Kinetic studies of σ-adduct formation and nucleophilic substitution in the reactions of ethyl 2,4,6-trinitrophenyl ether, some phenyl 2,4,6-trinitrophenyl ethers, and phenyl 2,4-dinitronaphthyl ether with aniline in dimethyl sulfoxide

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Abstract: The reaction of ethyl 2,4,6-trinitrophenyl ether with aniline in dimethyl sulfoxide containing Dabco occurs in two stages. The first gives **5**, the σ -adduct intermediate on the substitution pathway, which has been identified spectroscopically. The second yields 2,4,6-trinitrodiphenylamine, the substitution product. Kinetic studies show that proton transfer is rate limiting both in the formation of the intermediate and in its subsequent acid-catalysed decomposition. Phenoxide is a considerably better leaving group than ethoxide and the substitution reactions of phenyl 2,4,6-trinitrophenyl ethers and phenyl 2,4-dinitronaphthyl ether with aniline in DMSO occur without the accumulation of intermediates. The kinetics indicate both uncatalysed and base-catalysed pathways. The kinetic and equilibrium data for reaction of the ethyl and phenyl ethers are compared with data for σ -adduct formation from 1,3,5-trinitrobenzene and aniline.

Key words: nucleophilic substitution, proton transfer, base catalysis, σ -adducts.

Résumé : La réaction de l'oxyde d'éthyle et de 2,4,6-trinitrophényle avec l'aniline, dans le diméthylsulfoxyde contenant du DABCO, se produit en deux étapes. La première fournit le produit **5**, l'adduit- σ intermédiaire sur la voie de la substitution, que l'on a identifié par spectroscopie. La deuxième conduit à la 2,4,6-trinitrodiphénylamine, le produit de substitution. Des études cinétiques ont permis de montrer que le transfert de proton est l'étape cinétiquement limitante tant pour la formation de l'intermédiaire que pour sa décomposition acidocatalysée subséquente. L'ion phénolate est un bien meilleur groupe partant que l'éthanolate; les réactions de substitutions des oxydes de phényle et de 2,4,6-trinitrophényle, et de l'oxyde de phényle et de 2,4-dinitronaphtyle, avec l'aniline dans le DMSO se produisent sans accumulation d'intermédiaires. Les données cinétiques indiquent la présence de voies réactionnelles non catalysées et d'autres catalysées par les bases. On a comparé les données cinétiques et d'équilibre pour les réactions des oxydes d'éthyle et de phényle avec celles relatives à la formation de l'adduit- σ à partir du 1,3,5-trinitrobenzène et de l'aniline.

Mots clés : substitution nucléophile, transfert de proton, catalyse par les bases, adduits-o.

[Traduit par la rédaction]

Introduction

Whereas the reaction of 1,3,5-trinitrobenzene, TNB, with primary and secondary aliphatic amines in dimethyl sulfoxide, DMSO, spontaneously produces σ -adducts (1–3), reaction with aromatic amines requires the presence of a strong base. Buncel and co-workers showed, by use of ¹H NMR spectros-

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 Author to whom correspondence may be addressed. Telephone: +44 191 374 3130. Fax: +44 191 384 4737. E-mail: M.R.Crampton@durham.ac.uk copy, that reaction of the TNB–methoxide σ -adduct with aniline (4), or with ring-substituted anilines (5), resulted in the formation of TNB–anilide adducts, such as **1**.

Interestingly, kinetic studies (6, 7) showed that this conversion involved a dissociative mechanism rather than an $S_N 2$



displacement on the σ -adduct. It was later found that **1** may be formed directly from TNB and aniline in DMSO (8), or in acetonitrile (9), in the presence of a tertiary amine, B, such as Dabco or triethylamine, to act as a proton acceptor. The

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Fig. 1. Visible spectra of **3** $(4 \times 10^{-5} \text{ mol dm}^{-3})$ in DMSO containing aniline (0.1 mol dm⁻³), Dabco (0.05 mol dm⁻³), and Dabco hydrochloride (0.01 mol dm⁻³) taken after (*a*) 1 min, (*b*) 5 min, and (*c*) 3 h. The spectra show the rapid formation of **5** followed by the slower conversion to **6**.



