# Base Catalysis of σ-Complex Formation between 1,3,5-Trinitrobenzene and Aniline in Dimethyl Sulfoxide. Rate Limiting Proton Transfer

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Abstract: A kinetic and equilibrium study of the reaction between 1,3,5-trinitrobenzene (TNB), aniline, and 1,4-diazabicyclo-[2.2.2]octane (Dabco) in dimethyl sulfoxide solution, yielding the trinitrobenzene–anilide σ complex, has been performed. The rate of the forward reaction is first order with respect to TNB, $PhNH_2$, and Dabco, while the rate of the reverse reaction is first order with respect to TNB·NHPh⁻ and Dabco·H⁺. The preferred reaction mechanism invokes the preequilibrium formation of a zwitterionic complex, TNB·NH₂Ph±, followed by its rate-determining deprotonation, catalyzed solely by Dabco. The reaction thus provides a case in which the close to diffusion controlled rate of proton transfer between two nitrogen atoms constitutes the rate-determining step for the overall reaction. The significance of this study with regard to σ-complex formation between TNB and aliphatic amines, and to nucleophilic aromatic substitution, is considered. A rationalization is provided for the lack of σ-complex formation between TNB and aniline in the absence of Dabco.

Considerable interest has attached to the observation of base catalysis in activated nucleophilic aromatic substitution by primary or secondary amines and its significance.[1-5] In the most widely accepted mechanism of this S_NAr reaction, the base is assigned a catalytic role in deprotonation of the initially formed zwitterionic intermediate. This is shown in eq 1 by the
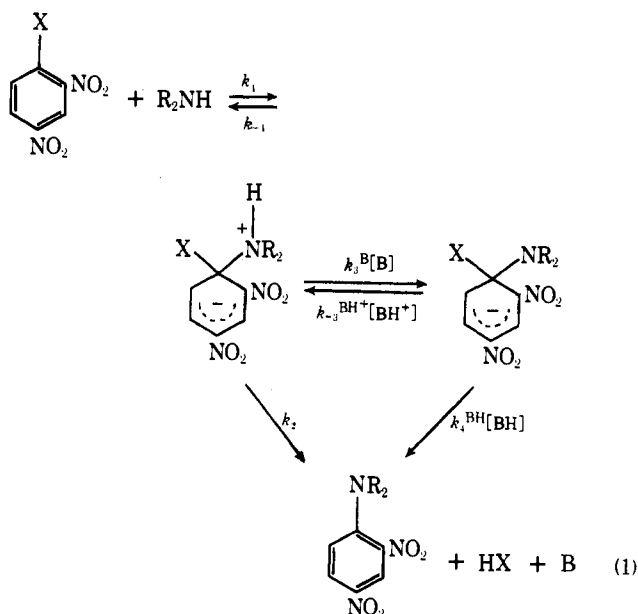

k_3^B pathway, while k_2 represents the uncatalyzed (solvent-assisted) reaction mode in product formation. The situation, however, is made complex by the number of elementary steps which appear to be required in the overall reaction in eq 1, and the consequent difficulty of identifying which of these is the rate-determining step. A further confusing aspect of the situation is the finding that reactions of this type are not in general subject to base catalysis.

Since the observation of base catalysis has, nevertheless, been considered to provide the strongest evidence for the intermediate complex mechanism in S_NAr reactions, studies of systems in which *stable* σ complexes are formed can potentially provide information pertinent to this problem. A variety of such stable σ complexes have been characterized from the interaction of polynitro aromatics with carbon, oxygen, nitrogen, etc., bases (eq 2),[6-11] including from 1,3,5-trinitrobenzene (TNB) and primary or secondary aliphatic amines. Recent
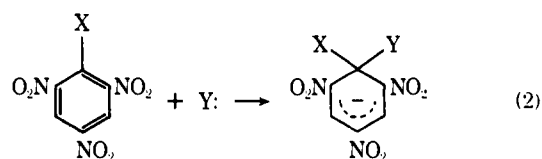
studies have focused on the catalytic processes involved in the formation and decomposition of spiro complexes,[12-15] i.e., eq 3 with Z being an oxygen or nitrogen nucleophilic center.
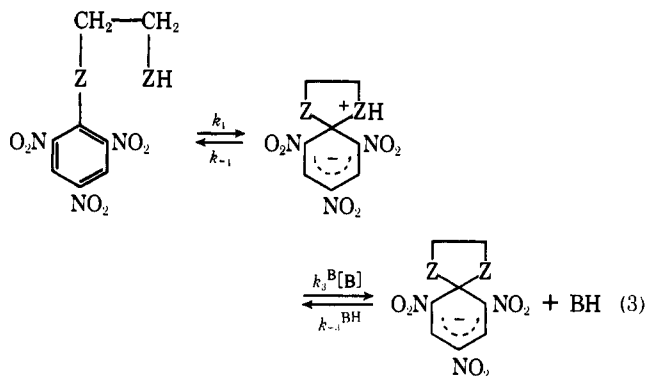
We now report the results of a kinetic study of σ-complex formation between TNB and aniline under catalysis by 1,4-diazabicyclo[2.2.2]octane (Dabco), in dimethyl sulfoxide (Me₂SO) solution. The reaction (eq 4) gives rise to the
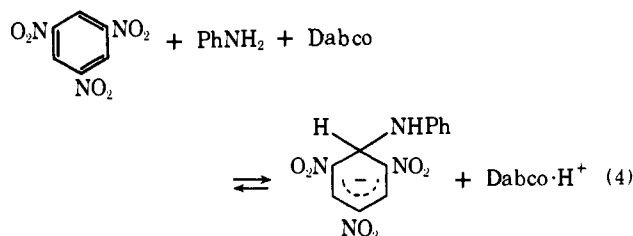
TNB–anilide σ complex, which is the first σ complex reported between a nitro aromatic compound and an aromatic amine.[16]

