Kinetics of the Reactions of Aniline and 2,2,2-Trifluoroethylamine with 1,3,5-Trinitrobenzene in Dimethyl Sulphoxide and Acetonitrile, and of 2,2,2-Trifluoroethylamine with 1-Fluoro- and 1-Chloro-2,4-dinitrobenzenes in these Solvents

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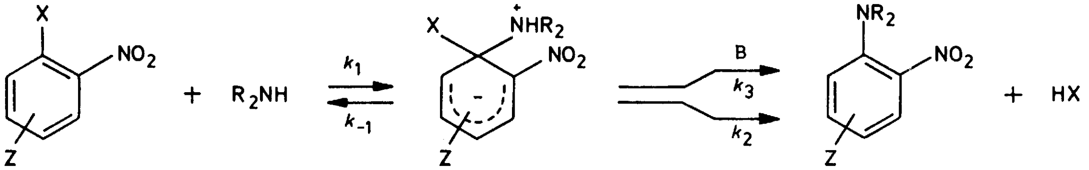
Meisenheimer complex formation between 1,3,5-trinitrobenzene (TNB) and the primary amines aniline and 2,2,2-trifluoroethylamine (TFE) has been studied in dimethyl sulphoxide and acetonitrile. The reaction with aniline is catalysed in both solvents by 1,4-diazabicyclo[2.2.2]octane (DABCO). With TFE, catalysis by both TFE and DABCO was observed in acetonitrile, but not in dimethyl sulphoxide. The reactions of TFE with 1-fluoro- and 1-chloro-2,4-dinitrobenzenes are not base catalysed in dimethyl sulphoxide or acetonitrile.

THE mechanism of aromatic bimolecular nucleophilic substitution when primary or secondary amines are the nucleophiles is given by equation (1), where B is a base which could be the nucleophile itself. Application of the steady state hypothesis gives equation (2) where k_A is the observed second-order rate constant.

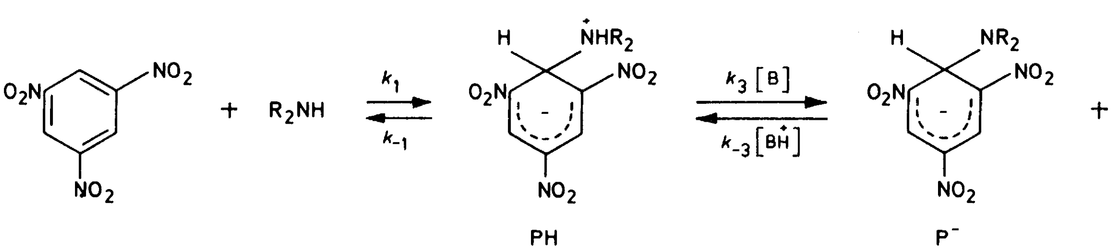


(1)

$$k_A = \frac{k_1(k_2 + k_3[B])}{k_{-1} + k_2 + k_3[B]} \qquad (2)$$

For the condition $k_{-1} \ll k_2 + k_3[B]$, $k_A = k_1$ and the reaction is independent of B; when $k_{-1} \gg k_2 + k_3[B]$, the reaction is base-catalysed. We have shown that for the reactions of 1-fluoro-2,4-dinitrobenzene in acetonitrile when n-butylamine or benzylamine are the nucleophiles, the reactions are not base-catalysed,[1] but when the nucleophile is aniline, then base-catalysis is observed.[2,3]

Both primary and secondary aliphatic amines form stable σ-complexes (Meisenheimer complexes) with 1,3,5-trinitrobenzene (TNB) and with other highly activated aromatic substrates in a variety of solvents;[4] the mechanism is shown in equation (3).



(3)

Until recently aromatic amines were thought not to participate in this type of reaction, but to form charge-transfer complexes.[5] Buncel and Leung[6] have, however, demonstrated that in the presence of tertiary amines such as triethylamine and 1,4-diazabicyclo[2.2.2]octane (DABCO), aniline forms a σ-complex with TNB in dimethyl sulphoxide. Buncel and Eggimann[7] have attributed this contrasting behaviour of aliphatic and aromatic amines towards TNB as being due to a thermodynamic factor, K_1 ($=k_1/k_{-1}$) in equation (3) being very much less for aromatic amines than for aliphatic ones. In spite of the relatively large equilibrium constant for the second stage ($PH + B = P^- + BH^+$), the overall equilibrium is disfavoured and σ-complex formation does not take place. The addition of DABCO, which is *ca.* 10^4 times more basic than aniline, increases the equilibrium constant for the deprotonation stage and the overall reaction becomes feasible.