reaction involves two steps, as shown in Scheme 1. The first step is thermodynamically unfavourable due to the weak basicity of aniline. However, the presence of a strong base renders the proton transfer step sufficiently favourable to allow formation of the anionic adduct. Nevertheless, kinetic studies (10, 11) showed that the proton transfer from the zwitterion, **2**, is rate limiting, corresponding to the condition $k_{-1} > k_{\rm B}$ [B]. When Dabco was used as the added base, a specific salt effect involving association of protonated Dabco with chloride ions was observed (12). There is also clear kinetic evidence for rate-limiting proton transfer in the reactions of TNB with aliphatic amines (13–15).

We have previously examined the kinetics of the reaction of ethyl 2,4,6-trinitrophenyl ether (16), **3**, and some ring-activated phenyl aryl ethers (17) with aliphatic amines in DMSO. In agreement with the classic work of Orvik and Bunnett (18), the results for **3** 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 observation of base catalysis in reactions of the phenyl aryl ethers was best explained in terms of rate-limiting proton transfer from a zwitterionic intermediate to base (17). Previous studies of nucleophilic substitution using aniline as the nucleophile have shown that in reaction with methyl 2,4,6trinitrophenyl ether there is competition between attack at the ring carbon atom to give a diphenylamine derivative, and at the side-chain carbon to give picric acid (19). Reactions of aniline with phenyl 2,4,6-trinitrophenyl ether yield the diphenylamine derivative and are subject to base catalysis in methanol, acetonitrile, tetrahydrofuran, ethyl acetate, and benzene (20). However, there was little evidence for catalysis in DMSO (19, 21).

Here we examine the kinetics of the reactions of **3**, and of some ring-activated phenyl aryl ethers with aniline in DMSO. Our results show that in these substitution reactions, as in the reaction of aniline with TNB, proton transfer may be the rate-limiting step.

Results and discussion

Kinetic and equilibrium measurements of the reactions with aniline were generally made in the presence of Dabco and Dabco hydrochloride. The pK_a values (22) in DMSO of the protonated forms of the bases are, for aniline, 3.82, and for Dabco, 9.06. Hence the value of the equilibrium constant, K'_a , for eq. [1] is 5.8×10^{-6} .

[1] aniline + DabcoH⁺ \rightleftharpoons aniline H⁺ + Dabco

$$K_{a}' = \frac{K_{a}(\text{DabcoH}^{+})}{K_{a}(\text{AnilineH}^{+})} = 5.8 \times 10^{-6}$$

Thus the concentrations of the reagents in the reaction mixture will be very similar to the stoichiometric concentrations; relatively little protonation of aniline will occur.

Reactions of ethyl 2,4,6-trinitrophenyl ether, 3

Ultraviolet–visible spectra of **3** in DMSO containing aniline (0.1 mol dm⁻³) indicated no reaction during 90 min. When the reaction was repeated with the addition of Dabco and DabcoH⁺ a biphasic reaction was observed. The spectra in Fig. 1 show that, in the first stage, a species with λ_{max} 430 nm and 500 nm is produced. The spectrum is typical of that for σ -adducts (2, 3) and ¹H NMR experiments confirm the formation of **5**, the intermediate on the substitution pathway. A second, much slower, reaction gave a species with λ_{max} 445 whose spectrum is identical to that of 2,4,6-trinitrodiphenylamine, **6**, in the reaction medium. Since the pK_a value (22) of **6** is 8.01, this species will be present largely in its deprotonated form, **7**.

The ¹H NMR spectrum of **3** in $[{}^{2}H_{6}]$ DMSO shows bands at

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Scheme 1.

Scheme 2.



Table 1. Kinetic and equilibrium data for the equilibration of 3 and 5 in DMSO at 25°C.

