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(13) The absence of a significant deuterium kinetic isotope effect for the $[Rh_2(CO)_4Cl_2]$-catalyzed rearrangement of **2** (i.e., $k_{2a} = k_{2b} = 8.6 \pm 0.4 \times 10^{-3}$ M^{-1} s^{-1} in C_6D_6 at 50 °C) is consistent with this interpretation.
(14) The equilibrium constant for the substitution reaction, $(1/2)[Rh(NOR)Cl]_2 + COD \rightleftharpoons (1/2)[Rh(COD)Cl]_2 + NOR$, is approximately 1 (J. Halpern and M. Takagi, unpublished results).
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Anomalous Rates of Proton Transfer to and from Nitrogen and Carbon in the Reactions of Amines with 1,1-Dinitro-2,2-diphenylethylene

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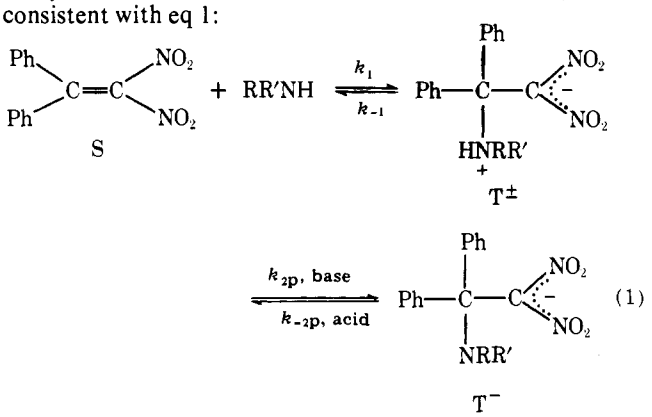
Abstract: Two kinetic processes are observed in the reactions of 1,1-dinitro-2,2-diphenylethylene with piperidine, morpholine, *n*-butylamine, and aniline in 50% aqueous dimethyl sulfoxide. The first, relatively fast and reversible, refers to nucleophilic addition of the amine to the 2 position of 1,1-dinitro-2,2-diphenylethylene to form a zwitterionic addition complex ($T^{\pm}$), which is subsequently deprotonated to the anionic addition complex (T^-). In the piperidine and *n*-butylamine reactions proton transfer is fast and nucleophilic attack is rate determining; in the morpholine and aniline reactions proton transfer is partially rate limiting. The second kinetic process, which is relatively slow, refers to protonation of T^- on carbon to form T^0, followed by rapid and irreversible cleavage of T^0 into $Ph_2C{=}O$ and $^-CH(NO_2)_2$. The rate constants for the various elementary steps were evaluated. They show a dramatic steric effect not only on the nucleophilic attack step but also on the proton transfer rates. For example, deprotonation by *N*-methylmorpholine of $T^{\pm}$ derived from morpholine has a rate constant of 2×10^3 M^{-1} s^{-1} instead of the 10^8–10^9 M^{-1} s^{-1} expected for a diffusion-controlled reaction. Rates of protonation of T^- on carbon by water and several general acids are as expected for similar dinitro compounds, but protonation by H^+ is 10^3–10^4 times faster than expected. This high rate is tentatively attributed to an intramolecular proton switch mechanism, $T^{\pm} \rightarrow T^0$.

This is the first paper in a series in which we will explore mechanistic features and structure-reactivity problems which not only relate to nucleophilic additions to olefins[1] but which are relevant to other classes of reactions such as nucleophilic vinylic substitutions,[2] ElcB eliminations,[3] and proton transfer reactions involving "normal" acids[4] as well as carbon acids.[5] The present paper deals with the reactions of piperidine, morpholine, *n*-butylamine, and aniline with 1,1-dinitro-2,2-diphenylethylene in 50% aqueous dimethyl sulfoxide (v/v). Two kinetic processes were observed. The first ($1/\tau_1$), relatively fast and reversible, was studied most thoroughly and is consistent with eq 1:



(1)

where k_{2p} and k_{-2p} refer to proton transfer and are defined as:

$$k_{2p} = k_{2p}^{w} + k_{2p}^{OH}[OH^-] + k_{2p}^{A}[RR'NH] + k_{2p}^{B}[B] \quad (2)$$

$$k_{-2p} = k_{-2p}^{H}[H^+] + k_{-2p}^{w} + k_{-2p}^{AH}[RR'NH_2^+] + k_{-2p}^{BH}[BH^+] \quad (3)$$

with k_{2p}^{w}, k_{2p}^{OH}, k_{2p}^{A}, and k_{2p}^{B} being the rate coefficients for the deprotonation of $T^{\pm}$ by the solvent, hydroxide ion, amine, and another base (buffer), which sometimes was added to the reaction solution, respectively, and k_{-2p}^{H}, k_{-2p}^{w}, k_{-2p}^{AH}, and k_{-2p}^{BH} being the rate coefficients for the protonation of T^- on nitrogen by the hydronium ion, the solvent, and the conjugate acids of the amine and of B, respectively.

The second process ($1/\tau_2$), which is relatively slow and irreversible, refers to the cleavage of T^- yielding benzophenone and dinitromethane anion.

Equation 1 can be regarded as a model for the initial two steps in the mechanism of base-catalyzed nucleophilic vinylic substitutions by amines;[6,7] in a "real" vinylic substitution reaction the substrate would have a nucleofugic leaving group (e.g., $Ph(X)C{=}C(NO_2)_2$) and there would be product-forming steps in which the leaving group departs from T^- (and possibly from $T^{\pm}$). A question of great relevance to the mechanism of base-catalyzed nucleophilic vinylic substitutions is whether proton transfer can always be assumed to be a rapid equilibrium step[6a-d] ($k_{2p} \gg k_{-1}$ in eq 1) or whether proton transfer may become rate limiting ($k_{2p} \ll k_{-1}$ in eq 1) under certain conditions.[7] Our results show the latter to be the case.

Results

General Features. When 1,1-dinitro-2,2-diphenylethylene (henceforth called S) is mixed with an amine in 50% aqueous

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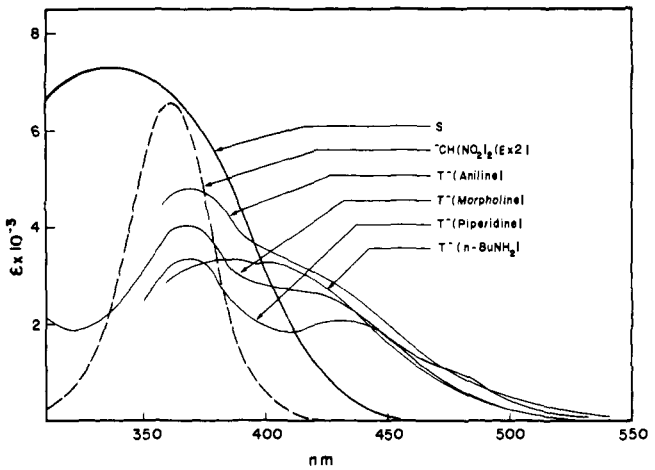


Figure 1. Absorption spectra of 1,1-dinitro-2,2-diphenylethylene (S), T$^-$, and of $\overline{C}H(NO_2)_2$ in 50% Me_2SO–50% water (v/v). For $\overline{C}H(NO_2)_2$, all ϵ values need to be multiplied by 2 (ϵ_{362} = 13 200).

dimethyl sulfoxide solution, there is a rapid formation of T$^-$ (eq 1), identified by its absorption spectrum whose λ_{max} is similar to that for the anion of dinitromethane as well as to those for the addition complexes between S and cyanide ion,[8a] ethoxide ion,[8a] trifluoroethoxide ion,[8b] and several tertiary amines.[8b] There is also NMR evidence that the complexes formed between various activated olefins and nucleophiles have structures which are analogous to that of T$^-$.[1b,9]

The absorption spectra, including those of S and of $^-CH(NO_2)_2$,[10] are shown in Figure 1. Those of T$^-$ were taken under conditions where S is virtually quantitatively converted into T$^-$; they were obtained in a stopped-flow spectrophotometer (see Experimental Section) because the solutions decomposed within a few minutes or less to yield benzophenone and $^-CH(NO_2)_2$ ("second kinetic process"). These latter products were identified by comparing the spectrum of the reaction solution after completion with that of a mock solution of the products as well as by showing that the sum of the spectra of separate solutions of benzophenone, amine, and $^-CH(NO_2)_2$ is identical with the spectrum of the reaction mixture after completion.

S also adds a hydroxide ion to form a complex analogous to T$^-$, which also decomposes to yield benzophenone and dinitromethane or its anion. However, under the conditions employed these reactions are much slower than the amine reactions[11] and did not interfere with our study.

Kinetics of Adduct Formation ($1/\tau_1$). The kinetics was studied in the stopped-flow spectrophotometer. In most cases the reactions were initiated by mixing S with a large excess of an amine–amine hydrochloride buffer, and the relaxation time was determined as a function of free amine concentration at constant pH by monitoring the appearance of T$^-$ at 450 nm. In cases where the equilibrium strongly favors the side of the reactants (low pH in aniline reaction), the experiments were performed by approaching the equilibrium from the T$^-$ side as follows: Substrate and amine were premixed at a high enough pH value in order to assure substantial or complete formation of T$^-$. This solution was then subjected to a pH jump by mixing it with an acidic buffer in the stopped-flow apparatus.

