in the former and between nitro and trifluoromethyl groups in the latter [44].

Kinetic results show that the substitution is first order in the aniline concentrations for the reaction with **1** in MeOH and AN and **2** in MeOH [13], AN, and Tol. This indicates that the reaction proceeds by pathway (a) of Scheme 1, where the nucleophilic attack to form zwitterion intermediates **I-1** and **I-2** is the ratedetermining step.



Unexpectedly, the reaction of **1** with aniline derivatives **3a–g** in Tol shows a second-order dependence on the aniline concentrations, indicating that this reaction involves catalysis, pathway (a) of Scheme 1, where either SB-GA or SB catalysis is the rate-determining step. It can be represented by the following equation:

$$k_{\rm A} = \frac{k_1(k_2 + k_{\rm Am}[\text{aniline}])}{k_{-1} + k_2 + k_{\rm Am}[\text{aniline}]}$$
(2)

If  $k_{-1} \ll k_2 + k_{Am}$  [aniline], Eq. (2) is reduced to Eq. (3), where  $k_1$  represents the rate-determining step of the uncatalyzed reaction:

$$k_{\rm A} = k_1 \tag{3}$$

whereas when  $k_{-1} \gg k_2 + k_{Am}$  [aniline], Eq. (2) is converted to Eq. (4), representing that the decomposition of intermediate is the rate-limiting step.

$$k_{\rm A} = K_1 k_2 + K_1 k_{\rm Am} \,[\text{aniline}] \tag{4}$$

The catalytic role in deprotonation of the initially formed zwitterion intermediate I to the Meisenheimer complex II is shown by Eq. (5) through pathway (a), where  $k_2$  the uncatalyzed pathway is negligible,  $k_{\text{Am}}$  represents the catalyzed step by aniline. An equivalent form is given by Eq. (6).

$$k_{\rm A} = \frac{k_1 k_{\rm Am}[\rm{aniline}]}{k_{-1} + k_{\rm Am}[\rm{aniline}]}$$
(5)

$$k_{\rm A} = \frac{K_1 k_{\rm Am}[\text{aniline}]}{1 + \frac{k_{\rm Am}}{k_{-1}}[\text{aniline}]} \tag{6}$$

This equation indicates that the breakdown of the zwitterion intermediate containing poor nucleofuge occurs by rate-limiting proton transfer [44].

#### Reaction of 1 and 2 with Anilines 3 a–g (Uncatalyzed Pathway)

**Solvent Effects.** The kinetics of the reaction of various concentrations of aniline derivatives with compound **1** in MeOH and AN and compound **2** in MeOH [13], AN, and Tol at 25°C was studied under pseudo-first-order condition. Values of the first-order rate constant,  $k_{\psi}$ , are available as supporting information (in Tables S1 and S2), and the second-order rate constants,  $k_A$ , are presented in Tables III and IV. It is found that  $k_A$  values vary linearly with amine concentrations. We interpreted these results in terms of Scheme 1 (pathway (a)), assuming that aniline attack is rate limiting (Eq. (3)). In all the cases, **1** and **2** were shown to give the expected substitution product. However, intermediates **II-1** and **II-2** were not detected spectroscopically.



Tables III and IV show that the order of decreasing reactivity for the reaction of a given nucleophile with compound 1 or 2 as follows:

$$k_{\rm A}({\rm MeOH}) > k_{\rm A}({\rm AN}) > k_{\rm A}({\rm Tol})$$

This is in agreement with the formation of a dipolar intermediate as seen from the effect of hydrogen bond donor  $\alpha$  compared to hydrogen bond acceptor  $\beta$ , polarity polarizability  $\pi^*$ , and Dimroth–Rechardt's  $E_{\rm T}$  solvatochromic parameters [45,46]. This reactivity order is due to the strong solvation of the

Table III	Second-Order Rate Constants for the
Reaction c	of <b>1</b> with Substituted Aniline, <b>3a–g</b> in MeOH
and AN at	25°C

		$10^3 k_{\rm A} ({\rm dm^3 mol^{-1}  s^{-1}})$		
Compound	Substituent	MeOH	AN	
<b>3</b> a	Н	$2.41\pm0.06$	$0.395 \pm 0.008$	
3b	4-OMe	$42 \pm 1$	$10.6\pm0.5$	
3c	4-Me	$11.3\pm0.3$	$2.48\pm0.06$	
3d	4-Cl	$0.286 \pm 0.003$	$0.040\pm0.02$	
3e	3-OMe	$1.580\pm0.02$	$0.192\pm0.007$	
3f	3-Me	$3.08\pm0.05$	$0.63\pm0.02$	
3g	3-Cl	$0.070\pm0.001$	$0.007 \pm 0.0002$	

Meisenheimer intermediate through intermolecular hydrogen bonding. Furthermore, this specific reaction becomes slower in media of high dielectric constant  $\varepsilon$ , because  $k_{\text{H(MeOH)}}/k_{\text{H(AN)}}$  is 6 and 3 for compounds 1 and 2, respectively. Also, the higher rate constant of 2 (ortho-like, contains an ortho nitro group with respect to the leaving Cl) over 1 (para-like, contains a para nitro group with respect to the leaving Cl) [ $k_{\text{A}}$  (4-Cl)/ $k_{\text{A}}$  (2-Cl)] is 6- and 12-folds in MeOH and AN, respectively, presumably indicating that the intermediate developing from the reaction of 2 is more polar than that developing from 1.