Whereas TNB had long been known to form σ complexes with primary or secondary aliphatic amines,[6-11] its interaction with corresponding aromatic amines had been reported to give rise only to the weaker charge-transfer π complexes.[17,18] In our first observation of the TNB–anilide σ complex[16] this was found to be formed from reaction of the TNB–methoxide σ

Table I. Dependence of Extent of Conversion and of the Equilibrium Constant on the Reagent Concentrations in Formation of the TNB-Anilide σ Complex in Me$_2$SO at 25 °C[a]

TNB, M	PhNH$_2$, M	Dabco, M	% convn	K, M^{-1}
5.0×10^{-4}	2.0×10^{-3}	2.0×10^{-3}	1.8	0.044
8.0×10^{-4}	2.0×10^{-3}	2.0×10^{-3}	2.0	0.087
8.0×10^{-4}	2.0×10^{-3}	4.0×10^{-3}	3.2	0.115
8.0×10^{-4}	2.0×10^{-3}	6.8×10^{-2}	15.1	0.170
8.0×10^{-4}	2.0×10^{-3}	1.9×10^{-1}	25.5	0.210
1.0×10^{-4}	4.0×10^{-4}	3.0×10^{-2}	6.6	0.039

[a] See text for effect of ionic strength on K values; see also Table III.

Table II. Typical Run Data for Formation of the TNB-Anilide σ Complex According to Equation 4 ([TNB]$_0$ = 0.99 $\times$ 10^{-4} M, [PhNH$_2$]$_0$ = 4.95 $\times$ 10^{-3} M, [Dabco]$_0$ = 1.98 $\times$ 10^{-3} M, [Et$_4$NCl]$_0$ = 0.1 M, in Me$_2$SO at 25 °C)

			% convn	
t, min	$A_{obsd}{}^{446a}$	$A_{cor}{}^{446a}$	b	c
0	0.020			
1.5	0.705	0.690	22.7	32.0
2.0	0.876	0.861	28.3	40.0
2.5	1.04	1.03	33.9	47.9
3.0	1.17	1.16	38.2	54.0
4.0	1.40	1.39	45.7	64.6
5.0	1.57	1.56	51.3	72.6
6.0	1.71	1.70	55.9	79.1
7.0	1.81	1.80	59.2	83.7
8.8	1.89	1.88	61.8	87.6
10.0	2.01	2.00	65.8	93.0
∞	2.16	2.15	70.7	100

[a] $A_{cor} = A_{obsd} - 0.02x/100$ where x is the percent conversion with reference to the equilibrium state. [b] With reference to complete conversion. [c] With reference to equilibrium state.

complex with aniline in Me$_2$SO. A number of TNB-aromatic amine σ complexes were obtained by this method and structurally characterized.[19,20] More recently we reported in a preliminary communication that the TNB-anilide σ complex can be formed more simply from TNB and aniline in the presence of a tertiary amine (Et$_3$N or Dabco).[21,22] The kinetic study of this reaction which we now report sheds light on the contrasting behavior between the reaction of TNB with aliphatic as compared to aromatic amines.

Results

When a solution of TNB in Me$_2$SO is added to a solution of aniline and Dabco in Me$_2$SO, a red-colored solution is obtained. The spectrum of this solution is characteristic of the TNB·NHPh$^-$ σ complex, which was previously found to have the following λ_{max} (ϵ) values: 446 nm (30 400 M^{-1} cm^{-1}), 522 (17 700).[19] Initially we determined the extent of conversion to TNB·NHPh$^-$ while varying the concentrations of TNB, PhNH$_2$, and Dabco. The equilibrium constant was calculated from

$$K = \frac{[TNB \cdot NHPh^-]_e [Dabco \cdot H^+]_e}{[TNB]_e [PhNH_2]_e [Dabco]_e} \quad (5a)$$

$$= \frac{(A_e/\epsilon l)^2}{([TNB]_0 - A_e/\epsilon l)([PhNH_2]_0 - A_e/\epsilon l)} \quad (5b)$$
$$([Dabco]_0 - A_e/\epsilon l)$$

where A_e is the equilibrium absorbance value of the TNB· NHPh$^-$ complex at 446 nm and ϵ is the molar extinction coefficient. A set of data is included in Table I in which the TNB and PhNH$_2$ concentrations were kept constant while varying the Dabco concentration. It is seen that the extent of conversion increases with [Dabco], which is as expected, but the calculated K values do not remain constant. Since in this reaction (eq 4) uncharged reactants are converted into charged products, it appeared that ionic strength effects could be important in this system and the subsequent work was carried out at a constant electrolyte concentration by addition of tetraethylammonium chloride. Under these conditions the calculated K values remained invariant, within the experimental error (vide infra).

The rate of approach to equilibrium could be measured by conventional spectrophotometric methods when the overall concentrations of the reagents were sufficiently small. Kinetic data were obtained under pseudo-first-order conditions, with PhNH$_2$ and Dabco in large excess over the TNB. Under these conditions eq 4 reduces to
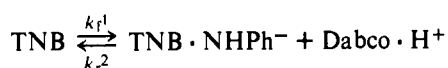
$$TNB \underset{k_r^2}{\overset{k_f^1}{\rightleftharpoons}} TNB \cdot NHPh^- + Dabco \cdot H^+$$

i.e., a mixed first-order (forward) and second-order (reverse) equilibrium process. The pseudo-first-order rate constant for the forward reaction, k_f^1, can then be obtained by means of[23]

