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Reaction of 4-chloro-3,5-dinitrobenzotrifluoride with aniline derivatives. Substituent effects

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N-(2,6-Dinitro-4-trifluoromethylphenyl)aniline derivatives were prepared by anilino-dechlorination of 4-chloro-3, 5-dinitrobenzotrifluoride. IR, UV and ^{1}H NMR studies suggested an intramolecular hydrogen bond between the amino hydrogen and one *o*-nitro group. An addition-elimination mechanism was suggested based on the second-order kinetics and the dependence of rates on the nature and the position of the substituent in the aniline ring, as well as the high negative values of ρ (–3.14, –3.16, –3.01). Such values indicate a positive charge on the aniline nitrogen in the transition state and that the rate is affected by the polar effect of the substituent. The β value (0.85 at 30°C) indicates an appreciable degree of bond formation in the transition state.

Keyword: 4-chloro-3,5-dinitrobenzotrifluoride, aniline, substituent effect

Nucleophilic substitution reactions of aromatic and heteroaromatic derivatives (S_NAr) with neutral and anionic nucleophiles have been recognised to be considerably affected by the properties of solvent, the type of nucleophile, the reactivity of substrate and the nature of substituents in the nucleophile or in the substrate as well as the possible steric hindrance.[1-13] High negative ρ values were reported for the reaction of 2-chloro-1,3,5-trinitrobenzene, 2-bromo-3,5-dinitrothiophene, 2-chloro-3,5-dinitropyridine and 2-chloro-5-nitropyridine with substituted anilines.[14-17] These values of ρ indicate that (a) a positive charge is developed on the aniline nitrogen in the transition state where no conjugation is possible with the substituent[18,19] and (b) the rates were facilitated by electron-releasing and retarded by electron-attracting substituents in the nucleophile.

In continuation of our previous studies in the field of nucleophilic aromatic substitutions,[16,17,20-26] this work is planned to study the kinetics and the effect of the substituent in the aniline ring on the reaction with 4-chloro-3,5-dinitrobenzotrifluoride (DNCBTF). A trifluoromethyl (-CF3) group was introduced in the substrate in an effort to gain understanding of its effect on rate compared to the nitro and the aza groups.

Experimental

Melting-points were uncorrected. ^{1}H NMR spectra $CDCl_3$ were recorded using a DRX 400 FTNMR Bruker-400 MHz instrument. IR spectra were taken on a Perkin-Elmer 1430 instrument. Elemental analyses were carried out at the microanalytical laboratory of the Faculty of Science King Abdulaziz University Jeddah, Kingdom of Saudi Arabia.

Starting material

4-chloro-3,5-dinitrobenzotrifluoride (DNCBTF), 3- and 4- substituted anilines and methanol were the purest available commercial samples.

General procedure

A mixture of (DNCBTF) (0.5 g, 1.8 mmol) and an appropriate substituted aniline (2.5 mmol) in 20 ml methanol were stirred at room temperature for 30-45 min. The precipitate solid was filtered and crystallised from methanol–water. The physical properties, UV, IR, ^{1}H NMR spectra and elemental analyses are given in Tables 1–3.

Kinetic measurements

The kinetics of DNCBTF with 3- and 4-substituted anilines in methanol were measured spectrophotometrically using a CECIL-CE 7200/Aquarius spectrophotometer and/or UV-VIS Shimadzu 160-A at three temperatures (30-50°C).

CAUTION: Methanol is toxic and causes blindness and death when ingested, inhaled or absorbed through the skin and high exposure to aniline derivatives can cause death, cyanosis, headaches, weakness, eye irritation, drowsiness, and shortness of breath. Protective gloves should be worn to avoid skin contact with aniline. Splash proof chemical goggles and a face shield should be used when working with aniline and its derivatives.

Kinetic runs were performed by following the appearance of the reaction product at λ = 410 nm. All reactions were carried out under pseudo first-order conditions with various concentrations of anilines (appropriate mol dm^{-3}) and concentration of DNCBTF (2×10^{-4} mol dm^{-3}). The pseudo-first order rate constants k_Ψ were determined by applying Eqn (1),

$$\ln (A_\infty - A_t) = -k_\Psi t + \ln (A_\infty - A_o) \qquad (1)$$

where A_o, A_t and A_∞ are the optical densities of the reaction mixture measured at zero time, time t and infinity respectively. The second-order rate constants, k_A, were obtained from the slopes of the plots of k_Ψ versus the concentration of substituted anilines. Rate coefficients were reproducible to ± 2%.