Although the differences in the reactions of the two types of amines both in Meisenheimer complex formation and in aromatic nucleophilic substitution can be explained by the difference in their basic strengths, the comparison is essentially between aromatic and aliphatic amines and this factor may have a considerable effect on the results; hence a comparison between aromatic and aliphatic amines of approximately the same base strength is desirable.

In aqueous solution, there is only a ten-fold difference between the basicities of aniline, pK_a 4.60,[8] and 2,2,2-trifluoroethylamine (TFE), pK_a 5.59,[9] and we assume this factor does not change drastically with change of solvent.

We have studied the kinetics of the reaction of TFE with 1-fluoro- and 1-chloro-2,4-dinitrobenzenes in dimethyl sulphoxide and acetonitrile for comparison with the results we have already obtained with aniline as the nucleophile,[3] and its reaction with TNB in these solvents. The reaction of aniline with TNB in acetonitrile has also been studied and for the sake of direct internal comparison some of the results of Buncel and Eggimann for this system in dimethyl sulphoxide have been repeated.

RESULTS AND DISCUSSION

(a) *Meisenheimer-complex Formation.*—(i) *Reactions of TNB with aniline.* Our measurements of the spectral characteristics of the red colour formed by TNB–aniline–DABCO mixtures in dimethyl sulphoxide confirmed the results of Buncel and his co-workers.[6,7] In acetonitrile the complex had maximum absorbances at 446 and 522 nm, the absorbance at the lower wavelength having the higher intensity. The value of the extinction coefficient at 446 nm obtained from Benesi–Hildebrand plots[10] in the presence of 0.1M tetraethylammonium chloride was 3.02 × 10^4 l mol^{-1} cm^{-1}.

In the kinetic investigations of reaction (4) the

$$\mathrm{TNB} + \mathrm{PhNH_2} + \mathrm{DABCO} \rightleftharpoons \mathrm{TNB{\cdot}NHPh^-} + \mathrm{DABCO\overset{+}{H}} \qquad (4)$$

concentrations of aniline and DABCO were in large excess over the substrate, and the system reduces to (5)

$$\mathrm{TNB} \overset{k_f^1}{\underset{k_r^2}{\rightleftharpoons}} \mathrm{TNB{\cdot}NHPh^-} + \mathrm{DABCO\overset{+}{H}} \qquad (5)$$

The experimental rate law (6) was demonstrated by

$$V = \mathrm{d[TNB{\cdot}NHPh^-]}/\mathrm{d}t = k_f^1[\mathrm{TNB}] - k_r^2[\mathrm{TNB{\cdot}NHPh^-}]^2 \qquad (6)$$

Buncel and Eggimann[7] and confirmed by us in both dimethyl sulphoxide and acetonitrile. The methodology and integrated rate equations we employed in obtaining k_f^1 were essentially those of these authors and the results are given in Tables 1—3. The additional quantities given in the Tables are defined as $k_f^2 = k_f^1/[\mathrm{PhNH_2}]$, $k_f^3 = k_f^1/[\mathrm{PhNH_2}][\mathrm{DABCO}]$, and * $k_r^2 = k_f^3/K$ where $K = [\mathrm{TNB{\cdot}NHPh^-}]_e[\mathrm{DABCO\overset{+}{H}}]_e/[\mathrm{TNB}]_e[\mathrm{PhNH_2}]_e[\mathrm{DABCO}]_e$.

The results in dimethyl sulphoxide are in full agreement with those of Buncel and Eggimann.[7] A plot of k_f^2 *versus* [DABCO] is linear, passing through the origin; a least-squares treatment gives slope 2.4 ± 0.1, intercept $-6.36 \times 10^{-5} \pm 3.94 \times 10^{-3}$, and r 0.993, and the assumption of third-order kinetics gives a constant value of k_f^3. In acetonitrile, the plot is again linear, but with a small intercept, a least-squares treatment giving slope 22.6 ± 0.3 and intercept $3.83 \pm 0.76 \times 10^{-2}$ and the assumption of third-order kinetics gives values of k_f^3 which fall slightly with increasing DABCO concentration.