$$\ln \frac{[TNB \cdot NHPh^-]_t([TNB]_0 - [TNB \cdot NHPh^-]_e)}{[TNB]_0([TNB \cdot NHPh^-]_e - [TNB \cdot NHPh^-]_t)}$$
$$+ [TNB]_0[TNB \cdot NHPh^-]_e$$

$$= \frac{2[TNB]_0 - [TNB \cdot NHPh^-]_e}{[TNB \cdot NHPh^-]_e} k_f^1 t \quad (6)$$

on plotting the left-hand term vs. time, after substituting [TNB · NHPh$^-$]$_e$ = $A_e/\epsilon l$ and [TNB·NHPh$^-$]$_t$ = $A_t/\epsilon l$. A linear plot is expected with slope = k_f' (2[TNB]$_0$ − [TNB· NHPh$^-$]$_e$)/[TNB·NHPh$^-$]$_e$. The second- and third-order forward rate coefficients, k_f^2 and k_f^3, are obtained from eq 7 and 8, respectively. The second-order reverse rate coefficient k_r^2 is given by eq 9.

$$k_f^2 = \frac{k_f^1}{[PhNH_2]} \quad (7)$$

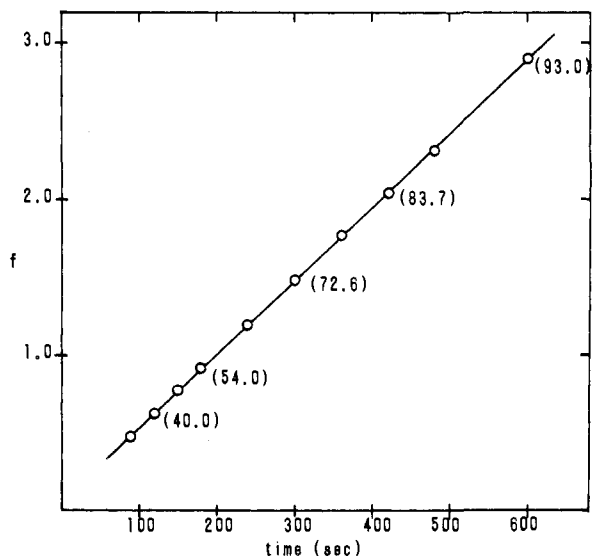$$k_f^3 = \frac{k_f^1}{[PhNH_2][Dabco]} \quad (8)$$

$$k_r^2 = \frac{k_f^3}{K} \quad (9)$$

The results for a typical run are as follows. Using the initial concentrations of reactants [TNB]$_0$ = 0.99 $\times$ 10^{-4} M, [PhNH$_2$]$_0$ = 4.95 $\times$ 10^{-3} M, and [Dabco]$_0$ = 1.98 $\times$ 10^{-3} M, and with [Et$_4$NCl] = 0.1 M, the equilibrium was established at 70.7% conversion. The absorbance values at various times are given in Table II. A plot of the data in Table II, according to eq 6, is given in Figure 1. (A Fortran program was used to calculate routinely the equilibrium constants according to eq 5 and the rate constants according to eq 6; computer plots of the rate data were also obtained.) In Figure 1, the numerical data in brackets beside the experimental points refer to the percent conversion with respect to the equilibrium position. It is seen that the experimental points are well on the straight line and that a curvature in the latter stages of reaction is not apparent. Under all conditions investigated, we observed linear behavior in such plots for more than 90% conversion (standard

Table III. Dependence of Rate and Equilibrium Data for Reaction in Equation 4 on Dabco Concentration ($[TNB] = 0.98 \times 10^{-4}$ M, $[PhNH_2] = 4.8 \times 10^{-3}$ M) at Two Concentrations of Electrolyte in Me_2SO at 25 °C

$[Et_4NCl]$, M	$[Dabco]$, M	% convn	K, M^{-1}	$k_f^1 \times 10^4$, s^{-1}	$k_f^2 \times 10^2$, $M^{-1} s^{-1}$	k_f^3, $M^{-2} s^{-1}$	k_r^2, $M^{-1} s^{-1}$
0.1	0.002	32.2	1.80	2.80	5.71	29.1	16.3
	0.010	56.1	1.52	12.6	25.7	26.0	17.1
	0.020	70.1	1.71	25.1	51.3	26.1	15.2
	0.040	79.3	1.65	52.4	107	26.9	16.3
0.5	0	(0.7)					
	0.002	58.2	9.32	3.89	7.94	40.5	4.35
	0.016	87.6	7.40	25.9	52.8	33.6	4.54
	0.040	97.6		63.2	129	32.5	

Figure 1. Illustrative plot for a kinetic run, in which the function f represents the left hand side of eq 6. The numerical data adjacent to the points refer to the percent conversion with respect to the equilibrium position.
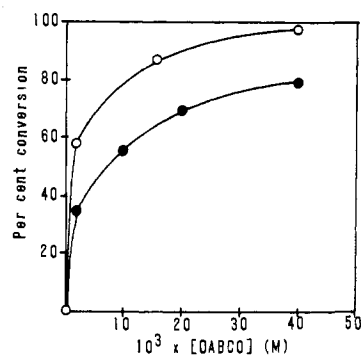
Figure 2. Dependence of the extent of conversion in the reaction of TNB (1.0×10^{-4} M), $PhNH_2$ (5.0×10^{-3} M), and Dabco in Me_2SO at 25 °C, to the anilide complex (eq 4), on the concentration of Dabco at constant tetraethylammonium chloride concentration. Full circles, $[Et_4NCl] = 0.1$ M; empty circles, $[Et_4NCl] = 0.5$ M.

deviation of slope = 0.5–1%) with respect to the equilibrium position, confirming the applicability of eq 6.

