methylaniline) exciplex indicating similar nature of their electronic structure.[11,25]

(5) Since the intramolecular exciplex formation and dissociation is a reversible process, k_{-1} only makes a partial contribution to the lifetime of E*, τ_{E*} (eq 8-10). Since values of $k_4 + k_5$ are appreciably larger than those of k_{-1} in different solvents (Table II), it is apparent that exciplex dissociation makes only a small contribution of τ_{E*}. Therefore, in contrast to τ_{A*}, τ_{E*} does not vary appreciably with the solvent viscosity as we have observed experimentally.

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Nucleophilic Addition to Activated Olefins. 3.[1] Reactions of Piperidine and Morpholine with Benzylidenemalononitrile in 50% Dimethyl Sulfoxide-50% Water. Intrinsic Barriers in Nucleophilic Additions

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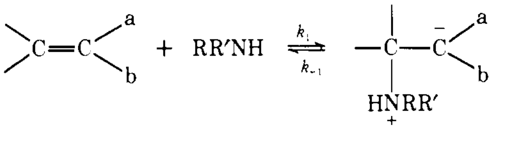
Abstract: The reactions of piperidine and morpholine with benzylidenemalononitrile give rise to two observable kinetic processes. The first is measurable by the stopped-flow temperature-jump technique and is associated with the formation of a zwitterionic addition complex ($T^{\pm}$ in Scheme I) and subsequent deprotonation to form the anionic complex T^-. The second process, which was monitored in the stopped-flow apparatus, refers to the cleavage of the addition complex T^- into benzaldehyde and malononitrile (Scheme II). In the first process nucleophilic attack is rate limiting for the piperidine reaction but proton transfer is partially rate limiting in the morpholine reaction at low amine concentrations. This result implies that base catalysis in nucleophilic vinylic substitutions by amines might be a consequence of rate-limiting proton transfer in some cases. For a given equilibrium constant for nucleophilic addition to an activated olefin the rate constants are higher for benzylidenemalononitrile (cyano activation) than for olefins activated by alkoxycarbonyl groups or the nitro group, implying a lower intrinsic barrier to nucleophilic attack in the former. The similarity of these results with findings on proton transfers involving carbon acids activated by the same substituents is discussed and related to a common origin. Analysis of the data referring to the cleavage of T^- shows that protonation of T^- on carbon, to form T^0, is rapid, while cleavage of T^0 into the iminium ion, $PhCH{=}N^+R_2$, and malononitrile anion is rate limiting.

Nucleophilic addition to the double bond of activated olefins is an important elementary process in organic chemistry.[2] Recently we have started a systematic study[3-5] of the reactions of amines with olefins bearing different electron-withdrawing substituents a and/or b (eq 1). In a preliminary report[3] we



(1)

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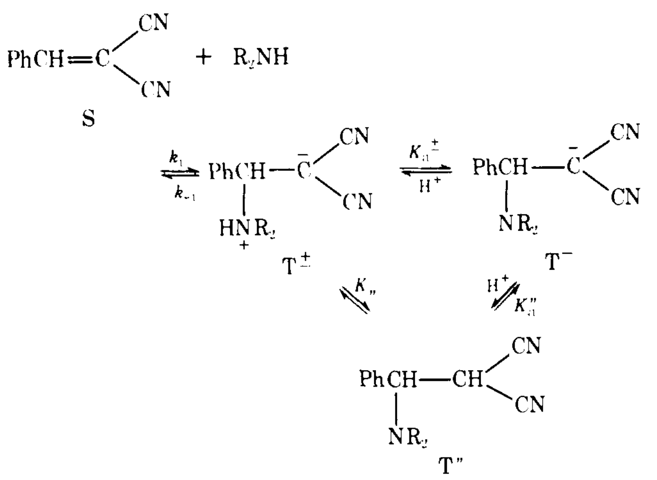
Scheme I



compared the addition of piperidine and morpholine to benzylidenemalononitrile (a = b = CN) with the addition of the same amines to β-nitrostyrene (a = H; b = NO_2). We found that for a given amine the equilibrium constants ($K_1 = k_1/k_{-1}$) have very similar values for the two olefins but that the rate constants are more than 100-fold higher for the dicyano compound compared to the nitro compound. These findings indicate that the kinetic barrier for nucleophilic addition is higher for the nitro compared to the cyano activated olefin, which is reminiscent of proton transfers involving carbon acids activated by cyano and nitro groups, respectively.