TABLE 1

Rate and equilibrium data for the reaction of TNB[a] and aniline[b] in the presence of DABCO at constant $[\mathrm{Et_4NCl}]$[c] in dimethyl sulphoxide and acetonitrile at 30.6°

Solvent					
Dimethyl sulphoxide	10^3[DABCO]/M	7.04	21.0	31.3	42.5
	$10K$l/mol^{-1}	8.65	9.02	7.21	6.67
	$10^4k_f^1/s^{-1}$	8.18	24.7	33.6	49.6
	$10k_f^2$/l mol^{-1} s^{-1}	1.72	5.18	7.04	10.4
	k_f^3/l^2 mol^{-2} s^{-1}	24.4	24.7	22.6	24.5
Acetonitrile	10^3[DABCO]/M	5.94	14.6	30.6	42.1
	10^2K/l mol^{-1}	10.6	7.44	7.24	7.92
	$10^4k_f^1/s^{-1}$	8.42	18.2	36.6	48.8
	$10k_f^2$/l mol^{-1} s^{-1}	1.70	3.68	7.39	9.84
	k_f^3/l^2 mol^{-2} s^{-1}	28.6	25.2	24.1	23.4

[a] $[\mathrm{TNB}]_0$ 1.01 × 10^{-4}M in $\mathrm{Me_2SO}$; 1.15 × 10^{-4}M in MeCN. [b] $[\mathrm{PhNH_2}]_0$ 4.77 × 10^{-3}M in $\mathrm{Me_2SO}$; 4.96 × 10^{-3}M in MeCN. [c] $[\mathrm{Et_4NCl}]$ 0.1M in all runs.

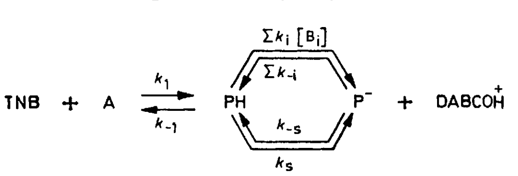
TABLE 2

Rate and equilibrium data for the reaction of TNB[a] and TFE at constant $[\mathrm{Et_4NCl}]$[b] in dimethyl sulphoxide and acetonitrile at 30.6°

Solvent						
Dimethyl sulphoxide	10^3[TFE]/M	1.901	2.377	4.752	9.504	
	$10K$/l mol^{-1}	9.65	5.04	10.1	6.03	
	$10^5k_f^1/s^{-1}$	5.59	7.63	14.6	27.7	
	$10^2k_f^2$/l mol^{-1} s^{-1}	2.94	3.21	3.08	2.91	
Acetonitrile	10^2[TFE]/M	3.45	4.31	6.89	8.61	10.33
	10^3K/l mol^{-1}	4.31	4.21	6.55	6.02	5.83
	$10^4k_f^1/s^{-1}$	3.25	4.41	12.1	18.8	27.7
	$10^3k_f^2$/l mol s^{-1}	9.42	10.2	17.6	21.8	26.8
	$10k_f^3/l^2$ mol^{-2} s^{-1}	2.73	2.37	2.55	2.53	2.60

[a] $[\mathrm{TNB}]_0$ 9.412 × 10^{-5}M in $\mathrm{Me_2SO}$; 1.006 × 10^{-4}M in MeCN. [b] $[\mathrm{Et_4NCl}]$ 0.1M in all runs.