The dependence of the $TNB/PhNH_2$ reaction on Dabco concentration was evaluated at two concentrations of Et_4NCl, 0.1 and 0.5 M, in the Me_2SO medium. The extent of conversion increased with [Dabco] in a nonlinear manner, as shown in Figure 2. The calculated values of K, k_f^2, k_f^3, and k_r^2 are given in Table III. The K values show satisfactory constancy in the series of runs at 0.1 M Et_4NCl but at 0.5 M Et_4NCl a much larger deviation is seen. This is accounted for by the fact that eq 5 which is used to calculate K is subject to large apparent errors at high percent conversion. Thus up to 60% conversion
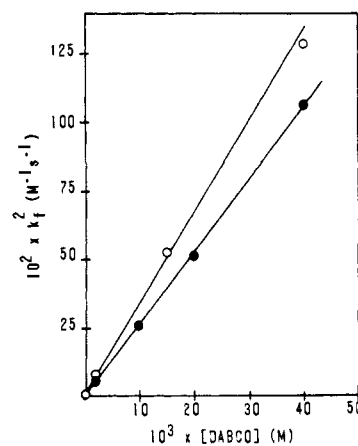
Figure 3. Plots showing the dependence of the second-order forward rate constant k_f^2 on the concentration of Dabco in the reaction of TNB (1.0×10^{-4} M) with aniline (5.0×10^{-3} M) in Me_2SO at 25 °C. Full circles, $[Et_4NCl] = 0.1$ M; empty circles, $[Et_4NCl] = 0.5$ M.

an error of ±3% in determination of the extent of conversion leads to an uncertainty in K of ±10%, while at 80% conversion the corresponding uncertainty in K is ±25%. The plots of k_f^2 vs. [Dabco] are linear at both Et_4NCl concentrations, passing through the origin (Figure 3).

Discussion

A number of significant conclusions follow from the rate and equilibrium constant data that we have presented in the preceding section for the reaction under study (eq 4). The linear increase of k_f^2 with [Dabco] and the fact that the plot in Figure 3 passes through the origin show that the forward reaction of TNB with aniline is base catalyzed and that Dabco acts as the sole basic catalyst (i.e., $PhNH_2$ and solvent Me_2SO are not significant contributors). Similarly, the reverse reaction is acid catalyzed by the species Dabco·H^+. Thus the transition state in the forward direction contains one molecule of TNB, $PhNH_2$, and Dabco, and the transition state in the reverse direction contains one molecule of TNB·$NHPh^-$ and Dabco·H^+, which is in accord with the principle of microscopic reversibility. The composition of the rate-determining transition state which has been deduced for the forward and reverse processes of the reaction in eq 4 can be accommodated on the basis of several possible mechanisms which will now be discussed.

Anilide Ion Intermediate Mechanism. In the reaction system, containing TNB, aniline, and Dabco in Me_2SO, there is the possibility of the formation of anilide ion via the protolytic equilibrium in eq 10, followed by rate-determining reaction of $PhNH^-$ with TNB (eq 11).

$$PhNH_2 + Dabco \underset{}{\overset{fast}{\rightleftarrows}} PhNH^- + Dabco \cdot H^+ \quad (10)$$

$$PhNH^- + TNB \underset{}{\overset{slow}{\rightleftarrows}} TNB \cdot NHPh^- \quad (11)$$

The feasibility of the formation of TNB·NHPh⁻ from reaction of TNB and PhNH⁻ was shown previously.[19] However, in that system potassium anilide was used as the reactant, in a concentration of ~0.5 M. In the PhNH₂/Dabco system, in contrast, the concentration of PhNH⁻ is expected to be extremely small, which could require that the rate constant in eq 11 exceed the diffusion-controlled value in order that the overall reaction occur at a finite rate.[24] A similar conclusion was reached previously for the TNB/aliphatic amine system,[26] the amide ion mechanism being disfavored in preference of the zwitterionic intermediate mechanism.

Concerted Mechanisms. A concerted pathway would readily account for the observed rate law in the formation and decomposition of the TNB–anilide σ complex. The rate-determining transition state in such a process would be given by **1**.

1

2
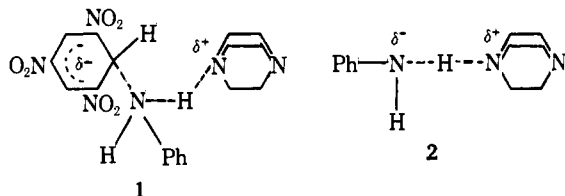
It should be noted that this does not necessitate a termolecular process (in the forward direction) since it is possible that aniline and Dabco could form a hydrogen-bonded complex, **2**, in a rapidly established preequilibrium.[27]

A possible alternative concerted mechanism would invoke initial formation of a π complex by a charge transfer interaction between TNB and aniline,[17] followed by rate-determining formation of the TNB·NHPh⁻ σ complex. In this reaction of the π complex with Dabco, proton transfer and covalent bond formation between the nitrogen of aniline and the TNB ring carbon would occur concertedly, and the transition state would be as in **1**.

Though concerted mechanisms of intermediate complex formation in S$_N$Ar processes appear to be plausible in many systems,[4] they perhaps lack the generality of the zwitterionic intermediate mechanism.[5] It will be shown in our consideration of the zwitterionic intermediate mechanism that a consistent and unified explanation is possible not only of the results obtained in this study but also of an extensive body of literature data.