The details of the reactions of benzylidenemalononitrile with piperidine and morpholine in 50% Me_2SO–50% water (v/v) are now reported and the problem of the kinetic barrier in the nucleophilic addition to olefins is discussed in more detail. The hydrolysis of benzylidenemalononitrile in the presence of piperidine, in the same solvent, to form benzaldehyde and malononitrile, and a complete analysis of its mechanism, is also discussed.

Results

General Features. When benzylidenemalononitrile is mixed with piperidine or morpholine in 50% Me_2SO–50% water (v/v), one observes two well-separated kinetic processes; they both manifest themselves by a decrease in absorbance at 310 nm which corresponds to λ_{max} of the substrate. The first process, with the relaxation time τ_1, can be measured in the stopped-flow apparatus at high pH (millisecond range) but becomes too fast for the stopped-flow method in the pH range where the amines act as buffers (50–500-μs range); under these conditions τ_1 can be measured by the stopped-flow temperature-jump method.

The kinetic and equilibrium data referring to the rapid process are consistent with the formation of the addition complexes $T^{\pm}$, T^-, and T^0 as shown in Scheme I.

We shall assume that with piperidine the T^0 form can be neglected but not with morpholine. Our reasoning is as follows. We have determined the pK_a of malononitrile in 50% Me_2SO–50% water to be 10.05. The $PhCHNR_2$ moiety in T^0 being electron withdrawing one expects the pK_a of T^0 to be <10.05. The pK_a of $T^{\pm}$ is expected to be in the vicinity of that of the parent $R_2NH_2^+$, which were found to be 11.00 for piperidine and 8.72 for morpholine in 50% Me_2SO–50% water. Hence we assume p$K_a^{\pm} \gg$ pK_a^0 implying $[T^{\pm}] \gg [T^0]$ in the case of piperidine but p$K_a^{\pm} <$ pK_a^0 implying $[T^{\pm}] < [T^0]$ for morpholine. Our data analysis presented below will confirm our assumptions.

Thus, with piperidine Scheme I simplifies to

$$S + R_2NH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} T^{\pm} \underset{H^+}{\overset{K_a^{\pm}}{\rightleftharpoons}} T^- \qquad (2)$$

which is analogous to the reactions of piperidine with 1,1-dinitro-2,2-diphenylethylene,[4] β-nitrostyrene,[3] and benzylidene Meldrum's acid and its derivatives.[5] In contrast to the systems mentioned,[3-5] no direct spectral evidence for T^- and/or $T^{\pm}$ could be obtained because of strong solvent absorption in the spectral range expected for $T^{\pm}$ and T^- derived from benzylidenemalononitrile.[6] However, in view of the close similarity to the above-mentioned systems with respect to kinetic and equilibrium behavior, there can be no doubt as to the identity of $T^{\pm}$ and T^-.

The second process which was monitored in the stopped-flow mode (τ_2 = 2–50 s) is associated with the cleavage of T^0 to form benzaldehyde and malononitrile. These latter products were also formed in the absence of amine, by direct hydrolysis of benzylidenemalononitrile, but with a rate which is much slower than the τ_2 process. Even though observed with both amines, the τ_2 process was studied in detail only with piperidine.

Reactions with Piperidine. Equilibrium measurements for adduct formation were performed by spectrophotometrically monitoring the decrease in substrate concentration at 310 nm with increasing piperidine concentration. Owing to the cleavage reaction these measurements had to be carried out in the stopped-flow apparatus. The results are summarized in Table S1;[7] they obey the equation

$$\frac{OD_0}{OD} - 1 = \left(K_1 + \frac{K_1 K_a^{\pm}}{a_{H^+}}\right)[R_2NH] \qquad (3)$$

where OD_0 and OD are the optical densities in the absence and in the presence of piperidine, respectively, and K_1 is the equilibrium constant for the first step of reaction 2. One obtains $K_1 = 15.4 \pm 2.5$ and $K_a^{\pm} = 5.2 \pm 2.0 \times 10^{-11}$ (p$K_a^{\pm}$ = 10.28 ± 0.14).

Kinetics of adduct formation was studied mainly by the stopped-flow temperature-jump method, with a few experiments at high pH conducted in the stopped-flow mode. In a typical experiment a solution of benzylidenemalononitrile (S) was mixed with a large excess of a piperidine buffer in the stopped-flow temperature-jump apparatus and after a delay of about 50 ms the mixture was subjected to a temperature jump of 3.5 °C, end temperature 20 °C. Chemical relaxation was monitored at 310 nm. The reciprocal relaxation time, τ_1^{-1}, was determined as a function of free piperidine concentration at pH 10.05, 10.40, and 11.00. The results are summarized in Table S2[7] and Figure 1.