The results can be interpreted in terms of the intermediate complex theory by equation (7). On the



(7)

assumption that PH can be treated as a steady state intermediate, equation (8) applies where $\Sigma k_i[\mathrm{B_i}] = k_A[\mathrm{A}] + k_D$ [DABCO] and refers to the removal of a proton from PH by aniline and DABCO: k_s refers to its removal by the solvent.

$$k_f^2 = \frac{k_1(k_s + \Sigma k_i[\mathrm{B_i}])}{(k_{-1} + k_s + \Sigma k_i[\mathrm{B_i}])} \qquad (8)$$

In both dimethyl sulphoxide and acetonitrile the linear dependence of k_f^2 on [DABCO] implies that $k_{-1} \gg k_s + \Sigma k_i[\mathrm{B_i}]$ and in dimethyl sulphoxide as the intercept

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* A referee has suggested that we comment on the k_r^2 values. Since this work was completed, however, Buncel and Eggimann[11] have shown that extensive heteroconjugation of the type $\mathrm{BH^+ + Cl^- \rightleftharpoons BH^+ \cdots Cl^-}$, occurs between the ammonium ions and the anion of the added electrolyte in dimethyl sulphoxide and that values of k_r^2 (and K) are very sensitive to the concentration of added electrolyte. As this effect probably occurs to a greater extent in acetonitrile, we have not attempted any analysis of k_r^2 or the comparison of K in the two solvents.

TABLE 3

Rate and equilibrium data for the reaction of TNB[a] and TFE[b] in the presence of DABCO in dimethyl sulphoxide and acetonitrile at 30.6° at constant [Et_4NCl][c]

Solvent							
Dimethyl sulphoxide	10^3[DABCO]/M	2.348	3.13	4.087	5.828		
	K/l mol^{-1}	1.58	1.56	1.61	1.47		
	$10^5 k_f^1/s^{-1}$	7.71	6.70	7.75	7.91		
	$10^2 k_f^2$/l mol^{-1} s^{-1}	4.06	3.52	4.08	4.16		
Acetonitrile	10^2[DABCO]/M	1.00	2.63	4.08	5.15	6.40	8.59
	$10^2 K$/l mol^{-1}	2.13	1.77	2.28	2.61	2.16	2.00
	$10^4 k_f^1/s^{-1}$	5.93	8.80	13.5	17.6	18.9	24.20
	$10^2 k_f^2$/l mol^{-1} s^{-1}	1.40	2.08	3.19	4.16	4.47	5.72

[a] $[TNB]_0$ 9.412×10^{-5}M in Me_2SO; 1.48×10^{-4}M in MeCN. [b] $[TFE]_0$ 1.901×10^{-3}M in Me_2SO; 4.23×10^{-2}M in MeCN. [c] [Et_4-NCl] 0.1M in all runs.

is zero, $k_D\,[DABCO] \gg k_s + k_A[A]$ hence leading to equation (9). As acetonitrile is an extremely weak base

$$k_f^2 = k_1 k_D[DABCO]/k_{-1} \qquad (9)$$

and k_s would be expected to be negligible in this solvent, the existence of a positive intercept implies equation (9a).

$$k_f^2 = k_1\,(k_A[A] + k_D\,[DABCO])/k_{-1} \qquad (9a)$$

The existence of a small catalytic effect due to aniline could be accounted for by the large (10^7-fold) increase in its base strength in going from dimethyl sulphoxide to acetonitrile.[12]

(ii) *Reactions of TNB with* 2,2,2-*trifluoroethylamine.* Unlike the case of aniline, there was an immediate formation of a red colour when TNB was mixed with TFE in both solvents. The solutions had the characteristic twin absorbance maxima of Meisenheimer complexes[4] at 450 and 526 nm, the lower wavelength having the higher intensity. The values of the extinction coefficient obtained by Benesi–Hildebrand plots in the presence of 0.1M-tetraethylammonium chloride at 450 nm are 3.25×10^4 mol^{-1} cm^{-1} in dimethyl sulphoxide and 3.05×10^4 mol^{-1} cm^{-1} in acetonitrile. The results of the kinetic investigation with TFE alone in both solvents are given in Table 2 and in the presence of DABCO in Table 3. The values of K in Table 2 refer to equilibrium (10) and

$$TNB + 2CF_3CH_2NH_2 \rightleftharpoons TNB{\cdot}\overset{-}{N}HCH_2CF_3 + CF_3CH_2\overset{+}{N}H_3 \qquad (10)$$

in Table 3, to (11).

$$TNB + CF_3CH_2NH_2 + DABCO \rightleftharpoons TNB{\cdot}\overset{-}{N}HCH_2CF_3 + DABCO\overset{+}{H} \qquad (11)$$