Zwitterionic Intermediate Mechanism. By analogy with the reaction of aliphatic amines with TNB, which is believed to proceed via a zwitterionic intermediate, we can formulate a corresponding mechanism for the TNB/aniline reaction. As shown in eq 12, the reaction would proceed in two stages, the

(12)
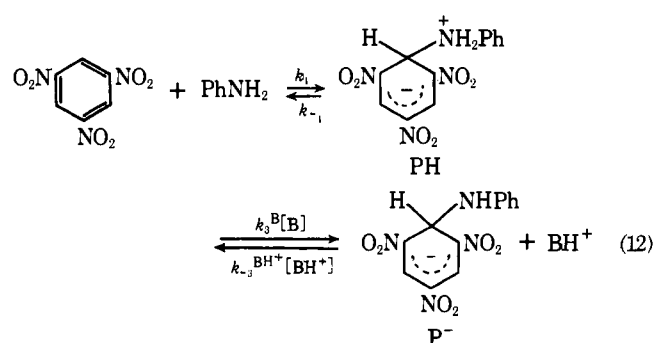
first being formation of the zwitterionic intermediate (PH), and the second stage being its deprotonation by the action of Dabco (B) with formation of the anionic complex (P⁻). The k_1, k_3^B nomenclature is retained in this equation, k_1 denoting the formation of the zwitterionic intermediate and k_3^B its base-assisted deprotonation, by analogy with related systems (e.g., eq 1).

On the assumption that the zwitterionic complex can be treated as a steady-state intermediate, the expressions for the forward and reverse rate coefficients will be given by

$$k_f^2 = \frac{k_1 k_3^B [B]}{k_{-1} + k_3^B [B]} \tag{13}$$

$$k_r^2 = \frac{k_{-1} k_{-3}^{BH}}{k_{-1} + k_3^B [B]} \tag{14}$$

Our finding of a linear dependence of k_f^2 on [Dabco] shows that the first stage in eq 12 is a rapidly established preequilibrium and that the second stage is rate determining, i.e., that $k_{-1} \gg k_3^B [B]$. Hence eq 13 and 14 reduce to eq 15 and 16, respectively.

$$k_f^2 = \frac{k_1 k_3^B [B]}{k_{-1}} \tag{15}$$

$$k_r^2 = k_{-3}^{BH} \tag{16}$$

The identification of k_{-3}^{BH} as equal to the experimentally measurable k_r^2 value will be referred to again in the subsequent discussion.

In the following sections we analyze our results in detail on the basis of the zwitterionic intermediate mechanism. Our treatment allows the derivation of estimates of the various specific rate constants pertaining to the two stages of eq 12 and of the equilibrium constants. In addition, a quantitative comparison of the present results with literature data is given.

Derivation of the Rate and Equilibrium Constants. For proton transfer from the zwitterionic complex (PH) to the base (B), k_3^B will be dependent on the relative magnitudes of the pK_as of PH and of BH.[28] In the cases examined hitherto (see Table IV), the zwitterionic complex is a stronger acid than the conjugate acid of the amine used to react with the nitro aromatic (i.e., $K_a^{PH} > K_a^{R_2NH_2^+}$), since the 2,4,6-trinitrohexadienate moiety is known to be electron withdrawing.[19,29,30] Provided that such a relationship holds in the present system (i.e., $K_a^{PH} > K_a^{PhNH_3^+}$), then the proton transfer from PH to Dabco (a stronger base than PhNH₂) is in the thermodynamically favored direction and one can assume as a first approximation that k_3^B will have a value close to the diffusion-controlled rate.

Thus assuming that in the TNB/PhNH₂/Dabco system the rate constant for proton transfer from TNB·NH₂Ph to Dabco is given by $k_3^B \sim 10^9$ M⁻¹ s⁻¹,[31] and since [B] $\sim 10^{-2}$ M, one obtains $k_3^B[B] \sim 10^7$ s⁻¹. We have shown kinetically that the condition $k_{-1} \gg k_3^B[B]$ must hold in our system, and hence $k_{-1} > 10^7$ s⁻¹. The k_1 value can be obtained from the measured kinetic data by use of eq 13, according to which a plot of $1/k_f^2$ vs. $1/[B]$ should be linear with intercept $1/k_1$. The plots, given in Figure 4, exhibit the required linearity but the small value of the intercept (~0.2 M s) places some uncertainty on the derived k_1 value. However, from this graph, k_1 may be estimated as >1 M⁻¹ s⁻¹. One thus obtains $K_1 = k_1/k_{-1} \sim 10^{-7}$.

The kinetic data that we have obtained also afford an estimate of K_a^{PH} for the zwitterionic species TNB·NH₂Ph. From eq 16 we obtained $k_{-3}^{BH} \sim 10$ M⁻¹ s⁻¹, and k_3^B has already been estimated as ~10^9 M⁻¹ s⁻¹, so that $K_3 \sim 10^8$. Now since $K_3 = K_a^{PH}/K_a^{Dabco·H^+}$, and substituting $K_a^{Dabco·H^+} = 2.5 \times 10^{-9}$ M, we obtain $K_a^{PH} \sim 0.25$ M.

The rate and equilibrium constants thus obtained for the present system are given in Table IV, along with the analogous values which have previously been obtained in other systems. In the remainder of this discussion we consider the results of the present system in the light of these other systems and address the question of the contrasting behavior of TNB and aliphatic vs. aromatic amines.