Generally, the nucleophilic substitution in 2,4,6triactivated is faster at position between two ortho nitro groups than at positions ortho and para to two nitro groups, e.g., there is a kinetic preference for reaction at 4-position in chloro-1-cyano-3,5dinitrobenzene [11] and in chloro-1-trifluromethyl-3,5-dinitrobenzene [26]. However, in compounds that lack a good leaving group the adduct formed by reaction at the 2-position has higher thermodynamic stability [13,14]. Accordingly, the observation that compound 2 is more reactive than 1 is in agreement with literature results [47,48].

For compounds 1 and 2, 2-chloro-3,5dinitropyridine, 1-chloro-2,4-dinitro-benzene, and 2-chloro-1,3,5-trinitrobenzene [23], the contribution of the bulky ortho substituents to the reaction center as well as its activating effect clearly has to be considered. The comparison shows that the reactivity order is  $NO_2 > ring N > CF_3 > H$ , and in general the ratios do not depend significantly on the nature of amine. We concluded that an o-NO<sub>2</sub> group is more activating than the ring nitrogen, whereas the o-CF<sub>3</sub> group has more profound steric effect. The steric argument of o-NO<sub>2</sub> may be unconvincing because the approach of the amine from a direction orthogonal to the ring in an o-substituted derivative will allow chlorine to be pushed out of the benzene plane [26].

			$10^3 k_{\rm A} ({\rm dm}^3 {\rm mol}^{-1} {\rm s}^{-1})$	)
Compound	Substituent	MeOH <sup>a</sup>	AN	Tol
3a	Н	$15 \pm 2$	$4.9 \pm 0.2$	$3.94 \pm 0.05$
3b	4-OMe	$140 \pm 2$	$78 \pm 2$	$67 \pm 3$
3c	4-Me	$52 \pm 1$	$27.8 \pm 0.8$	$18.4 \pm 0.8$
3d	4-Cl	$2.4 \pm 0.2$	$0.77\pm0.02$	$0.523 \pm 0.008$
3e	3-OMe	$6.4 \pm 0.4$	$2.24 \pm 0.09$	$2.040 \pm 0.001$
3f	3-Me	$24.8 \pm 0.1$	$7.2 \pm 0.2$	$3.98\pm0.07$
3g	3-C1	$0.90\pm0.01$	$0.14\pm0.05$	$0.076\pm0.001$

**Table IV**Second-Order Rate Constants, for the Reaction of 2 with Substituted Aniline 3a-g in MeOH, AN, and Tol at 25°C

<sup>a</sup>Extrapolated data from [13].

Other activating factor is presumably attributable to the efficient delocalization of the developed charge with the  $NO_2$  more than the aza group [19,22].

*Effect of Substituent on the Nucleophile.* The reactivity of the substituted anilines **3a–g** was found to decrease in the order 4-OMe > 4-Me > 3-Me > H > 3-OMe > 4-Cl > 3-Cl depending on the electronic nature and position of the substituent. The reactivity differences between compounds **1** and **2** with aniline derivatives may be ascribed to the electronic effect of the substituent on the aniline. This may be quantified by the use of a Hammett equation [49].

A good linear correlation between  $\log k_A$  for the reactions of compounds 1 and 2 with aniline derivatives versus  $\sigma$ -Hammett in all solvents at 25°C is established. The obtained  $\rho$  values are -4.07 and -4.62 for compound 1 in MeOH and AN, respectively, and -3.38, -4.11, and -4.34 for compound **2** in MeOH [13], AN, and Tol, respectively. The negative  $\rho$  values are comparatively in agreement with those of the Chapman et al. hypothesis of  $\rho$  (-3.1 and -3.5), which are characteristic of the displacement of the chlorine atom from an aromatic carbon by aromatic amines and suggesting the formation of an intermediate in the ratedetermining step [50]. The sign and magnitude of  $\rho$ indicates that (a) the substituent affects the rate of the reaction by the polar effect; (b) the negative  $\rho$  values are in agreement with the donor ability of aniline derivatives, and the positive charge is developed on the aniline nitrogen atom in the transition state; and (c) an anilino moiety participates in the bond formation in the transition state.