Results and discussion

The reaction of 4-chloro-3,5-dinitrobenzotrifluoride (DNCBTF) with 3- and 4- substituted anilines **2a–h** gave the corresponding substitution products **3a–h**. Elemental analyses, UV, IR and ^{1}H NMR spectra indicated the formation of *N*-(2,6-dinitro-4-trifluoromethylphenyl)aniline derivatives *via* an anilino-dechlorination process (see Scheme 1).

Applying the steady state treatment to the Eqn (1), the rate is as follows,

$$\frac{\text{Rate}}{[1][\text{amine}]} = k_A = \frac{k_2 k_1}{k_{-1} + k_2}$$

when $k_2 > k_{-1}$, $k_A = k_1 = \dfrac{k_\psi}{[\text{amine}]}$ (*i.e.* the first step is the rate-determining step).

The products, **3a–h**, showed a shift in the N–H stretching vibrations (ν 3239–3339 cm^{-1}) and in the vibrations of $-NO_2$ group, Table 1, indicating the possible formation of a hydrogen bond between an N-H and an *ortho*-nitro group in the dinitrobenzotrifluoride moiety[27-29] (Fig. 1).

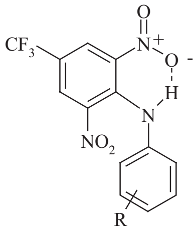

Fig. 1

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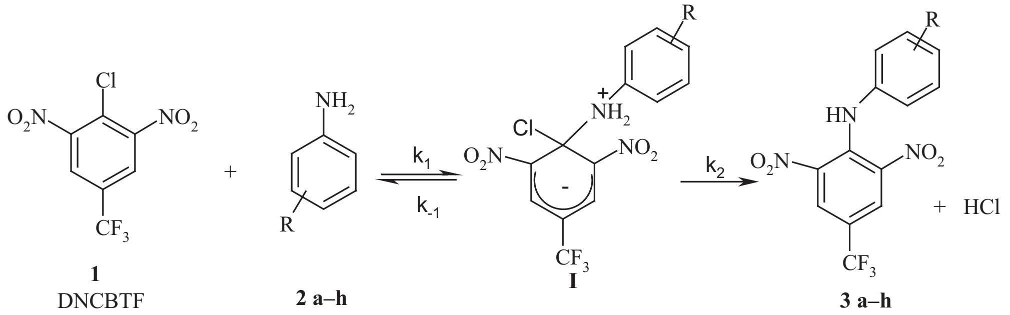

a, R = H; **b**, R = 4-OCH$_3$; **c**, R = 4-CH$_3$; **d**, R = 3-CH$_3$; **e**, R = 3-OCH$_3$; **f**, R = 4-Cl;
g, R =3-Cl ; **h**, R = 4-COCH$_3$

Scheme 1

Table 1 Physical properties, UV, IR spectra and elemental analyses of compounds **3a–h**

Compound	R	m.p./°C	Yield/%	λnm/ε	ν/cm^{-1} –NO$_2$ asym	ν/cm^{-1} –NO$_2$ sym	ν/cm^{-1} –NH	MF	Elemental analysis Calc'd (Found) C%	H%	N%
3a	H	120–121	87	220 (13000) 254 (14660) 411 (4730)	1537	1356	3331	$C_{13}H_8F_3N_3O_4$	47.72 (47.6)	2.46 (2.9)	12.84 (12.7)
3b	4-OCH$_3$	136–137	89	224 (16200) 250 (14500) 415 (5280)	1539	1358	3299	$C_{14}H_{10}F_3N_3O_5$	47.07 (47.7)	2.82 (3.2)	11.76 (11.5)
3c	4-CH$_3$	153–154	87	230 (17500) 251 (19160) 414 (6540)	1547	1360	3335	$C_{14}H_{10}F_3N_3O_4$	49.28 (49.15)	2.95 (3.3)	12.31 (11.85)
3d	3-CH$_3$	114–115	92	220 (13580) 258 (13000) 412 (5650)	1545	1364	3335	$C_{14}H_{10}F_3N_3O_4$	49.28 (49.6)	2.95 (2.5)	12.31 (11.9)
3e	3-OCH$_3$	128–129	84	223 (19660) 255 (16500) 409 (5770)	1533	1360	3339	$C_{14}H_{10}F_3N_3O_5$	47.07 (47.6)	2.82 (2.5)	11.76 (11.9)
3f	4-C1	102–103	82	250 (18270) 404 (5650)	1534	1350	3298	$C_{13}H_7ClF_3N_3O_4$	43.17 (43.0)	1.95 (2.4)	11.62 (11.5)
3g	3-Cl	147–148	76	220 (16700) 255 (17130) 403 (5410)	1541	1352	3339	$C_{13}H_7ClF_3N_3O_4$	43.17 (43.0)	1.95 (2.2)	11.62 (11.5)
3h	4-COCH$_3$	165–166	86	225 (18210) 301 (21140) 380 (6500)	1516	1360	3329	$C_{15}H_{10}F_3N_3O_5$	48.79 (48.5)	2.73 (2.3)	11.38 (11.5)