Comparison with Other Systems. The results obtained in this

Table IV. Comparison of Rate and Equilibrium Constants for the Trinitrobenzene/Aniline/Dabco System with the Trinitrobenzene/Aliphatic Amine and the Spiro Systems

	TNB/PhNH$_2$/Dabco (eq 12)[a]	TNB/R$_2$NH[c,d] (eq 17)[b]	Spiro system (eq 18)[e]
k_1, M^{-1}s^{-1}	>1	1.2 × 10^2 c ; 3.0 × 10^3 d	1.2 × 10^3
k_{-1}, s^{-1}	>10^7	2.0 × 10^4 c ; 1.5 × 10^4 d	1.9 × 10^5
$K_1 = k_1/k_{-1}$, M^{-1}	~10^{-7}	6.0 × 10^{-3} c ; 0.2 d	6.2 × 10^{-3}
$k_3{}^B$, M^{-1}s^{-1}	~10^9 (Dabco)		5.2 × 10^9 (OH$^-$) ; 1.4 × 10^4 (H$_2$O)
$k_{-3}{}^{BH}$, M^{-1}s^{-1}	~10 (Dabco·H$^+$)		8.0 (H$_2$O) ; 5.9 × 10^{10} (H$_3$O$^+$)
$K_a{}^{PH}$, M	~0.2	5.3 × 10^{-10} c ; 1.5 × 10^{-11} d	4.6 × 10^{-7}
$K_a{}^{R_2NH_2^+}$, M (or $K_a{}^{PhNH_3^+}$)	2.5 × 10^{-5} (PhNH$_3^+$)	2.1 × 10^{-11} (BuNH$_3^+$) ; 7.6 × 10^{-12} (Pip H$^+$)	2.8 × 10^{-9}
$K_a{}^{PH}/K_a{}^{R_2NH_2^+}$ (or $K_a{}^{PH}/K_a{}^{PhNH_3^+}$)	~10^4 (PhNH$_3^+$)	25 (BuNH$_3^+$) ; 2 (Pip H$^+$)	200

a This work; Me$_2$SO solvent, 25 °C. *b* Reference 27; 10% dioxane-90% water, 25 °C. *c* R$_2$NH = *n*-butylamine. *d* R$_2$NH = piperidine. *e* Reference 14; aqueous medium, 25 °C. In this case k_1 has units of s^{-1} and K_1 is dimensionless.
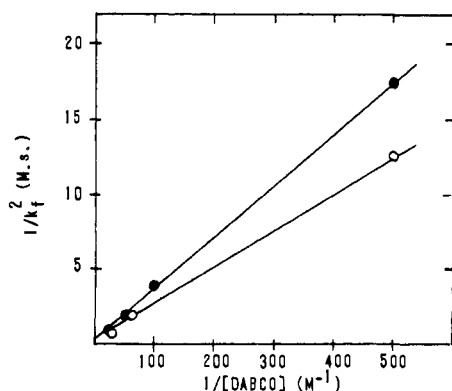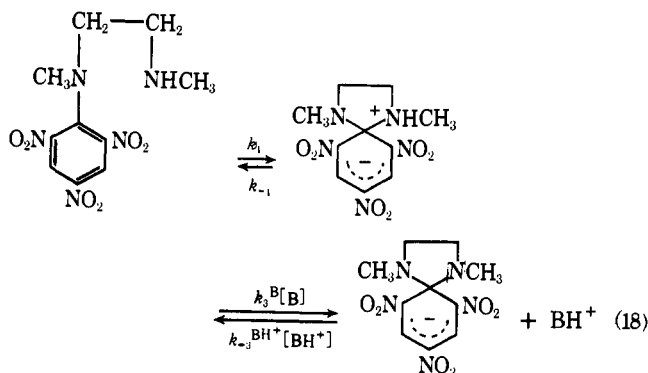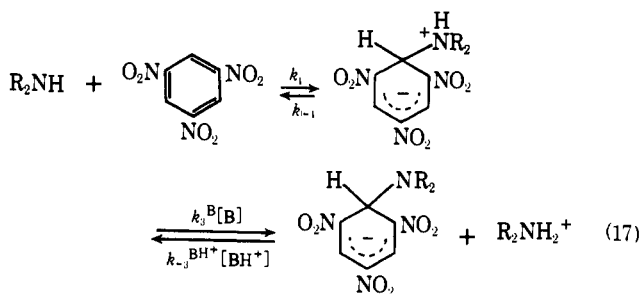

Figure 4. Plot of $1/k_f{}^2$ vs. $1/$[Dabco] (cf. eq 13). Full circles, [Et$_4$NCl] = 0.1 M; empty circles, [Et$_4$NCl] = 0.5 M.

work are of interest in relation to other studies, in particular σ-complex formation between TNB and aliphatic amines (eq 17)[26,32] and spiro complex formation by picrylethylenediamino

derivatives (eq 18).[14,15] As in our system, each of these reactions is believed to occur in two stages. However, the evidence shows that the nature of the rate-determining step in the three systems is not the same.

In the aliphatic amine system (R$_2$NH = butylamine, piperidine, and pyrrolidine in the cases investigated kinetically)[32] formation of the zwitterionic species is rate determining, i.e., $k_{-1} \ll k_3$[B]. The proton transfer reaction was found to be too fast to be measurable by the temperature-jump technique.

On the other hand, in the spiro system (eq 18) we have the interesting situation of an energy profile with the zwitterionic intermediate situated in a minimum such that the barrier for reversion to reactant is comparable in magnitude to the barrier for formation of product. Hence, depending on the concentration of B, one has the situations $k_{-1} > k_3{}^B$[B], $k_{-1} \sim k_3{}^B$[B], or $k_{-1} < k_3{}^B$[B]. This leads to the observation of a curvilinear dependence of rate with increasing buffer concentration, which has provided conclusive evidence of a change in rate-determining step.[14,33]

In the TNB–aniline case, however, we have found that the first stage is a preequilibrium process and the second stage is rate determining, i.e., $k_{-1} \gg k_3{}^B$[B]. Thus the three systems exhibit a gradation in behavior from a rate-determining first stage (eq 17), to either stage being rate determining (eq 18), and finally to a rate-determining second stage (eq 12).