On the other hand, our  $\rho$  values are similar to the values given by Wepster et al (-3.19) for the ionization of substituted anilinium ions [51]. The similarity of these  $\rho$  values can be explained on the basis of the following facts: (i) The conjugation of the amino group is

destroyed in the Meisenheimer complex-type intermediate formed, and (ii) the electron pair on the nitrogen atom of aniline is transferred to the nitrochlorobenzene transition states.

A significant feature of variable solvents and substituents in the anilines **3a–g** is shown by the plot of  $log(k/k_0)$  for the reaction of **1** against  $log(k/k_0)$  for the reaction of **2** in the same solvent, which gives a linear relationship with the slope close to unity (gradient = 0.81, r = 0.98)<sub>MeOH</sub> and (gradient = 0.93, r = 0.99)<sub>AN</sub>. Interestingly, this type of plot has the same behavior for **2** in toluene (gradient = 0.81, r = 0.99) Also, the  $\rho$  values for these reactions are quite the same (within experimental errors); the identity of these  $\rho$  values shows that the structure of the transition state does not alter significantly with the change in the nature and position of the substituents in aniline, the properties of solvent, and the position of the chlorine atom in compounds **1** and **2**.

### Reaction of 1 with Anilines 3a–c,e,f (Amine Catalysis)

The reaction of **1** with substituted anilines **3a–c,e,f** in toluene was studied in different amine concentrations at 25°C. The data of  $k_A$  values ( $k_{\Psi}$ /[aniline]), in Table V, show an amine concentration dependence, indicating that the proton transfer step  $k_{Am}$  is rate limiting or a dimer mechanism, pathway (a) or (c) of Scheme 1, respectively. This is another example of the base-catalyzed reaction for substrate that contains a chloro atom that is known as a good leaving group [52–57]. The dimer mechanism remains unproved and is difficult to distinguish it from mechanisms involving a consecutive reaction with two amine molecules. This mechanism is rejected on the ground that it does not show a parabolic dependence on the amine concentration [39–43].

	$\frac{10^4 k_{\rm A} ({\rm dm^3 \ mol^{-1} s^{-1}})}{10^4 k_{\rm A} ({\rm dm^3 \ mol^{-1} s^{-1}})}$						
Substituent [Am]	H ( <b>3a</b> )	4-OMe ( <b>3b</b> )	4-Me ( <b>3c</b> )	3-OMe ( <b>3e</b> )	3-Me ( <b>3f</b> )		
0.20		4.80					
0.25		6.88					
0.3		8.96	1.63				
0.35		10.94	1.77				
0.40		12.82	1.87				
0.45			1.95				
0.50			2.20		0.46		
0.60					0.50		
0.70	0.41				0.58		
0.80	0.47			0.22	0.70		
0.90				-	0.77		
1.00	0.55			0.28			
1.20	0.63			0.30			
1.40	0.79			0.36			
1.60				0.43			

**Table V**Reaction of 2-Chloro-3,5-dinitrobenzotrifluoride, 1 with Substituted Aniline 3a-g in Toluene at 25°C; SecondOrder ( $k_A$ )

The zwitterion **I-1** can undergo proton transfer in the rate-controlling step forming Meisenheimer intermediate **II-1** (general base catalysis) or the leaving group departure is the rate-limiting step (specific base general acid SB-GA). Since chloride is an extremely good leaving group, this is likely to be from the zwitterionic intermediate **I-1** to amine rather than from the protonated amine (AmH<sup>+</sup>) to the leaving group (the SB-GA mechanism).

It is found that a plot of  $k_A$  values from Table V versus aniline concentrations shows linear correlations with negligible intercepts (Fig. 1). In terms of Eq. (2), the contribution of  $k_2$  is negligible; hence Eq. (5) or the alternative Eq. (6) is applied, where  $k_{Am}$  represents



Figure 1 Variation of  $k_A$  for the reaction of 1 with substituted aniline concentration in toluene at 25°C.

	$10^3 k_{\rm A} ({\rm dm^3 \ mol^{-1} \ s^{-1}})$							
[DABCO] (mol dm <sup>-3</sup> )	H ( <b>3a</b> )	4-Me ( <b>3b</b> )	4-OMe ( <b>3c</b> )	4-Cl ( <b>3d</b> )	3-OMe ( <b>3e</b> )	3-Me ( <b>3f</b> )	3-Cl ( <b>3</b> g)	
0.0	0.05	0.896	1.00		0.03	1.06		
0.1	0.29	1.56	7.15		0.16	0.37		
0.2	0.47	2.95	12.65	0.06	0.28	0.71	0.02	
0.3	0.73	3.81	17.71	0.09	0.37	0.94	0.03	
0.4	0.99	4.93	21.41	0.11	0.46	1.15	0.04	
0.5	1.09							