The electronic spectra (UV-VIS) of 3a-h showed two or three main bands at λ 220–254 and 250–258 and 403–415 nm in methanol, Table 1. DNCBTF shows one absorption band at λ_{max} 221 nm. The observed shift presumably arises from the electronic transition[30] between the nitro groups and the amino one. The linear correlation of log λ values in the range 380–415 nm with Hammett σ-constants (gradient –3.699, r = 0.98) indicates the polar effect on this transition except **3h** (R = 4-COCH3), Table 1. The chemical shift of the NH proton presumably supports the existence of the intramolecular hydrogen bond between the amino hydrogen and an *o*-nitro group,[16] Figure 1 and Table 2.

The pseudo first-order rate constants (k_Ψ) of the reaction of DNCBTF with various substituted anilines **2a–h** in methanol at 30, 40 and 50°C were studied spectrophotometrically at λ_{max} = 410 nm, Table (3). The linear plots of k_Ψ vs. excess and variable aniline concentrations with null intercepts indicate that the reaction under investigation (i) obeys a clean a second-order overall reaction ($k_A = k_\Psi$/[amine]), (ii) is not amine-catalysed, ruling out the dimer mechanism[31] and also ruling out the possibility that the attack occurs at an unsubstituted ring position[32] (iii) has the formation of a σ-complex intermediate[5-8] as the rate-determining step.

The k_A values for the anilino-dechlorination of 1-chloro-2,4-dinitrobenzene (DNCB: 4.2 × 10^{-4} dm^3 mol^{-1} s^{-1} at 30°C),[33] 1-chloro-2,4,6-trinitrobenzene (TNCB: 1.16 dm^{3}mol^{-1}s^{-1} at 30°C) and 2-chloro-3,5-dinitropyridine (DNCP: 4.1 × 10^{-1} dm^{3}mol^{-1}s^{-1} at 30°C)[16] in methanol were compared with DNCBTF (1.85 × 10^{-2} dm^{3}mol^{-1}s^{-1}at 30°C, Table 3) to evaluate the difference in activating effect of the –CF$_3$ group compared to the –NO$_2$ and aza groups. This comparison indicated that: (i) the introduction of the –CF$_3$ group stabilises the developed negative charge of the intermediate more than its absence ($k_{DNCBTF}/k_{DNCB} \approx 44$); (ii) the delocalisation of the negative charge developed by the nitro group is greater than that of –CF$_3$ group in the intermediate ($k_{TNCIB}/k_{DNCBTF} \approx 62$); (iii) the activation by the –CF$_3$ group is comparable to that of the aza one ($k_{DNCBTF}/k_{DNCIP} \approx 0.04$). These points are in agreement