[Aniline]/mol dm ⁻³	[Dabco]/mol dm ⁻³	[Dabco H ⁺]/mol dm ⁻³	Abs ^{<i>a</i>} (430 nm)	$K_1 K_{\text{Dabco}} {}^b/\text{dm}^3 \text{ mol}^{-1}$	$k_{\rm fast}/10^{-3} {\rm ~s}^{-1}$	$k_{\rm calc} {}^c/10^{-3} {\rm s}^{-1}$
0.10	0.02	0.01	0.63	7.5	14	14
0.10	0.04	0.01	0.79	7.6	14	14
0.10	0.06	0.01	0.81	5.6	16	16
0.10	0.10	0.01	0.88	5.2	20	20
0.10	0.15	0.01	—		24	25
0.01	0.10	0.01	0.43	6.9	3.5	3.3
0.02	0.10	0.01	0.58	6.2	4.9	4.7
0.04	0.10	0.01	0.80	8.0	8.5	7.9
0.06	0.10	0.01	0.88	8.6	12	12
0.08	0.10	0.01	—	_	16	16

^a Absorbance at completion of fast reaction forming **5**.

Abs.[DabcoH⁺] ^b Calculated as $\frac{Aus.[Datc]}{(1.05 - Abs)[An][Dabco]}$

^c Calculated from eq. [6] with $K_1 k_{\text{Dabco}} = 1.17 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$, $k_{\text{DabcoH}} + = 0.2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and $k_{\text{An}} / k_{\text{Dabco}} = 0.46$.

δ 9.09 (ring hydrogens), 4.26 (q, J = 7 Hz, OCH₂), and 1.35 (t, CH₃). In the presence of aniline (1 equiv.) and Dabco (1 equiv.), bands due to 5 are observed at δ 8.62 (ring), 3.14 (q, J = 7 Hz, OCH₂), and 1.08 (t, CH₃). It is interesting (4, 5) that the anilide group of 5 shows a singlet at δ 5.98 attributed to the amino hydrogen together with spin-coupled, J = 8 Hz, bands due to ring hydrogens at δ 6.93(t), 6.52(t), and 6.35(d). Over a period of 1 h the bands due to 5 decrease in intensity while bands attributable to the substitution products, 7 and ethanol, increase in intensity. A small band at δ 8.58 is also observed, indicating the formation of some picric acid.

UV-visible measurements show that, in solutions containing Dabco but without aniline, 3 is very slowly converted to picric acid, $\lambda_{max} = 380$ nm. This reaction could be inhibited by the presence of Dabco hydrochloride. The latter observation indicates that picric acid formation is likely to be due to attack of hydroxide, formed from adventitious water in the solvent, at the 1-position rather than attack by Dabco at the side-chain ethyl group. All quantitative measurements involving aniline

were made in buffered solutions, Dabco with Dabco hydrochloride, to suppress picric acid formation.

Our kinetic and equilibrium results are interpreted in terms of Scheme 2, in which the zwitterion, 4, is expected to be an intermediate present in low concentrations. The first stage of the reaction, representing the equilibration of 3 and 5, was monitored at 430 nm. With concentrations of aniline (An), Dabco, and Dabco hydrochloride in large excess of the concentration of 3, first-order kinetics were observed. Rate constants, k_{fast} , and absorbances at completion of the equilibration are given in Table 1. All measurements were made in the presence of DabcoH⁺, 0.01 mol dm⁻³, to maintain constant ionic strength.

An equilibrium constant for formation of 5 may be defined in terms of the Dabco concentration by eq. [2]. The absorbance values in Table 1 lead to a value for $K_1 K_{\text{Dabco}}$ of $7 \pm 1 \text{ dm}^3 \text{ mol}^{-1}$.