**Table VI** Kinetic Results for the Reactions of **1** with Substituted Aniline (1.0 mol dm<sup>-3</sup>) except 4-OMe, 0.1 mol dm<sup>-3</sup>, and 4-Me, 0.3 mol dm<sup>-3</sup>) at Various DABCO Concentrations in Toluene at 25°C

the catalyzed pathway. Figure 1 shows that  $k_{\rm Am}/k_{-1}$ has lower values and then  $K_1k_{Am}$  is calculated from the slopes. To examine such catalysis, the reaction is subjected to general base catalysis by adding DABCO as an external base. The  $k_A$  values for the reaction of **1** with substituted anilines 3a-c,e,f (1.0 mol dm<sup>-3</sup> except 4-OMe, 0.1 mol dm<sup>-3</sup> and 4-Me, 0.3 mol dm<sup>-3</sup>) with various DABCO concentrations in toluene are given in Table VI. The values of  $K_1 k_{\text{DABCO}}$  (where  $k_{\text{DABCO}}$ represents the rate constant for the DABCO-catalyzed route) were obtained from the slopes of the linear plots of the data in Table VI. The reactions of 1 with different substituted aniline concentrations in the presence of constant DABCO, 0.1 mol dm<sup>-3</sup>, in toluene were performed, and the values of  $k_A$  are presented in Table VII. The values  $K_1 k_m$ ,  $K_1 k_{DABCO}$ , and  $k_{Am}/k_{Am}$  $k_{\text{DABCO}}$  are summarized in Table VIII, which reflects variations in the values of  $K_1 k_{Am}$  and in general  $k_{Am}$ / k<sub>DABCO</sub> increased with increasing electron-donating

0.350

0.400

0.500

 $0.800 \\ 0.900$ 

1.000

1.200

1.400

substituents. This agrees with the relatively high basicity values of 4-OMe and 4-Me aniline in toluene, presumably suggesting that the proton transfer process is the rate-controlling step.

## Comparison of 1 and 2 with 3a–g in MeOH, AN, and Toluene

The possibility of hydrogen bonding between the ammonium hydrogen atom and two *o*-nitro groups **I-2** causes the 4-chloro isomer to be less susceptible to catalysis than the 2-chloro one. Moreover, the hyperconjugation of the  $-CF_3$  group may pronounce a partial negative on the carbon atom bearing the leaving chlorine atom at 2-position of **1** more than the 4-position of **2** causing the former to undergo catalysis with ease. The important factor is that in toluene the value of  $k_{-1}$  will be relatively high because the polar intermediate will be poorly solvated, and  $k_{Am}$  will be reduced

			$10^3 k_{\rm A} ({\rm dm}^3 {\rm mol}^{-1}{\rm s})$	-1)	
[Aniline] (mol dm <sup><math>-3</math></sup> )	H ( <b>3a</b> )	4-Me ( <b>3b</b> )	4-OMe ( <b>3c</b> )	3-OMe ( <b>3e</b> )	3-Me ( <b>3f</b> )
0.05			2.83		
0.075			5.10		
0.100			7.15		
0.125			9.21		
0.150			11.26		
0.300		4.68			

5.50

6.57

8.32

2.48

2.95

3.35

3.63

**Table VII** Kinetic Results for the Reactions of 1 with Substituted Aniline, in the Presence of DABCO, 0.1 mol dm<sup>-3</sup>, in Toluene at 25°C

3.05

3.32

3.67

5.15

1.4

1.63

1.98

3.30

Substituent	$10^3 K_1 k_{\rm Am} ({\rm dm}^6 {\rm mol}^{-2} {\rm s}^{-1})$	$10^3 K_1 k_{\text{DABCO}} (\text{dm}^6 \text{mol}^{-2} \text{s}^{-1})$	k <sub>Am</sub> /k <sub>DABCO</sub>
Н	$0.06 \pm 0.01$	$2.1 \pm 0.1$	0.03
4-OMe	$3.01 \pm 0.1$	$11.0 \pm 0.6$	0.27
4-Me	$0.47\pm0.01$	$4.79 \pm 0.3$	0.09
4-Cl		$0.2\pm0.02$	
3-OME	$0.02\pm0$	$1.1 \pm 0.05$	0.02
3-Me	$0.08\pm0$	$2.7 \pm 0.01$	0.01
3-Cl		$0.08 \pm 0.0$	

Table VIII Summary of the Rate Constant Data for the Reaction of 1 with Substituted Anilines in Toluene

by steric and electrostatic repulsion between the approaching amine catalyst and the reaction center of compound **1**. This concept may be acceptable because the pervious work has shown that the CF<sub>3</sub> group is sterically demanding and is greater in size than the nitro group [10,11]. This is unlikely to affect values of  $k_1$  since nucleophilic attack occurs orthogonal to the ring.

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