The most striking feature of these results is the difference in the kinetic form in the two solvents. In dimethyl sulphoxide the reaction is second order and is not catalysed by either TFE or DABCO. In acetonitrile, a plot of k_f^2 against the concentration of TFE is linear, passing through the origin, a least-squares analysis giving slope 2.6 ± 0.1, intercept $-2 \pm 8 \times 10^{-4}$, and r 0.995, and the assumption of third-order kinetics gives constant values of k_f^3. At a constant concentration of TFE a plot of k_f^2 against DABCO concentration is linear with a definite intercept, regression analysis giving slope $5.9 \pm 0.4 \times 10^{-1}$, intercept $8 \pm 2 \times 10^{-3}$, and r 0.992.

The results can be interpreted by the intermediate complex theory of equation (7) when DABCO is present; when it is not, $DABCO\overset{+}{H}$ is replaced by $CF_3CH_2\overset{+}{N}H_3$. The results in dimethyl sulphoxide can be accommodated by the condition $k_s + \Sigma k_i[B_i] \gg k_{-1}$ and $k_f^2 = k_1$. In acetonitrile, the situation is the same as when aniline is the nucleophile, the linearity of the plots of k_f^2 *versus* [TFE] and [DABCO] requires $k_{-1} \gg k_s + \Sigma k_i[B_i]$. The third-order reaction observed when no DABCO is present implies that $k_A[TFE] \gg k_s$ hence $k_f^2 = k_1 k_A[TFE]/k_{-1}$. In the presence of DABCO, equation (12) holds. Hence in changing from dimethyl sulphoxide to

$$k_f^2 = k_1(k_A[TFE] + k_D[DABCO])/k_{-1} \qquad (12)$$

acetonitrile, there is a change from $(k_s + \Sigma k_i[B_i])/k_{-1} \gg 1$ to $(k_s + \Sigma k_i[B_i])/k_{-1} \ll 1$. This change is readily understood in terms of the solvents involved.

As k_s refers to the abstraction of a proton by the solvent, its magnitude will depend on the solvent basicity and dimethyl sulphoxide is more basic than acetonitrile[13] by the very large factor of 10^{10}. Additionally k_{-1} would be expected to be greater in acetonitrile than in dimethyl sulphoxide because of the former's inability to solvate cations.[14] To the best of our knowledge this is the first example of a change in the rate-determining step of Meisenheimer complex formation induced by a change of solvent.

From the above kinetic analysis the intercept obtained from the plot of k_f^2 in acetonitrile against the concentration of DABCO should be equal to $k_1 k_A[TFE]/k_{-1}$ where [TFE] is the constant value of the concentration of this nucleophile used in this set of runs, 4.23×10^{-2}M. The value $8 \pm 2 \times 10^{-3}$ l mol^{-1} s^{-1} obtained for the intercept is in reasonable agreement with the value of $10.7 \pm 0.6 \times 10^{-3}$ calculated for k_f^2 at this concentration of TFE using the slope of the plot of k_f^2 *versus* [TFE] when no DABCO was present.

(b) *The Reaction of* 2,2,2-*Trifluoroethylamine with* 1-*Fluoro- and* 1-*Chloro*-2,4-*dinitrobenzenes.*—The rates of reaction of 1-fluoro- and 1-chloro-2,4-dinitrobenzenes with TFE were followed spectrophotometrically with the amine in large enough excess to ensure first-order kinetics. The results are given in Table 4.

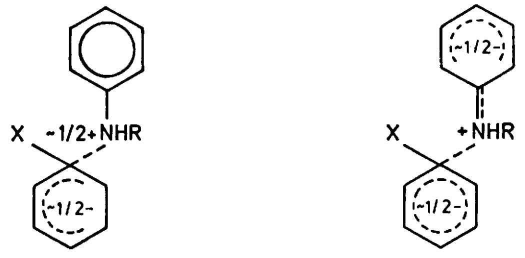
For both solvents, the second-order rate constants are independent of the amine concentration. The lack of base-catalysis and the high values of the $k_F : k_{Cl}$ ratios,[15] 118 in dimethyl sulphoxide and 178 in acetonitrile, show that the formation of the intermediate is rate-determining in all cases, *i.e.* $k_{-1} \ll k_2 + \Sigma k_i[B_i]$ in equation (2). The results for the chloro-compound are similar to those observed for this substrate when aniline is the nucleophile, but the results for the fluoro-compound differ.[3] The anilinodefluorination reaction is not base-catalysed in dimethyl sulphoxide, but in acetonitrile the second-order rate constant has a curvilinear dependence on the aniline concentration, the plot of k_A against concentration passing through the origin.[3] Hence for this reaction the conditions of equation (2) change from $k_{-1} \ll k_2 + \Sigma k_i[B_i]$ to $k_{-1} \gg k_2 + \Sigma k_i[B_i]$ with change of solvent.