The data are summarized in Tables S1–S4,[12] and Figures 2–5 show plots of reciprocal relaxation times vs. free amine concentration. These plots look different for each amine, but all results are easily rationalized by eq 1 if T$^\pm$ is assumed to be a steady-state intermediate; $1/\tau_1$ is then given by:

$$\frac{1}{\tau_1} = \frac{k_1 k_{2p}[RR'NH]}{k_{-1} + k_{2p}} + \frac{k_{-1}k_{-2p}}{k_{-1} + k_{2p}} \qquad (4)$$

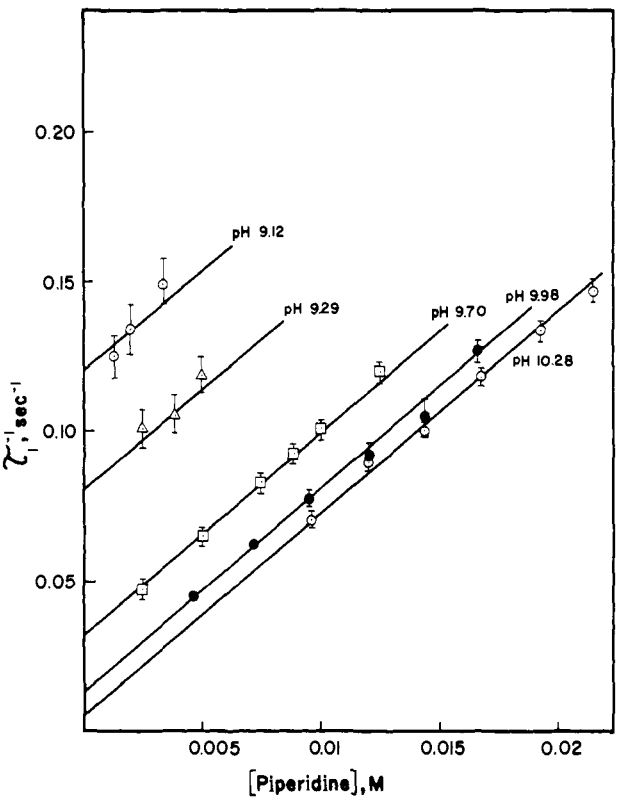


Figure 2. τ_1^{-1} for the reaction of 1,1-dinitro-2,2-diphenylethylene with piperidine.

The four types of behavior shown in Figures 2–5 can be understood as special cases of eq 4.

A. Rapid Proton Transfer ($k_{2p} \gg k_{-1}$). In this case nucleophilic attack is rate determining in the forward direction and eq 4 reduces to:

$$\frac{1}{\tau_1} = k_1[RR'NH] + k_{-1}\frac{[H^+]}{K_a^\pm} \qquad (5)[13]$$

where $K_a^\pm$ is the acid dissociation constant of T$^\pm$. Equation 5 describes the behavior of the piperidine reaction (Figure 2), i.e., a series of parallel straight lines with slope = k_1 and intercept = $k_{-1}[H^+]/K_a$. When $k_1[RR'NH] \gg k_{-1}[H^+]/K_a^\pm$, the intercepts become vanishingly small and the straight lines merge into one as in the reaction of *n*-butylamine (Figure 3).

From the intercepts, when measurable, only the ratio $k_{-1}/K_a^\pm$ can be obtained; in order to evaluate k_{-1} and $K_a^\pm$ separately, experiments at pH values close to or below p$K_a^\pm$ were needed. Since at these low pH values the equilibrium of eq 1 lies virtually completely on the side of the reactants ($k_1/k_{-1} = K_1$ small and amine is mainly present in protonated form), the experiments were performed as pH-jump experiments, as described above. The ensuing relaxation is essentially an irreversible breakdown of T$^-$, with $1/\tau_1$ given by:

$$\frac{1}{\tau_1} = k_{-1}\frac{[H^+]}{K_a^\pm + [H^+]} \qquad (6)$$

The results of these pH-jump experiments for the piperidine and *n*-butylamine reactions are summarized in Table I. From plots (not shown) according to eq 7, k_{-1} and $K_a^\pm$ were obtained. In the piperidine reactions the ratio $k_{-1}/K_a^\pm$ = 1.66 × 10^8 is virtually identical with $k_{-1}/K_a^\pm$ = 1.60 × 10^8 obtained at high pH from the intercepts in Figure 2, in support of our analysis.

$$\tau_1 = 1/k_{-1} + K_a^\pm/k_{-1}[H^+] \qquad (7)$$

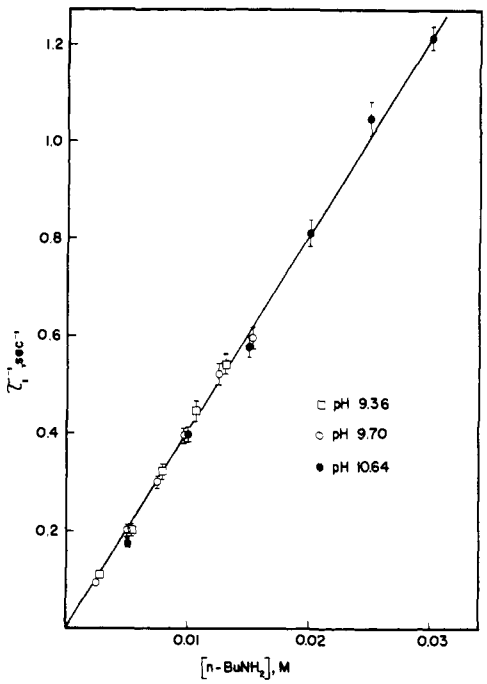


Figure 3. τ_1^{-1} for the reaction of 1,1-dinitro-2,2-diphenylethylene with *n*-butylamine.

With *n*-butylamine the situation is somewhat more complex. Plots (not shown) of $1/\tau_1$ vs. hydrogen ion concentration have a small but significant intercept which is inconsistent with eq 6. This intercept can be attributed to competing protonation of T^- on *carbon* as shown in eq 8:

$$S + RR'NH \underset{k_{-1}}{\rightleftharpoons} T^{\pm} \underset{H^+}{\overset{K_a^{\pm}}{\rightleftharpoons}} T^- \xrightarrow{k_{-3p},\ \text{acid}} \underset{NRR'\ NO_2}{\overset{Ph\quad H}{Ph{-}C{-}C{-}NO_2}} \quad T^0 \qquad (8)$$

where

$$k_{-3p} = k_{-3p}^{H}[H^+] + k_{-3p}^{w} + k_{-3p}^{AH}[RR'NH_2^+] + k_{-3p}^{BH}[BH^+] \qquad (9)$$

$1/\tau_1$ then becomes:

$$\frac{1}{\tau_1} = k_{-1}\frac{[H^+]}{K_a^{\pm} + [H^+]} + k_{-3p}\frac{K_a^{\pm}}{K_a^{\pm} + [H^+]} \qquad (10)$$

Supporting evidence for the reaction $T^- \rightarrow T^0$ comes from two observations. (1) Data summarized in Table II show that for the *n*-butylamine reaction $1/\tau_1$ increases linearly with cacodylic acid concentration, apparently due to an increase in the $k_{-3p}^{BH}[BH^+]$ term of eq 9. In the piperidine reaction where k_{-1} is much larger than in the *n*-butylamine reaction but k_{-3p} is expected to be similar, the $k_{-3p}K_a^{\pm}/(K_a^{\pm} + [H^+])$ term in eq 10 is expected to be negligible. In fact, buffer catalysis with acetic acid was hardly detectable, and the plot of $1/\tau_1$ vs. hydrogen ion concentration has no significant intercept. (2) At high pH the reaction $T^- \rightarrow T^0$, due to the fact that eq 1 is no longer "irreversible", gives rise to a separate relaxation process which was observed with all amines (τ_2; see under Kinetics of Cleavage Reaction).

In evaluating k_{-1} and $K_a^{\pm}$ via eq 7 from the data in Table I, we have corrected for the $k_{-3p}K_a^{\pm}/(K_a^{\pm} + [H^+])$ term in the *n*-butylamine reaction by subtracting the intercept of the plot of $1/\tau_1$ vs. $[H^+]$ from all $1/\tau_1$ values which yields $1/\tau_1$(corr). This procedure is not quite rigorous, since k_{-3p} is pH dependent, but in view of the smallness of the correction this is of no consequence. From plots of $1/\tau_1$ vs. $[BH^+]$, a value for k_{-3p}^{BH} for cacodylic acid was also obtained.