[2]
$$K_1 K_{\text{Dabco}} = \frac{k_1 k_{\text{Dabco}}}{k_{-1} k_{\text{DabcoH}^+}} = \frac{[5]}{[3]} \times \frac{[\text{DabcoH}^+]}{[\text{An}] [\text{Dabco}]}$$

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Alternatively, the equilibrium constant may be defined in terms of the aniline concentration in eq. [3]:

[3]
$$K_1 K_{An} = \frac{k_1}{k_{-1}} \times \frac{k_{An}}{k_{AnH}^+} = \frac{[5]}{[3]} \times \frac{[AnH^+]}{[An]^2}$$

Use of eq. [1] leads to eq. [4], showing that the value of K_1K_{An} will be many orders of magnitude lower than the value

of $K_1 K_{\text{Dabco}}$, and explaining why adduct formation is not observed in the absence of Dabco.

$$[4] K_1 K_{An} = K_1 K_{Dabco} K_a'$$

The variation of k_{fast} with values of the Dabco and aniline concentrations is compatible only with proton transfer being rate determining in the formation of **5**. Using the condition $k_{-1} > k_{\text{B}}[\text{B}]$ and treating **4** as a steady-state intermediate leads to the rate expression given in eq. [5]:

[5]
$$k_{\text{fast}} = \frac{k_1}{k_{-1}} [\text{An}](k_{\text{An}}[\text{An}] + k_{\text{Dabco}}[\text{Dabco}]) + k_{\text{DabcoH}^+}[\text{DabcoH}^+] + k_{\text{AnH}^+}[\text{AnH}^+]$$

Here k_{Dabco} and k_{An} represent k_{B} when reaction involves Dabco and aniline, respectively, while k_{DabcoH^+} and k_{AnH^+} represent k_{BH^+} for reactions with the appropriate conjugate acids.

Since K_{An}/K_{Dabco} has a constant value (eq. [4]) it is possible to reduce the number of variables in eq. [5] to give eq. [6]:

$$[6] k_{\text{fast}} = K_1 k_{\text{Dabco}} [\text{An}] \left([\text{Dabco}] + \frac{k_{\text{An}}}{k_{\text{Dabco}}} [\text{An}] \right) + k_{\text{DabcoH}^+} [\text{DabcoH}^+] \left(1 + \frac{k_{\text{An}}}{k_{\text{Dabco}}} \frac{[\text{An}]}{[\text{Dabco}]} \right)$$

Excellent agreement between the calculated and observed values of k_{fast} was obtained with K_1k_{Dabco} 1.17 ± 0.10 dm⁶ mol⁻² s⁻¹, k_{DabcoH^+} 0.20 ± 0.05 dm³ mol⁻¹ s⁻¹, and $k_{\text{An}}/k_{\text{Dabco}}$ 0.46 ± 0.10. The latter value indicates that aniline competes effectively with the much stronger base Dabco in the proton transfer step, **4** \Rightarrow **5**. This point is discussed later. It was not possible to obtain an acceptable fit between calculated and observed values of k_{fast} with lower values of the ratio $k_{\text{An}}/k_{\text{Dabco}}$. Combination of the values of K_1k_{Dabco} and k_{DabcoH^+} leads to a value of K_1K_{Dabco} of 5.9 dm³ mol⁻¹, in acceptable agreement with that obtained independently from absorbance measurements at equilibrium.

The slow product-forming reaction was measured at 445 nm. Values of the first-order rate constants, k_{slow} , are reported in Table 2. Making the assumption that **3** and **5** are in rapid equilibrium during this stage of the reaction leads to the rate expression of eq. [7].

[7]
$$k_{\text{slow}} = \left(k_{\text{sub,DabcoH}} [\text{DabcoH}]^+ + k_{\text{sub,AnH}} [\text{AnH}^+]\right) \left(\frac{K_1 K_{\text{Dabco}} [\text{Dabco}] [\text{An}]}{K_1 K_{\text{Dabco}} [\text{Dabco}] [\text{An}] + [\text{DabcoH}^+]}\right)$$

Here $k_{\text{sub,DabcoH}^+}$ and $k_{\text{sub,AnH}^+}$ are, respectively, the rate constants for the substitution reactions involving protonated Dabco and aniline. Use of eq. [1] results in eq. [8]:

[8]
$$k_{\text{slow}} = \left(k_{\text{sub,DabcoH}^{\dagger}} + k_{\text{sub,AnH}^{+}} \cdot \frac{[\text{Dabco}]}{[\text{An}]}\right) \left(\frac{K_1 K_{\text{Dabco}} [\text{Dabco}] [\text{An}] [\text{DabcoH}^{+}]}{K_1 K_{\text{Dabco}} [\text{Dabco}] [\text{An}] + [\text{DabcoH}^{+}]}\right)$$