In analyzing the different behaviors in these three systems, it is appropriate to compare the relative magnitudes of k_{-1} and $k_3{}^B$[B] since this ratio determines which step is rate controlling. The analysis simplifies to a comparison of the k_{-1} values, since $k_3{}^B$ appears to be close to diffusion controlled in all three systems. The value $k_{-1} > 10^7$ s^{-1} obtained in the present system can be compared (Table IV) with $k_{-1} \sim 10^4$ s^{-1} for the TNB/R$_2$NH system (eq 17)[32] and $k_{-1} \sim 10^5$ s^{-1} for the spiro system (eq 18).[14] The larger k_{-1} value in spiro compared to acyclic complexes has also been observed with the corresponding oxygen analogues and may have as origin the relief of strain.[12] However, the finding that k_{-1} for the TNB·NH$_2$Ph case is much larger than for the TNB·NHR$_2$ case is explicable on the ground that the ease of expulsion of amine from the zwitterionic intermediates will be in inverse order to the pK_as of these leaving groups (i.e., p$K_a{}^{PhNH_3^+}$ vs. p$K_a{}^{R_2NH_2^+}$).

It is an unexpected result of the present system that the ratio obtained for $K_a{}^{PH}/K_a{}^{PhNH_3^+}$ (~0.25/2.5 × 10^{-5} ~10^4) is considerably larger than the values in the previous studies (Table IV). It may be noted that a smaller value for $K_a{}^{PH}$, and hence for the $K_a{}^{PH}/K_a{}^{PhNH_3^+}$ ratio, is obtainable by appro-

priate choice of the rate constants pertaining to eq 12. Thus assuming that $k_3{}^B = 10^6$ M^{-1} s^{-1}, and using the condition k_{-1} > $k_3[B]$, one obtains k_{-1} > 10^4 s^{-1}. Further, if k_1 is allowed to retain the value >1 M^{-1} s^{-1}, one obtains $K_1 \sim 10^{-4}$ M^{-1}. The previously outlined method then yields $K_a{}^{PH} \sim 1.2 \times 10^{-3}$ M and $K_a{}^{PH}/K_a{}^{PhNH_3^+} \sim 50$. However, whereas the resulting $K_a{}^{PH}/K_a{}^{PhNH_3^+}$ value appears to be reasonable, the derived k_{-1} value appears to be unlikely as it about equals the k_{-1} value for the TNB-aliphatic amine case. This appears to be quite an unreasonable result in view of the large difference in basicity between aniline and the aliphatic amines. Alternatively, a differential medium effect[25] on the pK_a of PH relative to that of Dabco·H$^+$ and PhNH$_3^+$, on going from aqueous medium to Me$_2$SO, could also account for the large apparent value of the $K_a{}^{PH}/K_a{}^{PhNH_3^+}$ ratio. More data of this kind would be desirable before the significance of this finding can be evaluated.

The two-stage zwitterionic intermediate mechanism for the TNB/PhNH$_2$/Dabco system (eq 12) also provides an explanation for the contrasting behavior of TNB with aromatic as against aliphatic amines, i.e., that tnb and aniline alone do not react to yield a σ complex whereas there is facile σ-complex formation between TNB and primary or secondary aliphatic amines. It is noteworthy in this regard that eq 12 will be applicable to the TNB/PhNH$_2$ system in the absence of Dabco: the first stage will be unaffected but in the second stage the function of B will be taken by a second aniline molecule. Hence the information that we have obtained relating to the first stage in our analysis of the TNB/PhNH$_2$/Dabco system will be equally applicable to the system in the absence of Dabco.

Our results indicate that the formation of TNB·NH$_2$Ph is disfavored relative to TNB·NHR$_2$ both on account of a greater thermodynamic instability of the TNB·NH$_2$Ph species and due to a greater barrier height in formation of the activated complex. The former follows from the large difference (by 5 to 7 orders of magnitude) between the K_1 values (Table IV) for formation of TNB·NH$_2$Ph and TNB·NHR$_2$. The latter follows from the difference (between 2 and 3 orders of magnitude) in the corresponding k_1 values. These results also suggest that the thermodynamic factor dominates over the kinetic factor.

On the other hand, the second stage of the zwitterionic intermediate mechanism, involving the deprotonation of this intermediate, should be a thermodynamically favorable process in the TNB/PhNH$_2$ case as well as in the TNB/R$_2$NH case. This follows from the fact that the zwitterionic complex is a stronger acid than the conjugate acid of the amine used to react with the TNB. Indeed, as we have seen above, the $K_a{}^{PH}/K_a{}^{PhNH_3^+}$ ratio is at least as large in the aromatic amine case as the corresponding ratio in the aliphatic amine case.

In evaluating the effect of added Dabco on these processes, it is noteworthy that addition of Dabco to the TNB/PhNH$_2$ system causes the deprotonation of the zwitterionic intermediate to become more favorable. This is seen by reference to eq 19

$$\text{TNB} \cdot \text{NH}_2\text{Ph}^\pm + B \rightleftharpoons \text{TNB} \cdot \text{NHPh}^- + \text{BH}^+ \quad (19)$$

in which B is either PhNH$_2$ or Dabco. The equilibrium constant for this deprotonation process, with a given abstracting base B, is given by $K_3 = K_a{}^{PH}/K_a{}^{BH}$. Hence the ratio of the K_3 values is $K_3{}^{Dabco}/K_3{}^{PhNH_2} \sim 1 \times 10^4$. Thus the equilibrium transformation of the zwitterionic complex to the anionic σ complex, being directly related to the basicity of the abstracting amine, is favored in the Dabco system by $\sim 10^4$.