Table I. Reactions of 1,1-Dinitro-2,2-diphenylethylene with Piperidine and *n*-Butylamine, pH-Jump Experiments[a]

pH	τ_1^{-1},[b] s^{-1}	τ_1^{-1}(corr.),[c] s^{-1}
	Piperidine	
5.74[d]	77.1	77.1
5.75[d]	72.8	72.8
6.02[d]	59.3	59.3
6.04[d]	59.1	59.1
6.40[d]	41.8	41.8
6.44[d]	35.9	35.9
6.62[d]	27.1	27.1
6.70[d]	24.9	24.9
	n-Butylamine	
5.71[e]	22.7×10^{-2}	22.2×10^{-2}
5.99[e]	15.9×10^{-2}	15.4×10^{-2}
6.31[e]	9.62×10^{-2}	9.07×10^{-2}
6.36[f]	9.23×10^{-2}	8.68×10^{-2}
6.68[f]	5.74×10^{-2}	5.19×10^{-2}
7.09[f]	2.89×10^{-2}	2.34×10^{-2}
7.40[f]	1.78×10^{-2}	1.23×10^{-2}
8.00[f]	0.876×10^{-2}	0.326×10^{-2}

[a] μ = 0.5 M at 20 °C, KCl compensating electrolyte. [b] Error limit ±3%. [c] Corrected for protonation on carbon, see text. [d] pH maintained with acetic acid buffer, $[buffer]_{tot}$ = 0.005 M. [e] pH maintained with acetic acid buffer, $[buffer]_{tot}$ = 0.01 M. [f] pH maintained with cacodylic acid buffer, $[buffer]_{tot}$ = 0.01 M.

Table II. Reaction of 1,1-Dinitro-2,2-diphenylethylene with *n*-Butylamine; Cacodylic Acid Catalysis, pH-Jump Experiments[a]

pH	buffer ratio[b]	[BH[c]], M	$10^2\tau_1^{-1}$,[d] s^{-1}
6.97	3:1	0.0186	5.55
	3:1	0.0375	7.55
	3:1	0.0562	9.72
	3:1	0.075	11.4
7.45	1:1	0.0125	2.34
	1:1	0.025	3.85
	1:1	0.0375	5.33
	1:1	0.05	5.55

[a] μ = 0.5 M (KCl), $[RR'NH]_{tot} \leq 0.05$ M. [b] $[BH]/[B^-]$. [c] Cacodylic acid. [d] Error limit ±4%.

B. Rate-Limiting Proton Transfer ($k_{2p} \ll k_{-1}$). The reaction with morpholine (Figure 4) illustrates nicely the transition from rate-limiting proton transfer ($k_{2p} \ll k_{-1}$) to rate-limiting nucleophilic attack ($k_{2p} \gg k_{-1}$). Under the reaction conditions used we have $k_{2p}^{B}[B] = k_{-2p}^{BH}[BH^+] = 0$ (no buffer added), and also $k_{2p}^{OH}[OH^-] \ll k_{-1}$, $k_{2p}^{w} \ll k_{-1}$, $k_{2p}^{w} \gg k_{2p}^{OH}[OH^-]$ (and with it $k_{-2p}^{H}[H^+] \gg k_{-2p}^{w}$), as will be justified in the Discussion; thus eq 4 becomes:

$$\frac{1}{\tau_1} = \frac{k_1(k_{2p}^{w} + k_{2p}^{A}[RR'NH])[RR'NH]}{k_{-1} + k_{2p}^{A}[RR'NH]} + \frac{k_{-1}(k_{-2p}^{H}[H^+] + k_{-2p}^{AH}[RR'NH_2^+])}{k_{-1} + k_{2p}^{A}[RR'NH]} \qquad (11)$$

For very low amine concentrations we have $k_{2p}^{A}[RR'NH] \ll k_{-1}$, so that eq 11 reduces to:

$$\frac{1}{\tau_1} = \frac{k_1(k_{2p}^{w} + k_{2p}^{A}[RR'NH])[RR'NH]}{k_{-1}} + k_{-2p}^{H}[H^+] + k_{-2p}^{AH}[RR'NH_2^+] \qquad (12)$$

From eq 12 we obtain eq 13 for the intercepts, which allow determination of k_{-2p}^{H}, and eq 14 for the initial slopes with K_a^{AH} being the dissociation constant of $RR'NH_2^+$.[14]

$$\text{intercept} = k_{-2p}^{H}[H^+] \quad (13)$$

$$\text{initial slope} = \frac{k_1 k_{2p}^{w}}{k_{-1}} + \frac{k_1 k_{2p}^{A}[RR'NH]}{k_{-1}} + \frac{k_{-2p}^{AH}[H^+]}{K_a^{AH}} \quad (14)[14]$$

With respect to eq 14 we note that the $k_1 k_{2p}^{A}[RR'NH]/k_{-1}$ term cannot be large, otherwise the initial portion of the lines in Figure 4 would show significant upward curvature. It is also apparent that the increasingly steeper initial slopes in Figure 4 must result from an increasing importance of the $k_{-2p}^{AH}[H^+]/K_a^{AH}$ term; at pH 8.08 (lowest pH used) the initial slope is virtually completely dominated by this term and thus k_{-2p}^{AH} can be obtained.

As the amine concentration is increased, curvature sets in because the $k_{2p}^{A}[RR'NH]$ term in the denominator of eq 11 becomes significant; eventually, when $k_{2p}^{A}[RR'NH] \gg k_{-1}$, eq 11 reduces to eq 5, and the curves merge into a set of parallel lines with slope = k_1. Interestingly, at pH 9.2 (highest pH used) *all* points appear to lie on a straight line with a slope of k_1. Since $k_{2p}^{OH}[OH^-] \ll k_{-1}$ this cannot be due to the operation of eq 5, but is due to the sum of the three terms in eq 14 being approximately equal to k_1.

Extrapolation of the lines at high amine concentration to [RR'NH] = 0 (dashed lines in Figure 4) provides $k_{-1}[H^+]/K_a^{\pm}$ as intercepts and allows determination of $k_{-1}/K_a^{\pm}$. Unlike with the piperidine and *n*-butylamine reactions, $K_a^{\pm}$ and k_{-1} cannot be obtained separately from pH-jump experiments at low pH because of too fast rates. Hence $K_a^{\pm}$ was estimated based on the $pK_a^{\pm}$ of the *piperidine* adduct and assuming that the difference in pK_a between the free amine and the adduct is the same for the morpholine and the piperidine reaction, i.e., $pK_a^{AH}(morph) - pK_a^{\pm}(morph) = pK_a^{AH}(pip) - pK_a^{\pm}(pip)$. This then also allowed us to find k_{-1}.

Strong additional support for our interpretation of the curved plots in Figure 4 as being due to a change from rate-limiting proton transfer to rate-determining nucleophilic attack comes from experiments in the presence of added buffers of low nucleophilicity which catalyze proton transfer. The results are summarized in Table III. At high amine concentration $1/\tau_1$ should be unaffected by added buffers; this is borne out by the data (entry A in Table III). At low amine concentrations $1/\tau_1$ increases with buffer concentration (entries B, C, and D in Table III), as it should. With the sterically least hindered buffer, *p*-cyanophenoxide, $1/\tau_1$ quickly reaches a plateau, indicating $k_{2p}^{B}[B] \gg k_{-1}$; the plateau value corresponds, within experimental error, to $1/\tau_1$ calculated according to eq 5 for the pH and amine concentration used. With the sterically more bulky Dabco, the plateau cannot quite be reached, indicating that the proton transfer rate constant, k_{2p}^{B}, is substantially smaller than for *p*-cyanophenoxide; with the even bulkier *N*-methylmorpholine the acceleration is smaller still.

In order to further confirm that buffer catalysis is due to proton transfer rather than nucleophilic attack on the substrate, several control experiments were carried out in which the reaction of the substrate with the buffer was studied in the absence of morpholine. No significant OD changes could be observed with any of the buffers used, even at buffer and substrate concentrations higher than in the morpholine reaction.

Rate constants for proton transfer between the adduct and the buffers could be determined from initial slopes of plots (not shown) of $1/\tau_1$ vs. buffer base concentration. Here eq 4 takes

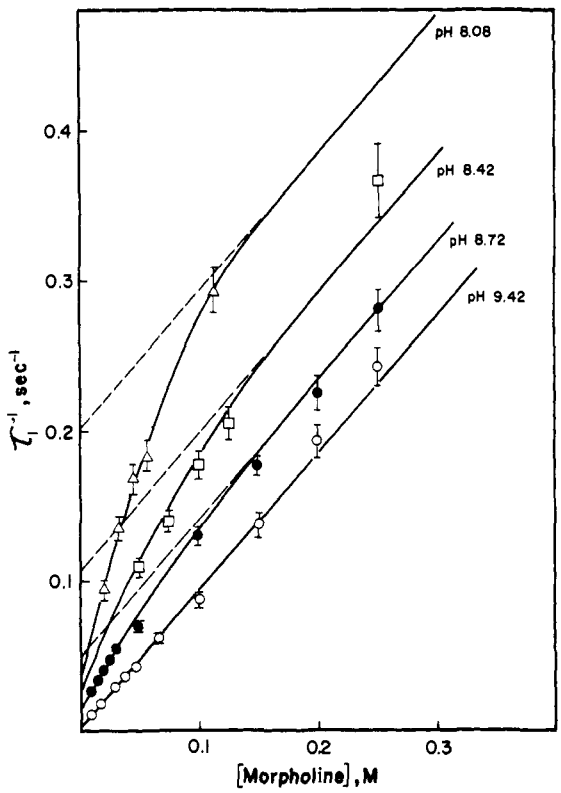


Figure 4. τ_1^{-1} for the reaction of 1,1-dinitro-2,2-diphenylethylene with morpholine.

on the form of:

$$\frac{1}{\tau_1} = \frac{k_1(k_{2p}^{w} + k_{2p}^{A}[RR'NH] + k_{2p}^{B}[B])[RR'NH]}{k_{-1} + k_{-2p}^{H}[H^+] + k_{-2p}^{AH}[RR'NH_2^+] + k_{-2p}^{BH}[BH^+]} \quad (15)$$

Since at the low amine concentrations used the first term in eq 15 is negligible, the initial slope is given by:

$$\text{initial slope} = k_{-2p}^{BH}[H^+]/K_a^{BH} \quad (16)[15]$$

where K_a^{BH} is the acid dissociation constant of BH^+ [15]; k_{2p}^{B} is then obtained as $k_{2p}^{B} = k_{-2p}^{BH}K_a^{\pm}/K_a^{BH}$.