Analysis of the results using the known value for K_1K_{Dabco} of 7 dm³ mol⁻¹ showed that most of the reaction flux involved the protonated Dabco. Agreement between observed and calculated values of k_{slow} was optimized with values of $0.06 \pm 0.01 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for $k_{\text{sub,DabcoH}^+}$ and $0.005 \pm 0.002 \text{ dm}^3 \text{ mol}^{-1}$ s⁻¹ for $k_{\text{sub,AnH}^+}K_a'$. Using the known value of K_a' leads to a value for $k_{\text{sub,AnH}^+}$ of 860 dm³ mol⁻¹ s⁻¹.

Reactions of phenyl 2,4,6-trinitrophenyl ethers, 8

Reactions of **8a–c** with aniline in DMSO proceeded in a single stage. UV–visible spectra, and NMR spectra (in more concentrated solutions), at completion of reaction were identical to those of **6**, the expected substitution product, in the reaction medium.

Kinetic measurements were made with aniline and with solutions containing aniline, Dabco, and Dabco hydrochloride. With these concentrations in large excess of the substrate concentration, first-order kinetics were observed. Data obtained with aniline alone are shown in Fig. 2. Plots of the second-order rate constant, k_{obs} /[aniline], versus aniline concentration were linear with positive intercepts. At a constant aniline concentration, values of the first-order rate constant, k_{obs} , increased linearly with Dabco concentration, as shown in Fig. 3. These results are interpreted in terms of the process shown in Scheme 3. It is known (17, 23) that phenoxide is a considerably better leaving group than ethoxide, by a factor of ca. 10⁶. Our failure to observe **10**, the intermediate on the substitution pathway, may be attributed to its rapid decomposition by loss of phenoxide. The assumption that **9** may be treated as a steady-state intermediate leads to the rate expression of eq. [9], where k_{An} and k_{Dabco} represent k_{B} for the respective bases.

[9]
$$k_{\text{obs}} = \frac{k_1[\text{An}] \left(k_2 + k_{\text{An}}[\text{An}] + k_{\text{Dabco}}[\text{Dabco}]\right)}{k_{-1} + k_2 + k_{\text{An}}[\text{An}] + k_{\text{Dabco}}[\text{Dabco}]}$$

Our results, which provide evidence for base catalysis, indicate that the condition $k_{-1} >> k_2 + k_{An}[An] + k_{Dabco}[Dabco]$ applies so that eq. [9] reduces to eq. [10].

[10] $k_{obs} = K_1[An](k_2 + k_{An}[An] + k_{Dabco}[Dabco])$

Values obtained for K_1k_2 , K_1k_{An} , and K_1k_{Dabco} can be found in Table 3.

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Table 2. Kinetic data for the formation of the product, **6**, in DMSO at 25°C.

[Aniline]/	[Dabco]/	[DabcoH ⁺]/		
mol dm ⁻³	mol dm ⁻³	mol dm ⁻³	$k_{\rm slow}/10^{-4} {\rm s}^{-1}$	$k_{\rm calc} a / 10^{-4} {\rm s}^{-1}$
0.10	0.02	0.01	3.4	3.5
0.10	0.04	0.01	4.3	4.5
0.10	0.06	0.01	5.1	5.1
0.10	0.10	0.01	5.5	5.7
0.10	0.15	0.01	5.9	6.1
0.01	0.10	0.01	4.7	4.5
0.02	0.10	0.01	5.1	5.0
0.04	0.10	0.01	5.5	5.3
0.06	0.10	0.01	5.6	5.5
0.08	0.10	0.01	5.7	5.6
0.05	0.05	0.003^{b}	1.8	1.7
0.05	0.05	0.005^{b}	2.6	2.5
0.05	0.05	0.007^{b}	3.4	3.3
0.05	0.05	0.010	4.3	4.1

^{*a*} Calculated from eq. [8] with $k_{sub,DabcoH^+} 0.060 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$,

 $k_{\text{sub},\text{AnH}^+} \cdot K_a' 0.005 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and $K_1 K_{\text{Dabco}} 7.0 \text{ dm}^3 \text{ mol}^{-1}$. ^{*b*} Ionic strength was maintained at 0.01 mol dm⁻³ using tetrabutylammonium chloride.