TABLE 4

Rate constants (l mol^{-1} s^{-1}) for the reactions of 1-X-2,4-dinitrobenzenes with TFE in dimethyl sulphoxide and acetonitrile at 30.6 °C

Solvent	X						$k_F : k_{Cl}$
Dimethyl sulphoxide	F	10^3[amine]/M	6.65	13.3	19.9		118
		10^2k_A	9.35	9.02	9.35		
	Cl	10^2[amine]/M	1.70	7.27	24.24		
		10^4k_A	7.43	7.81	8.29		
Acetonitrile	F	10^2[amine]/M	1.25	2.50	4.39	6.59	178
		10^3k_A	1.59	1.55	1.41	1.68	
	Cl	10[amine]/M	1.39	2.31	4.32		
		10^6k_A	9.01	8.65	8.67		

Comparison of the Behaviour of Aniline and 2,2,2-*Trifluoroethylamine.*—The most striking features are the changes in kinetic form associated with change of nucleophile in (a) Meisenheimer complex formation in dimethyl sulphoxide and (b) the reactions of 1-fluoro-2,4-dinitrobenzene in acetonitrile. In both cases the changes are due to a shift from the condition $k_{-1} \ll k_2 + \Sigma k_i[B_i]$ to $k_{-1} \gg k_2 + k_i[B_i]$ when the nucleophile is changed from TFE to aniline. Usually when amines of the same type and under the same conditions react by different mechanisms, there is a considerable difference in their basicities [1,16] and the change is ascribed to a decrease in the strength of the C–N bond with decrease in amine basicity, leading to an increase in k_{-1}. If this is the explanation in the present case, then the effect must be very sensitive to amine basicity, as the ΔpK in water of the amines employed is only *ca.* 1. There is, however, an alternative explanation. In the decomposition to reactants of adducts formed from aromatic and aliphatic amines of the same basicity, the transition state for the reaction of the aromatic amine will be stabilised relative to that of the aliphatic one by interaction with the aromatic ring of the partially liberated lone pair of electrons in the nitrogen atom as shown in the Figure, hence k_{-1} for aromatic amines will be greater than that for aliphatic amines of the same basicity.



(a) (b)

EXPERIMENTAL

Materials.—The purification of dimethyl sulphoxide,[17] acetonitrile,[18] aniline,[19] 1-chloro- and 1-fluoro-2,4-dinitrobenzene [20] has been described previously. TFE was displaced from its hydrochloride by the method of Gilman and Jones [21] and dissolved directly in the relevant solvent. Its concentration was determined by titration with perchloric acid using the method of Keen and Fritz.[22] DABCO and TNB were commercial products purified by recrystallization twice from benzene (DABCO) and ethanol (TNB). Tetraethylammonium iodide was prepared by the reaction of triethylamine with ethyl iodide in acetone and an aqueous solution of the purified product passed through a column of Amberlite resin IR A-400 (chloride form). The effluant was evaporated to dryness under reduced pressure and the resulting chloride recrystallised twice from a 1 : 1 v/v mixture of benzene and acetonitrile.

Kinetic Procedure.—The rates of formation of the product of the reaction of 1-fluoro- and 1-chloro-2,4-dinitrobenzene with TFE were followed spectrophotometrically at 400 nm using the pipette procedure already described.[20]

The rates of formation of the Meisenheimer complexes were measured in the thermostatted cell compartment of a Gilford 2400 spectrophotometer by following the change in absorbance at 446 (aniline) and 450 nm (TFE). Reactions were initiated by injecting 50 μl of a concentrated solution of TNB into 2—2.5 ml of a solution of the amine contained in a 1-cm cell.

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