The kinetic behavior of the aniline reaction is similar to that of the morpholine reaction in some respects and dissimilar in others. Under the conditions used we can again safely assume $k_{2p}^{OH}[OH^-] \ll k_{-1}$, $k_{2p}^{w} \gg k_{2p}^{OH}[OH^-]$ (and with it $k_{-2p}^{H}[H^+] \gg k_{-2p}^{w}$), but not necessarily $k_{2p}^{w} \ll k_{-1}$. Furthermore, except at pH 4.85 where aniline acts as its own buffer, a buffer was added in small concentration ($k_{2p}^{B}[B] \ll k_{-1}$) for effective pH control. Hence eq 4 becomes:

$$\frac{1}{\tau_1} = \frac{k_1(k_{2p}^{w} + k_{2p}^{A}[RR'NH] + k_{2p}^{B}[B])[RR'NH])}{k_{-1} + k_{2p}^{w} + k_{2p}^{A}[RR'NH]} + \frac{k_{-1}(k_{-2p}^{H}[H^+] + k_{-2p}^{AH}[RR'NH_2^+] + k_{-2p}^{BH}[BH^+])}{k_{-1} + k_{2p}^{w} + k_{2p}^{A}[RR'NH]} \quad (17)$$

and the initial slopes ($k_{2p}^{A}[RR'NH] \ll k_{-1}$) are given by:

$$\text{initial slope} = \frac{k_1 k_{2p}^{w}}{k_{-1} + k_{2p}^{w}} + \frac{k_1 k_{2p}^{A}[RR'NH]}{k_{-1} + k_{2p}^{w}} + \frac{k_1 k_{2p}^{B}[B]}{k_{-1} + k_{2p}^{w}} + \frac{k_{-1}k_{-2p}^{AH}[H^+]/K_a^{AH}}{k_{-1} + k_{2p}} \quad (18)$$

There is some indication of an initial upward curvature in some of the plots in Figure 5 (dashed lines), suggesting that,

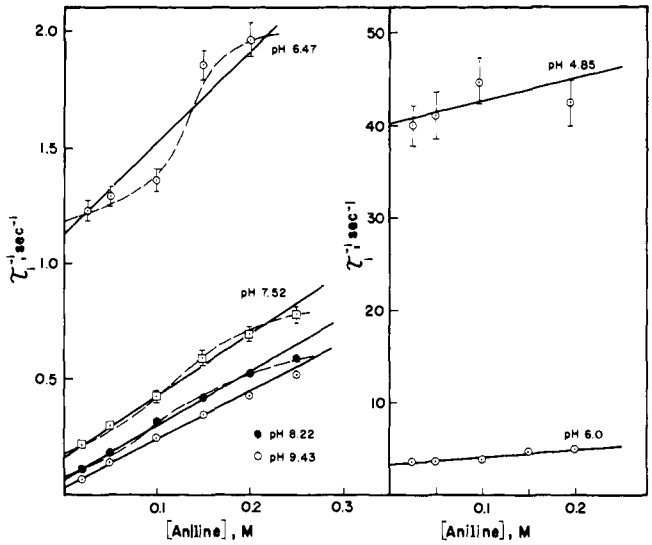


Figure 5. τ_1^{-1} for the reaction of 1,1-dinitro-2,2-diphenylethylene with aniline.

in contrast to the morpholine reaction, the $k_1k_2^A[RR'NH]/(k_{-1} + k_{2p}^w)$ term in eq 18 may not be negligible at high pH. Since the data can also be fitted by straight lines this point will not be pursued further.

From the data in Figure 5 it appears that no leveling off, which would indicate $k_{2p} \gg k_{-1}$, has occurred even at the highest amine concentrations used. This is confirmed by the fact that increasing acetate buffer concentration enhances $1/\tau_1$ not only at low (Table IV, entry A) but also at high aniline concentrations (Table IV, entry B). This shows that proton transfer is rate limiting, or at least partially so, under all conditions employed.

The rate constants for some of the elementary steps were estimated as follows. At the buffer concentrations used in the experiments of Figure 5 (0.02 M total buffer concentration), the $k_{2p}^B[B]$ and $k_{-2p}^{BH}[BH^+]$ terms in eq 17 can, to a first approximation, be neglected; this is borne out by the data in Table IV which show the buffer effect to be small at these concentrations. Hence the intercepts in Figure 5 are approximated by:

$$\text{intercept} = \frac{k_{-1}k_{-2p}^H[H^+]}{k_{-1} + k_{2p}^w} \qquad (19)$$

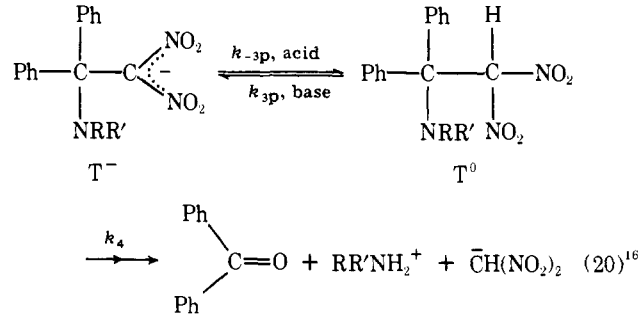
from which we can obtain $k_{-1}k_{-2p}^H/(k_{-1} + k_{2p}^w)$. Since the evidence presented above shows that proton transfer is significantly rate limiting under all conditions, k_{2p}^w cannot be much larger than k_{-1} and probably we have $k_{2p}^w \lesssim k_{-1}$. Thus assuming k_{2p}^w to be negligible in eq 19 and equating the intercepts with $k_{-2p}^H[H^+]$ will not introduce an error of more than a factor of two in our estimate of k_{-2p}^H.

The $pK_a^{\pm}$ is estimated from the $pK_a^{\pm}$ of the *n*-butylamine adduct and assuming pK_a^{AH}(aniline) − $pK_a^{\pm}$(aniline) = pK_a^{AH}(*n*-BuNH$_2$) − $pK_a^{\pm}$(*n*-BuNH$_2$), as for the piperidine-morpholine pair. This then allows us to obtain $k_{2p}^w = K_a^{\pm}k_{-2p}^H$.

The approximation $k_{2p}^w \ll k_{-1}$ also allows eq 18 to be reduced to eq 14 at low buffer concentrations. At the lowest pH values the $k_{-2p}^{AH}[H^+]/K_a^{AH}$ term obviously dominates the initial slopes and k_{-2p}^{AH} can thus be obtained. At high pH the first two terms in eq 14 dominate and at very low amine concentration the slope is approximated by $k_1k_{2p}^w/k_{-1}$, from which k_1/k_{-1} can now be calculated. Assuming further that $k_{2p} \lesssim k_{-1}$ gives us an estimate for k_1 and k_{-1}.

Finally, an approximate value for k_{-2p}^{BH} in the case of acetic acid can be found by applying eq 16 to the data summarized in Table IV.

Kinetics of Cleavage Reaction. $1/\tau_2$ was measured by monitoring the disappearance of T^- at 450 nm on a Gilford kinetic spectrophotometer; it was determined as a function of the respective amine-amine hydrochloride buffer and, in the aniline reaction, also as a function of cacodylic acid concentration. The results are summarized in Tables V and VI. We now show that they are consistent with eq 20 where k_{-3p} and



k_{3p} refer to proton transfer to and from carbon, respectively; k_{-3p} is defined by eq 9, whereas k_{3p} is defined in a similar way as k_{2p} (eq 2).

Assuming T^0 to be a steady-state intermediate and treating the reactions in eq 1 as rapid preequilibria, $1/\tau_2$ is given by:

$$\frac{1}{\tau_2} = \frac{K'}{1 + K'}\frac{k_{-3p}k_4}{k_{3p} + k_4} \qquad (21)$$

with

$$K' = \frac{K_1K_a[RR'NH]}{[H^+]} \qquad (22)$$

Rearranging eq 21 provides "adjusted" $1/\tau_2$ values (included in Tables V and VI) given by:

$$\frac{1}{\tau_2}(\text{adj}) = \frac{1}{\tau_2}\frac{1 + K'}{K'} = \frac{k_{-3p}k_4}{k_{3p} + k_4} \qquad (23)$$

In the piperidine and *n*-butylamine reactions we found $1/\tau_2 \approx 1/\tau_2$(adj), but in the morpholine and aniline reactions the two values differ significantly.