Reactions of phenyl 2,4-dinitronaphthyl ether, 11

UV–visible and ¹H NMR studies showed that in the presence of aniline, or aniline with Dabco, **11** was smoothly converted into *N*-phenyl-2,4-dinitronaphthylamine. Kinetic measurements at 440 nm showed a single first-order process. Values of the rate constant, k_{obs} , are given in Table 4. Data are interpreted in a manner similar to that given for **8** so that Scheme 3 is applicable and eq. [10] will apply. Values calculated with K_1k_2 2.0×10^{-4} dm³ mol⁻¹ s⁻¹, K_1k_{An} 1.1×10^{-2} dm⁶ mol⁻² s⁻¹, and K_1k_{Dabco} 0.24 dm⁶ mol⁻² s⁻¹ give excellent agreement with values of k_{obs} .



Comparisons

Data for reactions of 3, 8, and 11 are collected in Table 3, where they are compared with values for the formation of 1 from TNB. The value of $K_1 K_{\text{Dabco}}$, the overall equilibrium constant for formation of the adduct 5 from 3, is ca. 20 times larger than that for formation of 1 by reaction at an unsubstituted ring position of TNB. The major effect is likely to be an increase in K_1 due to relief of steric strain present in the parent (16, 24) when the ethoxy group is twisted from the ring plane. Stereoelectronic stabilization of 5 relative to 1 may also contribute, as described in related systems by Buncel et al. (25). The polar effect of the ethoxy group will be expected to result in an increase in the value of K_1 and may also give rise to a small increase in K_{Dabco} . For comparison (16), the equilibrium constant for formation of 12 from 3 and *n*-butylamine has a value 50 times larger than that for the corresponding formation of 13. We have not observed an adduct formed by attack of **Fig. 2.** Plots of the second-order rate constant, k_{obs} /[aniline], versus aniline concentration for reactions of **8a**, **8b**, and **8c** with aniline in DMSO.



Fig. 3. Plots of k_{obs} versus [Dabco] for reactions of **8a**, **8b**, and **8c** with aniline (0.02 mol dm⁻³) in DMSO containing Dabco hydrochloride (0.05 mol dm⁻³).



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Scheme 3.

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Table 3. Comparison of data in DMSO at 25°C.

Reactant	$K_1 k_{ m An} / \ { m dm^6 \ mol^{-2} \ s^{-1}}$	$K_1 k_{ m Dabco} / dm^6 mol^{-2} s^{-1}$	$\frac{K_1k_2}{dm^3 mol^{-1} s^{-1}}$	$k_{\mathrm{DabcoH}^{+}}$ dm ³ mol ⁻¹ s ⁻¹	$K_1 K_{\text{Dabco}} / $ dm ³ mol ⁻¹	$k_{\rm An}/k_{\rm Dabco}$	$k_{\mathrm{An}}/k_2 \mathrm{dm^3 mol^{-1}}$
3	0.54	1.17	_	0.2	7	0.46	_
TNB^{a}		26	_	74	0.35		
8a	0.42	1.2	0.055	—	_	0.35	8
8b	0.27	1.6	0.050	—	_	0.17	5.4
8c	0.65	0.9	0.32			0.72	2
11	0.011	0.24	0.0002	—	_	0.045	55

^a From ref. 12. Values quoted are in presence of tetraethylammonium chloride 0.01 mol dm⁻³, to correspond with data for reactant 3.



aniline at the unsubstituted 3-position of **3**. This may be explained by the much lower thermodynamic stability expected for this adduct compared with its isomer **5** or with the adduct **1** formed from TNB. Attack at the 3-position of **3** will not relieve the steric strain present in the parent, and work with aliphatic amines (16) suggests that the adduct so formed would have a stability ca. 100 times lower than that of the adduct **1** from TNB.