It follows from the above discussion that the difference in behavior between aromatic and aliphatic amines in their reaction with TNB has as origin primarily the unfavorable thermodynamic factor associated with formation of the zwitterionic complex in the aromatic amine case. The equilibrium

constant associated with the first stage is so small in the aromatic amine case that in spite of the relatively large equilibrium constant associated with the second stage the overall equilibrium is disfavored and σ-complex formation does not occur. Such a proposal was previously given on the basis of our study of the TNB/PhNH$_2$/MeOK system.[34] The present study shows, however, that the addition of the tertiary amine Dabco increases the equilibrium constant for deprotonation of the zwitterionic intermediate to the extent that now the overall reaction becomes feasible and formation of the σ complex is observed.

Conclusion

In conclusion, we have found that the formation of the anionic TNB·NHPh$^-$ σ complex from TNB, PhNH$_2$, and Dabco involves rate-determining proton transfer, in Me$_2$SO solvent, from the ammonio function of the zwitterionic complex TNB·NH$_2$Ph. Reactions involving rate-determining proton transfer from nitrogen are unusual but not without precedent,[35-37] though this appears to be the first reported case involving such proton transfer in Me$_2$SO.[38] Whereas proton transfer between the two nitrogen atoms is expected to occur close to the diffusion-controlled rate, in a multistage reaction such a step can still be rate determining when preceded by a highly unfavorable equilibrium.[36,37] This finding also has relevance to substitution reactions (eq 1) in which the proton transfer stage could be rate controlling under appropriate circumstances. This possibility was first raised some time ago[39] but it is only recently that it has been substantiated by this kind of evidence.[40,41]

Experimental Section

Materials. TNB was recrystallized from ethanol and dried in vacuo, mp 123 °C. Aniline was distilled twice from zinc dust in a dry nitrogen atmosphere, under reduced pressure, and stored under nitrogen in the dark. Dabco was recrystallized twice from benzene and dried in vacuo. The resulting material was mixed with an equal amount of barium oxide and sublimed twice to yield white crystals, mp 157 °C. Tetraethylammonium chloride was recrystallized twice from a mixture of benzene-acetonitrile (1:1 v/v) and dried in vacuo. Me$_2$SO (Fisher Certified Reagent) was distilled from barium oxide under nitrogen.

Kinetic Measurements. The reactions were followed spectrophotometrically by monitoring the increase in the absorption due to product as a function of time. Kinetic measurements were taken at 446 nm, the wavelength of the absorption maximum of the TNB-anilide σ complex, and at the completion of the reaction the spectra were taken in full. The reactions were carried out directly in the spectrophotometric cell, which allowed the absorbance to be recorded continuously as well to be read from a digital display. A Beckman Acta IV UV/vis spectrophotometer fitted with a thermostated cell compartment was used throughout this work. The temperature was maintained at 25.0 ± 0.05 °C. The stock solutions were made up in a drybox and were protected from light.

A typical run, using the concentrations 0.99×10^{-4} M TNB, 4.95×10^{-3} M PhNH$_2$, 1.98×10^{-3} M Dabco, and a given electrolyte concentration, was performed as follows. To 3 mL of a Me$_2$SO solution containing the appropriate electrolyte concentration in a 1-cm cell were added 30 μL of a solution of aniline (0.5 M) and 30 μL of the Dabco solution (0.2 M). After mixing and temperature equilibration in the cell compartment, 6 μL of a TNB stock solution in Me$_2$SO (5×10^{-2} M) was introduced, the resulting solution was quickly mixed, and the increasing absorbance at 446 nm was followed with time. Table II contains the absorbance values for a typical run as a function of time. Correction of the measured absorbances was necessary, since extrapolation of the absorbance at fixed wavelength to the time of mixing yielded a small but not negligible absorbance value (ca. 0.02). The measured absorbances were corrected assuming that the "zero absorption" decreased proportionally to the extent of conversion of the reaction. The plot for this run is given in Figure 1.

The molar extinction coefficient for the TNB-anilide complex was

obtained by increasing the concentration of aniline and/or Dabco until complete conversion resulted. The previously reported value[19] of ϵ 30 400 M^{-1} cm^{-1} at λ_{max} 446 nm was confirmed.

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Carbenium Ion Stabilities in the Gas Phase and Solution. An Ion Cyclotron Resonance Study of Bromide Transfer Reactions Involving Alkali Ions, Alkyl Carbenium Ions, Acyl Cations, and Cyclic Halonium Ions

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Abstract: Ion cyclotron resonance techniques are used to measure relative heterolytic bond dissociation energies $D(R^+-Br^-)$ in the gas phase for a series of alkali cations, alkyl carbenium ions, acyl cations, and cyclic halonium ions. $D(R^+-Br^-)$ for adamantyl cation is found to be less than for *tert*-butyl cation. A proton affinity for norbornene of $D(B-H^+) = 198.8 \pm 2$ kcal/mol is determined from which $D(R^+-Br^-) = 146.8 \pm 2.3$ kcal/mol is calculated for norbornyl cation, 16 kcal/mol less than for cyclopentyl cation. In several cases additional thermochemical data useful in assessing absolute $D(R^+-Br^-)$ heterolytic bond dissociation energies are provided by photoionization mass spectrometry. Relative enthalpies of solvation for carbenium ions are estimated via appropriate thermochemical cycles by combining the gas phase data with heats of ionization in a HSO_3F/SbF_5 medium. The results show that solvation enthalpies are related to ion size with smaller ions being better solvated. Relative stabilities of cyclic bromonium ions are the same in the gas phase and solution. Stability increases with increasing ring size and in the three-membered rings with methyl substitution. However, solvent has an appreciable effect in attenuating the observed range.

The quantitative assessment of the energetics of carbenium ion formation and solvation is a difficult problem in organic chemistry. Relatively few stable carbenium ions have been thoroughly studied in aqueous media, where more often these species are invoked as transient intermediates in a wide range of chemical transformations.[2] Only recently has it been possible to devise conditions compatible with the existence of these reactive species for periods of time which permit their