Plots (not shown) of $1/\tau_2$(adj) vs. morpholinium ion concentration for the morpholine reaction afford parallel straight lines (pH independent slopes) with intercepts which increase with decreasing pH. This demonstrates general acid catalysis and is consistent with $k_4 \gg k_{3p}$ which reduces eq 23 to:

$$\frac{1}{\tau_2}(\text{adj}) = k_{-3p} = k_{-3p}^H[H^+] + k_{-3p}^w + k_{-3p}^{AH}[RR'NH_2^+] \qquad (24)$$

The data permit calculation of the rate constants k_{-3p}^H, k_{-3p}^w, and k_{-3p}^{AH} for protonation on carbon by the hydronium ion, the solvent, and by morpholinium ion, respectively.

In the aniline reaction, plots (not shown) of $1/\tau_2$(adj) vs. cacodylic acid concentration also form a series of parallel straight lines, again demonstrating general acid catalysis. Here k_{-3p} contains an additional term, $k_{-3p}^{BH}[BH]$, for cacodylic acid (eq 9). On the other hand $k_{-3p}^H[H^+]$ and k_{-3p}^w contribute too little to k_{-3p} to be measurable; this is also the case in the *n*-butylamine and piperidine reactions where only k_{-3p}^{AH} could be determined. The various rate constants for protonation on carbon are summarized in Table IX.

Discussion

Rate coefficients for the various elementary reactions are summarized in Tables VII–IX.

Nucleophilic Attack (k_1, k_{-1}). The order of nucleophilic reactivity (k_1) is *n*-BuNH$_2$ > piperidine ≳ aniline > morpholine (Table VII). This is a very unusual order; commonly one finds piperidine ≫ *n*-BuNH$_2$, and piperidine ≫ aniline

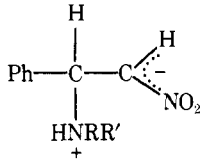
Table III. Reaction of 1,1-Dinitro-2,2-diphenylethylene with Morpholine; Buffer Catalysis[a]

pH	[base],[b] M	$10^2\tau_1^{-1}$,[c] s^{-1}
A. *p*-Cyanophenoxide at [Morpholine][d] = 0.2 M		
9.43	0	17.7
	0.01	18.0
	0.02	18.9
	0.04	17.7
	0.06	17.8
	0.08	17.1
B. *p*-Cyanophenoxide at [Morpholine][d] = 0.01 M		
8.45	0	4.60
	0.005	8.38
	0.01	10.2
	0.025	12.5
	0.05	12.1
C. Dabco at [Morpholine][d] = 0.01 M		
8.37	0.0074	6.37
	0.0185	8.02
	0.037	8.94
	0.056	9.22
	0.074	10.0
	0.925	9.29
D. *N*-Methylmorpholine at [Morpholine][d] = 0.01 M		
8.44	0.05	5.71
	0.10	5.49
	0.15	5.53
	0.20	5.88
	0.25	6.61

[a] At 20 °C, μ = 0.5 M (KCl). [b] Free base. [c] Error limit ±3%. [d] Free amine.

for nucleophilic attack on a variety of electrophiles.[17] The observed order is undoubtedly due to steric hindrance by the two phenyl groups in S; this is not surprising since amine addition even to unhindered olefins is known to be quite sensitive to steric effects in the nucleophile.[17b]

The steric interpretation is consistent with three additional observations. (a) Nucleophilic attack by the same amines on the less hindered β-nitrostyrene, to form **1**, follows the normal



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reactivity order.[11] (b) Nucleophilic attack on β-nitrostyrene is about as fast as attack on S with *n*-butylamine and aniline, and about 200-fold faster than on S with the bulkier piperidine and morpholine,[11] despite the smaller electronic activation. (c) 1,1-Dinitro-2-phenylethylene (one phenyl group only) is so much more reactive than S that it hydrolyzes virtually instantaneously in aqueous solution, precluding a kinetic study.

The rather large $k_{-1}^{Pip}/k_{-1}^{n\text{-}BuNH_2}$ ratio of 280 is also a consequence of the steric effect; the analogous ratio for β-nitrostyrene is 29,[11] that for 1,3,5-trinitrobenzene (Meisenheimer complexes) is ~10.[18]

Based on a comparison between piperidine and morpholine which have the same steric requirement, we have calculated β_{nuc} = 0.37(k_1) and β_{lg} = −0.61(k_{-1})[19]; the β_{nuc} values compare well with those of other electrophiles.[11,21]

Acidity of $T^{\pm}$ ($pK_a^{\pm}$). It is quite remarkable that, despite its negative charge, the $\overline{C}(NO_2)_2$ moiety is so strongly electron withdrawing that $T^{\pm}$ is almost 5 pK_a units more acidic than its parent $RR'NH_2^+$ (Table VII). In comparison, the acidifying effect of the $\overline{C}HNO_2$ group in **1** lowers the pK_a of **1** by 2–2.5 units relative to $RR'NH_2^+$,[11] which is similar to the effect of the $C_6H_2(NO_2)_3^-$ group in Meisenheimer complexes formed from amines and 1,3,5-trinitrobenzene.[18]

Proton Transfer between $T^{\pm}$ and T^-. One of the most interesting findings of this study is that many of the rate constants for proton transfer between $T^{\pm}$ and T^- are substantially lower than expected for normal acids and bases.[4] This effect is particularly pronounced in the morpholine reaction; deprotonation of $T^{\pm}$ by morpholine, *N*-methylmorpholine, Dabco, and *p*-cyanophenoxide ion is thermodynamically fa-

Table IV. Reaction of 1,1-Dinitro-2,2-diphenylethylene with Aniline; Buffer Catalysis[a]

pH	[AcO^-],[b] M	τ_1^{-1},[f] s^{-1}
A. Acetate at [Aniline][c] = 0.02 M		
8.13[d]	0	8.72×10^{-2}
	0.05	10.7×10^{-2}
	0.10	11.0×10^{-2}
	0.15	12.9×10^{-2}
	0.20	13.9×10^{-2}
	0.25	13.9×10^{-2}
B. Acetate at [Aniline][c] = 0.2 M		
6.08[e]	0.05	4.31
	0.10	4.84
	0.15	5.39
	0.20	6.35
	0.25	7.13

[a] At 20 °C, μ = 0.5 M (KCl). [b] Free base. [c] Free amine. [d] pH maintained by Dabco buffer, $[buffer]_{tot}$ = 0.01 M. [e] pH maintained by acetate buffer. [f] Error limit ±3%.

Table V. Cleavage Reaction with Morpholine, Piperidine, and *n*-Butylamine[a]

pH	[RR'NH], M	[$RR'NH_2^+$], M	$10^3\tau_2^{-1}$, s^{-1}	$10^3\tau_2^{-1}$(adj), s^{-1}
		A. Morpholine		
8.41	0.01	0.02	0.815	8.70
	0.02	0.04	2.30	13.4
	0.03	0.06	3.80	16.0
	0.04	0.08	5.56	19.8
8.71	0.01	0.01	0.78	4.58
	0.02	0.02	1.78	6.12
	0.03	0.03	2.86	7.46
	0.04	0.04	4.19	9.25
	0.05	0.05	5.22	10.3
	0.06	0.06	6.37	11.5
9.41	0.02	0.004	1.02	1.52
	0.06	0.012	2.29	2.66
	0.10	0.02	3.04	3.36
		B. Piperidine		
11.03	0.02	0.02	0.762	0.762
	0.04	0.04	1.08	1.08
	0.06	0.06	1.42	1.42
	0.08	0.08	1.66	1.66
		C. *n*-Butylamine		
9.92	0.02	0.10	1.33	1.33
	0.03	0.15	2.03	2.03
	0.04	0.20	2.75	2.75
10.65	0.05	0.05	0.72	0.72
	0.10	0.10	1.48	1.48
	0.15	0.15	2.34	2.34
	0.20	0.20	3.18	3.18

[a] At 20 °C, μ = 0.5 M (KCl).

Table VI. Cleavage Reaction with Aniline[a]

pH	[RR'NH], M	[RR'NH$_2^+$], M	[B$^-$],[b] M	[BH],[b] M	$10^2\tau_2^{-1}$, s^{-1}	$10^2\tau_2^{-1}$(adj), s^{-1}
7.46	0.05	3.08×10^{-5}	0.095	0.105	1.81	3.76
	0.10	6.17×10^{-5}	0.095	0.105	2.72	4.19
	0.15	9.25×10^{-5}	0.095	0.105	3.29	4.47
	0.20	1.23×10^{-4}	0.095	0.105	3.73	4.73
7.02	0.10	1.70×10^{-4}	0.00125	0.00375	0.843	2.10
	0.10	1.70×10^{-4}	0.0025	0.0075	1.37	3.41
	0.10	1.70×10^{-4}	0.0038	0.0114	1.87	4.66
	0.10	1.70×10^{-4}	0.005	0.015	2.42	6.03
7.50	0.10	5.62×10^{-5}	0.005	0.005	1.43	2.13
	0.10	5.62×10^{-5}	0.01	0.01	2.53	3.77
	0.10	5.62×10^{-5}	0.015	0.015	3.74	5.57
	0.10	5.62×10^{-5}	0.02	0.02	4.62	6.88
8.07	0.10	1.51×10^{-5}	0.008	0.0021	0.835	0.944
	0.10	1.51×10^{-5}	0.016	0.0042	1.48	1.67
	0.10	1.51×10^{-5}	0.024	0.064	2.18	2.46
	0.10	1.51×10^{-5}	0.032	0.085	2.78	3.14

[a] At 20 °C, μ = 0.5 M (KCl). [b] BH = cacodylic acid.