Buncel et al. (10, 11) showed that, in the formation of **1** from TNB and aniline, the proton transfer step is rate limiting. Similarly in the formation of **5** our results indicate rate-limiting proton transfer. From eqs. [1] and [4], K_{An}/K_{Dabco} has the value 5.8×10^{-6} , showing that the equilibrium constant for the proton-transfer step is very much smaller when the reaction involves aniline than when it involves Dabco. Nevertheless the ratio of 0.46 obtained for k_{An}/k_{Dabco} shows that *kinetically* aniline may compete effectively with Dabco, a much stronger base, in the proton-transfer step. This may seem surprising; however, it should be remembered that the proton-transfer

Table 4. Kinetic results for reaction of phenyl 2.4-dinitronaphthyl ether with aniline in DMSO at 25°C.

[Aniline]/	[Dabco]/	kaha/	$k_{\rm colo} a/$
mol dm ⁻³	mol dm ⁻³	10^{-5} s^{-1}	10^{-5} s^{-1}
0.02	_	0.84	0.84
0.04		2.5	2.6
0.07	_	6.7	6.8
0.10	—	14	13
0.15		29	28
0.20	—	50	48
0.11	0.01	44	42
0.11	0.02	71	68
0.11	0.03	92	95
0.11	0.05	150	150
0.11	0.10	280	280

^{*a*} Calculated from eq. [10] with $K_1k_2 2.0 \times 10^{-4}$ dm³ mol⁻¹ s⁻¹, $K_1k_{An} 1.1 \times 10^{-2}$ dm⁶ mol⁻² s⁻¹, and $K_1k_{Dabco} 0.24$ dm⁶ mol⁻² s⁻¹.

step, $4 \Rightarrow 5$, in Scheme 2 will be thermodynamically favourable even when the reaction involves aniline as B and the anilinium ion as BH⁺. Thus it is known (5, 26) that the trinitrocyclohexadienate group, even though negatively charged, is electron withdrawing relative to hydrogen. Hence 4 will be more acidic than the anilinium ion. Values of k_{An} and k_{Dabco} will be affected by steric factors rather than the relative basicities of the amines. It is likely that the proton to be transferred from **4** will be hydrogen bonded to a DMSO molecule in the solvent (13, 27, 28) and this, together with steric hindrance to the approach of the reagents, will reduce values of rate constants below the diffusion limit.

It is interesting to speculate on values of rate constants for the proton-transfer step. It has previously been estimated (15, 16) that the presence of the trinitrocyclohexadienate ring in zwitterions such as 4 will acidify the adjacent ammonium protons by a factor of ca. 500, as indicated in eq. [11]:

[11]
$$K_a(4)/K_a(AnH^+) = 500$$

Use of eq. [1] allows the comparison of the relative acidities of **4** and protonated Dabco as shown in eq. [12]:

[12]
$$K_a$$
 (4)/ K_a (DabcoH⁺) = $\frac{500}{5.8 \times 10^{-6}}$ = 8.6 × 10²

The ratio obtained corresponds to $k_{\text{Dabco}} / k_{\text{DabcoH}^+}$ and since k_{DabcoH^+} has been found experimentally to be 0.2 dm³ mol⁻¹ s⁻¹ we obtain a value for k_{Dabco} of 1.7×10^7 dm³ mol⁻¹ s⁻¹. This allows the calculation of values for k_{An} of 8×10^6 dm³ mol⁻¹ s⁻¹ and for K_1 of 7×10^{-8} dm³ mol⁻¹. Since the ratio given in eq. [11] is not known precisely, the values calculated using it should be regarded only as estimates.

The data in Table 3 indicate that values of rate constants for proton transfer are larger in the formation of **1** from TNB, than in the formation of **5**. Here reaction occurs at an unsubstituted ring position so that there is less steric congestion at the reaction centre. A calculation analogous to that given above leads here to a value for k_{Dabco} in excess of $10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

The formation of **6** from **5** involves general acid-catalysed expulsion of the ethoxy group. Values of the rate constants for reaction with the anilinium ion, 860 dm³ mol⁻¹ s⁻¹, and Dab-coH⁺, 0.06 dm³ mol⁻¹ s⁻¹, may be used in conjunction with eq. [1] to calculate a Brønsted α value of 0.80.