Table 2 ^1H NMR spectra of compounds **3a–h**

				dppm ($CDCl_3$)			
Compound	R	NH	H-2, 6	H-2', 6′	H-3', 5'	H-4'	
3a	H	9.96 (s)	8.68 (s)	7.05 (d) (*J* = 7.8)	7.36 (t) (*J* = 7.8, 7.4)	7.24 (t) (J = 7.4 Hz)	
3b	4-OCH_3[a]	9.95 (s)	8.43 (s)	6.99 (m)[f] (*J** = 8.8 Hz)	6.86 (m)[f] (*J** = 8.8 Hz)		
3c	4-CH_3[b]	9.96 (s)	8.45 (s)	7.15 (m)[f] (*J** = 8.2 Hz)	6.94 (m)[f] (*J** = 8.2 Hz)		
3f	4-Cl	9.88 (s)	8.48 (s)	6.99 (m)[f] (*J** = 6.8 Hz)	7.30 (m)[f] (*J** = 6.8 Hz)		
3h	4-$COCH_3$[e]	9.90 (s)	8.52 (s)	7.09 (m)[f] (*J** = 8.6 Hz)	7.96 (m)[f] (*J** = 8.6 Hz)		
				H-2'[g]	**H-4'**[g]	**H-5'**[g]	**H-6'**[g]
3d	3-CH_3[c]	9.94 (s)	8.46 (s)	6.84(d) (*J* = 2.1 Hz)	7.04 (d) (*J* = 7.9 Hz)	7.24 (t) (*J* = 8.3 Hz)	7.22 (d) (*J* = 7.5 Hz)
3e	3-OCH_3[d]	9.93 (s)	8.47 (s)	6.56 (d) (*J* = 2.0 Hz)	6.61 (d) (*J* = 7.8 Hz)	6.77 (t) (*J* = 7.6 Hz)	7.24 (d) (*J* = 7.3 Hz)
3g	3-Cl	9.68 (s)	8.49 (s)	7.07 (s) (*J* = 2.0 Hz)	7.29 (d) (*J* = 8.0 Hz)	7.21 (t) (*J* = 8.3 Hz)	6.93 (d) (*J* = 7.8 Hz)

[a] 4-OCH_3 protons appear at δ 3.81 (s) ppm; [b] 4-CH_3 protons appear at δ 2.34 (s) ppm; [c] 3-CH_3 protons appear at δ 2.33(s) ppm; [d] 3-OCH_3 protons appear at δ 3.79 (s) ppm; [e] 4-$COCH_3$ protons appear at δ 2.59 (s) ppm. [f] AA′ XX′ system ($J^* = J_{23} = J_{25}$)[g] H-2', 3' 4', 5', 6' aromatic hydrogens of the phenylamino moiety.

with substituent constant values for $-CF_3$ ($\sigma_p = 0.54$), and of $-NO_2$ ($\sigma_p = 0.76$).

It was found that, the rate constants for the reaction of aniline derivatives with [TNCB],[34] [DNCP],[16] and [DNCBTF] (contains two *ortho* nitro groups) are greater than 1-chloro-2,4-dinitrobenzene [DNCB],[33] 2-nitrochlorobenzene[34] and 3-nitro-2- chloropyridine[17] (contains one *ortho*-nitro group). This increase in rates is presumably explicable by the electronic effect of the activating group and its proximity to the leaving one. This is based on the steric effect of *o*-nitro groups in the former compounds TNCB, DNCP and DNCBTF and is unconvincing because the approach of the amine from a direction orthogonal to the ring results in the chlorine atom being pushed back from the ring plane.[7,8] Another explanation is that one of the two nitro group rotates to achieve better hydrogen bonding with the amino group and the second *o*-nitro group is then twisted more to relieve steric strain.[14,31] The substitution by arylamines instead of the chloro atom will replace a repulsive interaction with an attractive one and thus, at least partially, restore the planar conformation.[35,36] Consequently, the twist with respect to the ring of the nitro group in the *o*-positions in **3a**–**h** is reduced in comparison to the twist in DNCBTF. We assume that the most likely conformation of **3a–h** has one of the *o*-nitro groups oriented to achieve better hydrogen bonding with the amino group and the second *o*-nitro group is then twisted more to relieve steric strain.[37] This concept is in agreement with the spectroscopic data of **3a**–**h**, Tables 1and 2.

Table 3 shows that the variation of the rate constants depend on the nature and position of the substituents in the aniline derivatives. The order of decreasing reactivity of substituted anilines is found to be as follows: 4-OCH_3, 4-CH_3, 3-CH_3, H, 3-OCH_3,4-Cl, 3-Cl, 4-$COCH_3$. Good linear correlations between log k_A for the reaction of DNCBTF with 3- and 4-substituted anilines and the Hammett σ-constants are obtained at all temperatures with ρ values (–3.14, –3.16, –3.01). These values are similar to the value given by Chapman's hypothesis[38] and indicate that there is extensive transfer of charge from the aniline to the dinitrobenzotrifluoride ring in the transition state.[39] The sign and magnitude of

Table 3 Rate constants and activation parameters for the reaction of 4-chloro-3,5-dinitrobenzotrifluoride **1** (2×10^{-4} mol dm^{-3}) with substituted anilines **2a–h** (1×10^{-3}-5×10^{-1} mol dm^{-3}) in absolute MeOH