Table VII. Rate and Equilibrium Constants for the Reactions of Amines with 1,1-Dinitro-2,2-diphenylethylene in 50% Me_2SO–50% Water at 20 °C[a]

	piperidine	morpholine	*n*-butylamine	aniline
k_1, M^{-1} s^{-1}	6.8	0.95	40	~1
k_{-1}, s^{-1}	100	2.4×10^3	0.36	$\sim 5 \times 10^6$
$K_1 = k_1/k_{-1}$, M^{-1}	6.8×10^{-2}	4×10^{-4}	1.1×10^2	$\sim 2 \times 10^{-7}$
p$K_a^{\pm}$	6.22	~3.94[b]	5.91	~−0.5[c]
pK_a^{AH}[d]	11.00	8.72	10.60	4.25
$K_1K_a^{\pm}$[e]	4.11×10^{-8}	4.58×10^{-8}	1.35×10^{-4}	6.32×10^{-7}[f]

[a] μ = 0.5, KCl compensating electrolyte. [b] Estimated as pK_a^{AH} − 4.78 where 4.78 = pK_a^{AH} − p$K_a^{\pm}$ for piperidine. [c] Esimated as pK_a^{AH} − 4.79 where 4.79 = pK_a^{AH} − p$K_a^{\pm}$ for *n*-butylamine. [d] pK_a^{AH} determined potentiometrically. [e] $K_1K_a^{\pm}$ is a measure of the stability of T$^-$ relative to S. Note that for piperidine and morpholine they are about the same, which means that for a given amine concentration and pH the same percentage of S is converted into T$^-$, leading to roughly the same OD, as observed. [f] Independent spectrophotometric measurement yielded $K_1K_a^{\pm} = 6.43 \times 10^{-7}$

Table VIII. Rate Coefficients for Proton Transfers between T$^{\pm}$ and T$^-$ in the Reaction of 1,1-Dinitro-2,2-diphenylethylene with Morpholine and Aniline in 50% Me_2SO–50% Water at 20 °C[a]

	morpholine (catalyst)	ΔpK[b]	aniline (catalyst)	ΔpK[b]
k_{2p}^{w}, s^{-1}	4.2×10^2 (H_2O)	−5.38	~9×10^6 (H_2O)	−0.94
$k_{2p}^{w}/[H_2O]$, M^{-1} s^{-1}	1.52×10 (H_2O)	−5.38	~3.3×10^5 (H_2O)	−0.94
k_{-2p}^{H}, M^{-1} s^{-1}	4.2×10^6 (H^+)	5.38	~3×10^6 (H^+)	0.94
k_{2p}^{A}, M^{-1} s^{-1}	3.8×10^4 (morph)	4.78	~6×10^6 ($PhNH_2$)	4.79
k_{-2p}^{AH}, M^{-1} s^{-1}	0.63 (morph-H^+)	−4.78	~100 ($PhNH_3^+$)	−4.79
k_{2p}^{B}, M^{-1} s^{-1}	2×10^3 (*N*-methylmorph)	3.62	~7×10^7 (AcO^-)	6.24
	1.1×10^4 (Dabco)	4.86		
	5×10^5 (*p*-$CNC_6H_4O^-$)	4.76		
k_{-2p}^{BH}, M^{-1} s^{-1}	0.48 (*N*-methylmorph-H^+)	−3.62	~40 (AcOH)	−6.24
	0.15 (Dabco-H^+)	−4.86		
	8.5 (*p*-CNC_6H_4OH)	−4.76		

[a] μ = 0.5 M (KCl). [b] ΔpK = pK_a (acceptor) − pK_a (donor), e.g., for k_{2p}^{A}: ΔpK = pK_a^{AH} − p$K_a^{\pm}$; for k_{-2p}^{AH}: ΔpK = p$K_a^{\pm}$ − pK_a^{AH}, etc.; pK_a^{AH} and p$K_a^{\pm}$ from Table VI; pK_a^{BH} determined potentiometrically: 7.56 (*N*-methylmorpholine), 8.80 (Dabco), 8.70 (*p*-cyanophenol), 5.74 (acetic acid); pK_s = 15.9, determined from pH measurements in dilute KOH solution; p$K_a(H_3O^+)$ = −log $[H_2O]$ = −1.44, p$K_a(H_2O)$ = pK_s + log $[H_2O]$ = 17.34; $\Delta pK > 0$ means thermodynamically favored reaction.

vored by several pK units and should approach diffusion control with rate constants in the order of 10^8 to 10^9 M^{-1} s^{-1},[4] but in fact the highest rate constant is only 5×10^6 M^{-1} s^{-1} (*p*-cyanophenoxide ion) and the one for *N*-methylmorpholine is as low as 2×10^3 M^{-1} s^{-1}.

These dramatic rate depressions are another manifestation of the great steric bulkiness of T$^{\pm}$ which, as can be clearly seen with molecular models, makes the proton very inaccessible. The fact that the rate depression becomes stronger with increasing bulkiness of the *base* (*N*-methylmorpholine is the bulkiest, *p*-cyanophenoxide ion the least bulky) is further evidence for a steric effect, and so is the observation that in the case of the less bulky **1** comparable deprotonation rate constants have normal values in the order of 10^9 M^{-1} s^{-1}.[11] The steric effect also retards the protonation of the morpholine T$^-$ adduct by the hydronium ion (k_{-2p}^{H}) by at least three orders of magnitude.[22]

In the aniline reaction the rate depressions are much less dramatic, apparently because T$^-$ is a secondary rather than a tertiary amine which reduces the steric effect. For example, for the same ΔpK, deprotonation of the aniline T$^{\pm}$ adduct by aniline is 150 times (or 12 times) faster than the deprotonation of the morpholine T$^{\pm}$ adduct by morpholine (or *p*-cyanophenoxide ion). Based on these results one would also expect the

protonation of T^- by the hydronium ion to be substantially faster for aniline compared to morpholine. We find however that k_{-2p}^H is about the same for both amines. This is because ΔpK is quite small in the aniline reaction which depresses k_{-2p}^H.[4]

Steric retardations of proton transfers between normal general acids and bases have been observed in other systems,[4,20,24] although they are usually less dramatic.[25] Reports on steric retardation of the protonation of a normal base by the *hydronium ion* are practically nonexistent; we have shown recently that the protonation of 2,6-di-*tert*-butylpyridine by the hydronium ion is about 50 to 70 times slower than that of pyridine.[28]

Alternative Interpretation for Slow Proton Transfer? A referee has suggested that intramolecular hydrogen bonding between amino nitrogen and nitro oxygen in $T^\pm$ might be a contributing factor in the slowness of the proton transfer. Intramolecular hydrogen bonding is in fact known to strongly reduce proton transfer rates,[4,27,29] but the following points show that this cannot be a major factor in our system. (1) The deprotonation of the morpholine-$T^\pm$ becomes progressively slower with increasing bulkiness of the base; this cannot be explained by hydrogen bonding but is consistent with the steric interpretation. (2) Since the aniline-$T^\pm$ is significantly more acidic than the morpholine-$T^\pm$, hydrogen bonding should be stronger in the aniline case and should lead to a larger rate reduction than in the morpholine case. This is opposite to the observed behavior. (3) Intramolecular hydrogen bonding, if it occurs at all, should be stronger in **1** than in the $T^\pm$ adducts because the negative charge is delocalized into one nitro group only, making it a better hydrogen bond acceptor. Hence one would expect even more dramatic rate reductions in the deprotonation of **1**. We found however that the rates are normal[11] in the Eigen[4] sense. (4) The large rate reduction in the reaction $T^- + H^+ \rightarrow T^\pm$ cannot possibly be explained by intramolecular hydrogen bonding since it is a protonation rather than a *de*protonation.

Estimate of Experimentally Inaccessible Proton Transfer Rates. k_{2p}^A and k_{-2p}^{AH} in the piperidine reaction must be virtually identical with those in the morpholine reaction (3.8×10^4 and $0.63\ M^{-1}\ s^{-1}$, respectively), since the steric situation and ΔpK are the same in both systems. k_{2p}^A and k_{-2p}^{AH} in the *n*-butylamine reaction must be similar to those in the aniline reaction (same ΔpK) or perhaps slightly higher due to a somewhat smaller steric effect (estimated $k_{2p}^A \approx 1\text{-}5 \times 10^7\ M^{-1}\ s^{-1}$, $k_{-2p}^{AH} \approx 2\text{-}10 \times 10^2\ M^{-1}\ s^{-1}$). k_{-2p}^H in the piperidine reaction should be comparable to that for the morpholine reaction (same steric effect) or perhaps slightly higher because of a larger pK (estimated $k_{-2p}^H \approx 0.5\text{-}2 \times 10^7\ M^{-1}\ s^{-1}$). k_{-2p}^H in the *n*-butylamine reaction will be substantially higher than in the aniline reaction because it is not depressed due to a small ΔpK, and because of a somewhat reduced steric effect (estimated $k_{-2p}^H \approx 10^8\text{-}10^9\ M^{-1}\ s^{-1}$).

k_{2p}^{OH} is not accessible experimentally in any of the reactions. Taking into account the steric effect, we estimate it to be $10^6\text{-}10^7\ M^{-1}\ s^{-1}$ in the piperidine and morpholine reactions, $0.5\text{-}2 \times 10^9\ M^{-1}\ s^{-1}$ in the aniline reaction, and $1\text{-}3 \times 10^9$ in the *n*-butylamine reaction. From this we can now see that our original assumptions that, for the morpholine and *n*-butylamine reactions, $k_{2p}^{OH}[OH^-] \ll k_{-1}$ and $k_{2p}^{OH}[OH^-] \ll k_{2p}^w$ under all experimental conditions are justified.