Phenoxide is known to be a considerably better leaving group than ethoxide (17, 23), and we did not observe intermediates in the substitution reactions of the phenyl ethers 8a-c. We interpret the increases in the rate constant shown in Figs. 2 and 3 as base catalysis. Previous work (19, 21), at lower base concentrations, did not find evidence for base catalysis. The effects we have observed are not particularly large. However, values calculated for $K_1 k_{An}$ and $K_1 k_{Dabco}$ for reactions of **8a–c** are similar to those found for reaction of 3, where there is genuine base catalysis. These similarities are to be expected if proton transfer from zwitterion, 9 or 4, to base is rate limiting. The presence of a phenoxy group rather than an ethoxy group at the 1-position is not expected to drastically affect the value of K_1 for formation of the zwitterion (29). Nor will this change be expected to greatly alter the values of k_{An} or k_{Dabco} for the proton-transfer step. A major difference between the phenyl ethers, 8, and the ethyl ether, 4, is that in the former case much of the reaction flux involves the direct uncatalysed decomposition of the zwitterions, 9, by the k_2 step. This step is likely to involve intramolecular proton transfer from nitrogen to oxygen coupled with carbon-oxygen bond cleavage. Leavinggroup expulsion is part of the rate-limiting step here, so that reaction of the 4-nitrophenoxy derivative, 8c, is six times faster than that of the phenoxy derivative, 8b (Table 3).

Comparison of data for reaction of phenyl

2,4-dinitronaphthyl ether, **11**, with that for phenyl 2,4,6-trinitrophenyl ether, **8b**, shows decreases in K_1k_2 , K_1k_{An} , and K_1k_{Dabco} by factors of 250, 24, and 7, respectively. These changes may be attributed (2, 3) to two main factors: the decrease in ring activation in **11** compared to **8b**, and the reduction in steric crowding at the reaction centre in the zwitterionic



intermediate **14** compared to that in the corresponding intermediate, **9b**. The first factor will result in a decrease in the value of K_1 and hence in the value of K_1k_2 . That the decreases observed for K_1k_{An} and K_1k_{Dabco} are smaller than that observed for K_1k_2 may be attributed to the second factor. A reduction in steric crowding in **14** compared to **9b** may allow the easier approach of a base molecule to accept a proton from the zwitterionic intermediate. Hence values of k_{An} and k_{Dabco} may be larger in the 2,4-dinitronaphthyl system. The k_{An}/k_{Dabco} ratio is somewhat decreased in the dinitronaphthyl system and this may indicate that the situation is being approached in which the reduction in the electron-withdrawing ability of the ring system renders the proton transfer from **14** to aniline thermodynamically unfavourable.

Experimental

Ethyl 2,4,6-trinitrophenyl ether (16), **3**, phenyl 2,4,6-trinitrophenyl ether (17), **8b**, and phenyl 2,4-dinitronaphthyl ether (17), **11**, were available from previous work. The 4-substituted phenyl 2,4,6-trinitrophenyl ethers **8a** and **8c** were prepared by reaction at 45°C for 3 h of picryl chloride (1 equiv.) with sodium hydroxide (1 equiv.) in an excess of the appropriate 4-substituted phenol containing a little water. On completion, water was added to remove any picric acid produced and recrystallization from ethanol yielded **8a**, mp 100°C (lit. (30) mp 103°C) and **8c**, mp 163°C (lit. (30) mp 157°C). 2,4,6-Trinitrodiphenylamine, **6**, and *N*-phenyl-2,4-dinitronaphthylamine were available from previous work (22). Solvent, amines, and amine salts were prepared and (or) purified as described previously (22).

¹H NMR spectra were recorded using Varian-200 XL or VXR-400 spectrometers. UV–visible spectra and kinetic measurements were made with Beckman Lambda 2 or Applied Photophysics SX.17 MV stopped-flow spectrophotometers at 25°C. Reported rate constants are the means of several determinations and are precise to $\pm 5\%$.

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