Cpd	R	10^2 k_A mol^{-1} s^{-1}			ΔH$^\#$/kcal mol^{-1}	–ΔS $^\#$/cal mol^{-1} K^{-1}
		30°C	40°C	50°C		
3a	H	1.85 ± 0.05	2.63 ± 0. 06	4.08 ± 0. 05	29.7 ± 2.6	180.4 ± 8.4
3b	4-OCH_3	16.75 ± 0.22	22.26 ± 0.23	30.80 ± 0.84	22.3 ± 1.4	186.4 ± 4.4
3c	4-CH_3	7.02 ± 0.10	10.20 ± 0.19	15.33 ± 0.26	29.3 ± 1.4	170.5 ± 4.4
3d	3-CH_3	3.09 ± 0.01	4.72 ± 0.07	6.92 ± 0.06	30.4 ± 0.4	173.8 ± 1.1
3e	3-OCH_3	0.82 ± 0.04	1.33 ± 0.12	2.07 ± 0.16	35.2 ± 0.2	168.7 ± 0.8
3f	4-Cl	0.31 ± 0.02	0.49 ± 0.02	0.74 ± 0.03	32.9 ± 0.4	184.3 ± 1.3
3g	3-Cl	0.12 ± 0.05	0.22 ± 0.04	0.36 ± 0.01	42.3 ± 1.8	161.3 ± 5.9
3h	4-$COCH_3$	0.04 ± 0.001	0.08 ± 0.001	0.16 ± 0. 001	53.6 ± 0.01	133.3 ± 2.0
ρ		–3.14 ± 0.04	–3.16 ± 0.05	–3.01 ± 0.07		
		(r = 0.99)	(r = 0.99)	(r = 0.99)		

β = 0.85 ± 0.1 (r = 0.97) at 30°C.

ρ values indicate that: (a) the negative ρ values are in agreement with the donor ability of aniline derivatives;[40] (b) a positive charge is developed on the aniline nitrogen atom as the transition state is formed;[41] (c) the substituent affects the rate by its polar effect; (d) the aniline derivative in the developed activated complex has become appreciably bonded to the carbon of DNCBTF.

Several reports have indicated that β values are dependent on the property of solvent and the nature of the amine as well as the reactivity of the nitro halo derivatives.[42-45] Since the dissociation of anilinium ions[39] and the reaction of DNCBTF with substituted anilines give good Hammett plots, the latter reaction must also give a Brønsted-like plot of the form $\log k_A = \beta \mathrm{pka} + \mathrm{constant}$. The effect of the basicity of the nucleophile on aromatic nucleophilic substitutions was shown by the dependence of the rates of structurally related nucleophiles.[46-48] Bordwell has pointed out that Brønsted plots reported in the literature,[37-43] for reactions in which bond formation to the nucleophile is rate-limiting have an almost symmetric position of the transition state along the reaction coordinate.[8] The Brønsted plot for the titled reaction at 30°C, gave a straight line with β equal to 0.85 ± 0.1 (r = 0.97), which is comparable with those reported.[46-48] The positive sign and the relatively high value of β is expected for a nucleophilic substitution reaction[49,50] and suggests a high extent of charge transfer from the nucleophile to the substrate in the transition state[52] (*i.e.* an appreciable degree of bond formation in the transition state[49,50]) and that bond formation to the aniline derivatives is rate-limiting.

The activation parameter values indicate that this reaction is slightly enthalpically controlled, but that it is substituent dependent, Table 3. This suggestion is corroborated by the calculation of the isokinetic temperature (252°C) for the title reaction (the temperature at which the substituent effect is supposed to be reversed) and this is far from the temperatures used in the kinetic runs. The ΔS# values are negative as expected for bimolecular nucleophilic substitution.[53] This is presumably due to the transition state exhibiting much greater charge separation than that existing in the reactants which will be accompanied by a considerable loss of solvent freedom. Furthermore the mechanism for the reaction series is common for all members as indicated by the excellent straight plot of log k30 against log k50 (gradient 1.12 ± 0.02, r = 0.99).

On the basis of no observation of an intermediate, the effects of substituent; no amine catalysis and high negative ρ values, it is evident that the reaction between DNCBTF and substituted anilines **2a–h** proceeds by a two stage mechanism with the first stage rate-determining.

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