Mechanism of Base Catalysis in Nucleophilic Vinylic Substitutions. With sluggish leaving groups base catalysis in nucleophilic vinylic substitutions by amines has been reported in a number of cases.[6,7] In acetonitrile the mechanism for base catalysis appears to consist of a rapid equilibrium deprotonation of the $T^\pm$-like adduct to form the T^--like adduct, followed by rate-limiting general acid catalyzed leaving group departure,[6] although in their most recent study Rappoport and Peled[7] prefer a mechanism whereby proton transfer is rate limiting.

Table IX. Rate Coefficients, k_{-3p}^{cat}, for Protonation of T^- on Carbon

nucleophile	catalyst (pK_a^{cat})	k_{-3p}^{cat},[a] $M^{-1}\ s^{-1}$
morpholine	H_2O (17.34)	4×10^{-4} [b]
piperidine	piperidinium ion (11.0)	1.56×10^{-2}
n-butylamine	*n*-$BuNH_3^+$ (10.60)	1.44×10^{-2}
morpholine	morpholinium ion (8.70)	1.34×10^{-1}
n-butylamine	cacodylic acid (7.50)	1.38
aniline	cacodylic acid (7.50)	3.50
aniline	$PhNH_3^+$ (4.25)	9.90×10
morpholine	H_3O^+ (−1.44)	1.6×10^6

[a] k_{-3p}^{cat} stands for k_{-3p}^{AH}, k_{-3p}^{BH}, k_{-3p}^{H}, and k_{-3p}^{w}, respectively. [b] s^{-1}; $k_{-3p}^w/[H_2O] = 1.45 \times 10^{-5}\ M^{-1}\ s^{-1}$.

The results of the present study show that for a vinylic substrate with electronic and steric effects similar to those of 1,1-dinitro-2,2-diphenylethylene proton transfer can be rate limiting in the formation of the T^--like adduct in a partially aqueous solvent. Whether proton transfer can be rate limiting for the *overall* substitution reaction would depend on the rate of leaving group departure relative to the rate of the reversion of the T^--like adduct to the $T^\pm$-like adduct.[30] Work currently in progress in our laboratory will hopefully answer this question.

Protonation on Carbon. In comparing our results, summarized in Table IX, with the deprotonation-protonation rates and equilibria of 1,1-dinitroethane and its derivatives we note that our $k_{-3p}^w = 4.0 \times 10^{-4}\ s^{-1}$ (protonation of T^- by the solvent) is comparable to that for the solvent protonation of the anion of 1,1-dinitroethane ($5.7 \times 10^{-4}\ s^{-1}$).[32] Also, the protonation rates of T^- by piperidinium ion, morpholinium ion, *n*-$BuNH_3^+$, $PhNH_3^+$, and cacodylic acid are of the same order of magnitude as the rates of protonation of the anion of 1,1-dinitroethane by general acids of comparable pK_a.[32] Thus, it appears safe to conclude that T^0 must have a pK_a value of the same order of magnitude as 1,1-dinitroethane ($pK_a = 5.24$).[32] This conclusion is reenforced by an independent estimate of the pK_a of T^0 based on substituent effect data by Dronov and Tselinsky.[33]

On the other hand our rate constant of $1.6 \times 10^6\ M^{-1}\ s^{-1}$ for the protonation of T^- by the hydronium ion (k_{-3p}^H) is completely out of line with that for the 1,1-dinitroethane anion ($2.1 \times 10^2\ M^{-1}\ s^{-1}$)[32] or the anions of a great many 1,1-dinitroethane derivatives ($10^2\text{-}2 \times 10^3\ M^{-1}\ s^{-1}$),[33] except for $HOOCCH_2CH_2\overline{C}(NO_2)_2$ where $k_{H+} = 1.6 \times 10^7$.[33] Two possible interpretations come to mind. In the first the high rate may be attributed to the presence of Me_2SO, which is known to enhance proton transfer to and from carbon.[34] However with this interpretation it is difficult to rationalize why the rate of protonation of T^- by acids other than the hydronium ion is not enhanced.

A more attractive explanation of our high rate is that protonation occurs on nitrogen, to form $T^\pm$, which then undergoes an *intra*molecular proton switch as shown in eq 25:

$$T^- + H^+ \underset{k_{2p}^w}{\overset{k_{-2p}^H}{\rightleftharpoons}} T^\pm \xrightarrow{k_i} T^0 \qquad (25)$$

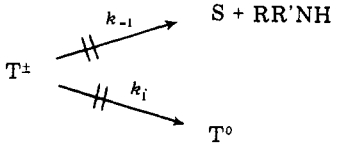
with k_{-3p}^H given by:

$$k_{-3p}^H = \frac{k_{-2p}^H k_i}{k_{2p}^w + k_i} \qquad (26)$$

A similar intramolecular proton transfer involving the carboxylic group of $HOOCCH_2CH_2\overline{C}(NO_2)_2$ could explain the anomalous rate for this latter compound.[33]

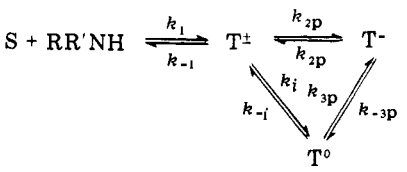
In further support for this interpretation we determined spectrophotometrically how much S is recovered in experi-

ments where S is first quantitatively converted into T^- (at high morpholine concentration and high pH) and then subjected to a pH jump (end pH 3-4) by mixing with an HCl solution. The amount of S recovered varied somewhat from one experiment to another but was generally in the range of 90-95%. This would suggest that $k_i/k_{-1} \approx 0.05$-0.1, assuming that the entire loss in S is due to conversion to T^0 (eq 27). This is in agreement with $k_i/k_{-1} \approx 0.1$, estimated from $k_{-1} = 2400\ s^{-1}$ (Table VII), and $k_i = 240\ s^{-1}$ obtained by solving eq 26 for k_i.



(27)

Alternative Reaction Schemes. Our conclusion that the intramolecular proton switch, $T^{\pm} \rightarrow T^0$, is probably a significant reaction raises the question whether eq 1 should be expanded to include T^0 (eq 28). If the pathway via T^0 were significant



(28)

this could alter the mechanistic interpretation of some of the calculated rate constants. The fact that the reaction leading to T^0 can be observed as a separate, slower relaxation effect (τ_2) shows however that the pathway $T^{\pm} \rightleftharpoons T^0 \rightleftharpoons T^-$ must be significantly slower than the direct pathway $T^{\pm} \rightleftharpoons T^-$.

A referee also suggested that a possible involvement of the aci form of T^0 might lead to complications. This possibility can be discarded as follows. If the aci form were an important species under our conditions, this would manifest itself in the pH dependence of $1/\tau_1$ and $1/\tau_2$. For example, if eq 29 instead of eq 1 would apply:

$$S + RR'NH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} T^{\pm} \underset{k_{-2p}}{\overset{k_{2p}}{\rightleftharpoons}} T^- \underset{K_a^{aci}}{\overset{H^+}{\rightleftharpoons}} T_{aci}^0 \qquad (29)$$

eq 4 would become:

$$\frac{1}{\tau_1} = \frac{k_1 k_{2p}[RR'NH]}{k_{-1} + k_{2p}} + \frac{k_{-1}k_{-2p}}{k_{-1} + k_{2p}} \cdot \frac{K_a^{aci}}{K_a^{aci} + [H^+]} \qquad (30)$$

and the intercept in plots of $1/\tau_1$ vs. amine concentration would show a different pH dependence than observed if $K_a^{aci} \lesssim [H^+]$. Strict adherence of our data to eq 5, 6, 13, etc., indicates that $K_a^{aci} \gg [H^+]$ under all conditions employed. This is consistent with the fact that protonation of the anion of 1,1-dinitroethane in water is strictly first order with respect to $[H^+]$[32] for $[H^+] \leq 10^{-3}$ M, which implies $pK_a^{aci} \ll 3$ for 1,1-dinitroethane. The pK_a^{aci} of our T_{aci}^0 can be expected to be at least as low and probably lower because of the electron-withdrawing effect of the RR'N group and the different solvent. Since all our measurements were carried out at pH $\geq$4.85 and most of them at pH $\geq$6, T_{aci}^0 can never be an important species in our systems.

Spectra. The spectra of T^- shown in Figure 1 deserve some comment. The long tail extending almost up to 550 nm indicates a rather strong interaction of the RR'N group with the $C(NO_2)_2^-$ chromophore. We further note that the spectrum of the *n*-butylamine adduct is distinctly different from that of the other three amine adducts; this is most likely another manifestation of the steric effect.

Experimental Section

Materials. 1,1-Dinitro-2,2-diphenylethylene was a gift from Professor Zvi Rappoport. Morpholine, piperidine, *n*-butylamine, and *N*-methylmorpholine were refluxed over sodium for 8 h and distilled under dry nitrogen. The middle 50% was kept and stored in the dark and cold. Aniline was distilled twice, once from KOH and once from zinc dust. Dabco (1,4-diaza[2.2.2]bicyclooctane) was purified by sublimation. *p*-Cyanophenol was recrystallized from ethanol. Glacial acetic acid, potassium acetate, cacodylic acid, and KCl were used without further purification. Dimethyl sulfoxide was stored over 4A molecular sieves prior to use.

Reaction Solutions, pH and pK_a Determinations. The solutions were prepared by adding appropriate amounts of aqueous stock solutions to a measured amount of Me_2SO that would correspond to 50% of the final solution volume. pH measurements were performed on a Corning Digital 110 pH meter with a Corning No. 476022 glass electrode and a Beckman No. 39400 calomel reference electrode placed into a salt bridge containing 50% aqueous Me_2SO_4 saturated with KCl. The pH meter was calibrated with buffers described by Hallé et al.[35] $[H^+]$ is defined as 10^{-pH} throughout this paper, where pH is directly taken from the pH meter without correction for activity coefficients. The pK_a values for the amines and buffers were determined in 50% aqueous Me_2SO_4, μ = 0.5 M, 20 °C, by extrapolating the pH values of solutions containing the acid and base forms in a 1:1 ratio to zero concentration. The pK_a values of piperidine and *n*-butylamine were also determined by a complete potentiometric titration which gave the same result, within 0.02 pK unit, as the above method.

Spectra. The spectra of all "stable" solutions (substrate, products of cleavage reaction) were taken on a Cary 14 spectrophotometer. In order to obtain the spectra of the adducts T^-, the OD of the reaction solution at a given wavelength was measured on a Durrum-Gibson stopped-flow spectrophotometer shortly after mixing the substrate and the amine, i.e., before the cleavage reaction had made significant progress. In some cases, where the cleavage reaction was relatively rapid, it was necessary to extrapolate the OD reading to time zero. This procedure was repeated at various different wavelengths, at 10-nm intervals, from 350 to 540 nm (Figure 1).

Rate Measurements. $1/\tau_1$ was measured in a Durrum-Gibson stopped-flow spectrophotometer at 450 nm. The pH of the reaction solution was determined in mock mixing experiments; these mock experiments allowed us to establish beforehand how much excess acid or base was needed to achieve a certain desired pH in the reaction solution. $1/\tau_2$ was measured in a Gilford spectrophotometer at 450 nm. The pH of the reaction solution was adjusted and measured before 2 to 5 μL of a concentrated Me_2SO solution of the substrate was added to it.

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Supplementary Material Available: Tables S1-S4 summarizing $1/\tau_1$ values as a function of amine concentration and pH for the reactions of 1,1-dinitro-2,2-diphenylethylene with piperidine, *n*-butylamine, morpholine, and aniline (5 pages). Ordering information is given on any current masthead page.

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(10) Obtained by hydrolyzing S in alkaline solution which yields $\bar{C}H(NO_2)_2$ and benzophenone.[11]
(11) C. F. Bernasconi and D. J. Carré, to be published.
(12) See paragraph concerning supplementary material at the end of this paper.
(13) Note that the second term in eq 4 becomes $k_{-1}k_{-2p}/k_{2p}$ and that $k_{-2p}/k_{2p} = k_{-2p}^{H}[H^+]/k_{2p}^{w} = k_{-2p}^{w}/k_{2p}^{OH}[OH^-] = k_{-2p}^{AH}[RR'NH_2^+]/k_{2p}^{A}[RR'NH] = k_{-2p}^{BH}[BH^+]/k_{2p}^{B}[B] = [H^+]/K_a^{\pm}$.
(14) Note that the $k_{-2p}^{AH}[RR'NH_2^+]$ term in eq 12 is equivalent to $k_{-2p}^{AH}[H^+][RR'NH]/K_a^{AH}$.
(15) Note that the $k_{-2p}^{BH}[BH^+]$ term in eq 15 is equivalent to $k_{-2p}^{BH}[H^+]\cdot[B]/K_a^{BH}$.
(16) The k_4 process probably involves the two steps $T_0 \rightarrow Ph_2C{=}N^+RR' + {}^-CH(NO_2)_2\ (H_2O) \rightarrow Ph_2C{=}O + RR'NH_2^+$.
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(19) It is interesting to compare our k_{-1} values with the rate constant for trifluoroethoxide ion departure from the addition complex between S and trifluoroethoxide ion in acetonitrile, $k \approx 10^{-5}\ s^{-1}$.[8b] Using $\beta_{lg} = -0.61$ we calculate $k_{-1} \approx 3.5\ s^{-1}$ for a hypothetical secondary cyclic amine whose pK_a is the same as that of trifluoroethanol, estimated to be 13.4 in 50% aqueous dimethyl sulfoxide. This would give a ratio $k_{-1}^{amine}/k_{-1}^{CF_3CH_2O^-} \approx 3.5 \times 10^5$. It seems unlikely that the entire ratio is due to the different solvents; part of this ratio probably reflects a better leaving group ability of the amine. If in vinylic systems alkoxide ions are intrinsically about equal or perhaps even slightly better leaving groups than amines of the same pK_a as seems to be the case in aromatic systems,[18,20] our present comparison with trifluoroethoxide ion would again suggest that part of the large $k_{-1}^{amine}/k_{-1}^{CF_3CH_2O^-}$ ratio is a consequence of steric acceleration in the case of the amine leaving groups.
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(22) Protonation of tertiary amines by the hydronium ion in aqueous solution proceeds usually with rate constants $\geq 10^{10}\ M^{-1}\ s^{-1}$.[4a,b] Allowing for a threefold reduction of the diffusion rate due to the threefold higher viscosity[23] of 50% Me_2SO would still lead to $k \geq 3 \times 10^9\ M^{-1}\ s^{-1}$.
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Rate of Protonation of 2,6-Di-*tert*-butylpyridine by the Hydronium Ion. Steric Hindrance to Proton Transfer

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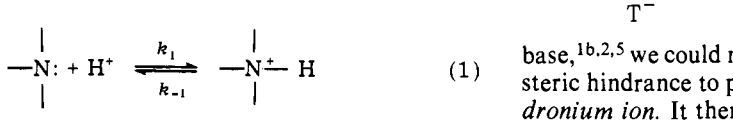
Abstract: The rate of protonation of 2,6-di-*tert*-butylpyridine by the hydronium ion was measured by the temperature-jump method in 20% dioxane–80% water (v/v) at 25 °C. The rate constant is $3.7 \pm 0.8 \times 10^8\ M^{-1}\ s^{-1}$, which is about 50 to 70 times lower than expected for a diffusion-controlled reaction. The rate reduction is attributed to a steric effect and represents one of the first cases where steric hindrance is seen to affect the rate of protonation of a nitrogen base by the *hydronium ion.* The results support the notion that the abnormally low basicity of 2,6-di-*tert*-butylpyridine is due to steric hindrance of solvation rather than due to steric compression of the N–H bond in the protonated base.

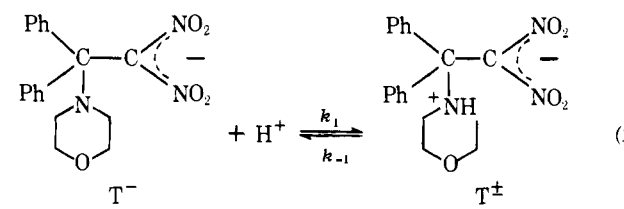
Most chemists know by now that thermodynamically favored proton transfers between oxygen or nitrogen acids and bases are usually diffusion controlled or nearly so.[1] In particular, the reaction of an amine with the hydronium ion in aqueous solution (eq 1) has k_1 values in the order of $10^{10}\ M^{-1}\ s^{-1}$ or slightly higher. Table I summarizes some typical rate constants.



(1)

In a recent study of the nucleophilic addition of amines to 1,1-dinitro-2,2-diphenylethylene, we found that protonation of the morpholine adduct T^- on nitrogen by H^+ in 50% aqueous dimethyl sulfoxide (v/v) (eq 2) has a $k_1 = 4.2 \times 10^6\ M^{-1}\ s^{-1}$.[2] This is nearly 10^4 times lower than typical k_1 values for tertiary amines in water (Table I) and was attributed to a steric effect.[3]

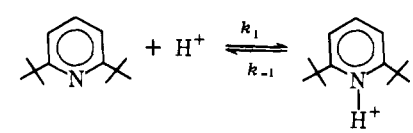
Even though there are numerous precedents of steric hindrance to proton transfer from a *general acid* to a nitrogen base, or from a protonated amine to hydroxide ion or a general



(2)

base,[1b,2,5] we could not find any report in the literature about steric hindrance to protonation of a nitrogen base by the *hydronium ion.* It therefore appeared desirable to look for examples other than reaction 2 where this phenomenon would be observable.[6]

In view of the rather large steric effect of the two *tert*-butyl groups on the pK_a of di-*tert*-butylpyridine,[7,8] we expected that steric hindrance might significantly lower k_1 in reaction 3. We



(3)

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