The figure shows that, at least above a piperidine concentration of 0.01 M, the data correspond to a family of parallel straight lines with pH-dependent intercepts. This is consistent with the equation

$$\frac{1}{\tau_1} = k_1[R_2NH] + k_{-1}\frac{a_{H^+}}{K_a^{\pm} + a_{H^+}} \qquad (4)$$

which is derived for reaction 2 under the assumption that the proton-transfer equilibrium $T^{\pm} \rightleftharpoons T^-$ is rapidly established. The average slope of the three lines affords $k_1 = 1.85 \pm 0.20 \times 10^5\ M^{-1}\ s^{-1}$.

At amine concentrations below 0.01 M there is an indication of some downward curvature which is reminiscent of the reaction of 1,1-dinitro-2,2-diphenylethylene with certain amines[4] and could be suggestive of a (partially) rate-limiting proton transfer at low amine concentration. Since the experimental error is substantial, we do not consider curvature firmly established and will not pursue this point further. On the other hand, in the morpholine reaction discussed below the curvature is very pronounced (Figure 3) and definitely indicates rate-limiting proton transfer at low amine concentrations.

Some additional experiments were carried out between pH 9.66 and 10.32 and at pH 13.92. The experiments at low pH were aimed at obtaining more data on the $k_{-1}a_{H^+}/(K_a^{\pm} +$

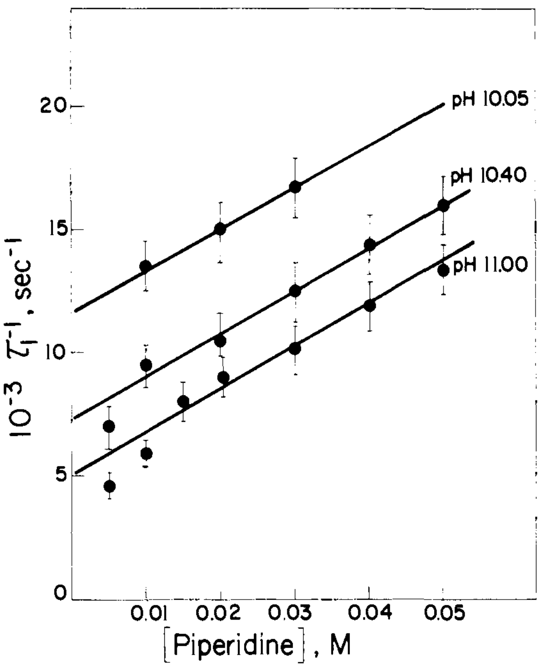


Figure 1. Reaction of benzylidenemalononitrile with piperidine. Kinetics of adduct formation, stopped-flow temperature-jump experiments.

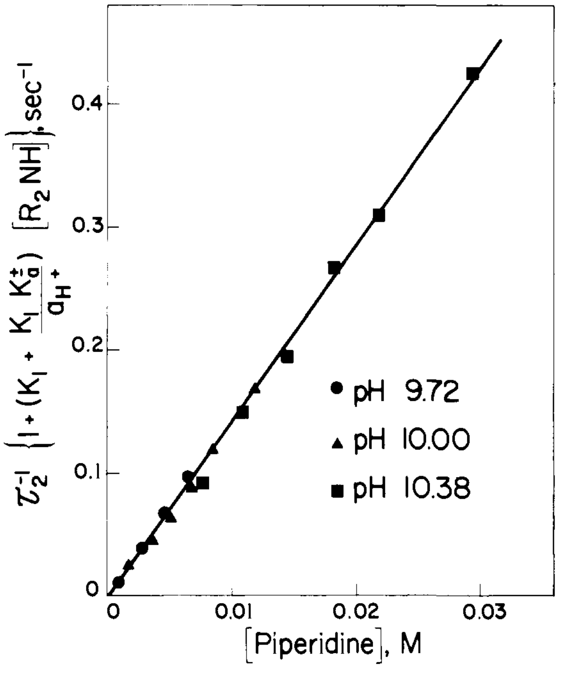


Figure 2. Reaction of benzylidenemalononitrile with piperidine. Kinetics of cleavage reaction, data plotted according to eq 7, stopped-flow experiments.

a_{H^+}) term in eq 4 (intercepts in Figure 1). τ_1^{-1} was determined at single amine concentrations and $k_{-1}a_{H^+}/(K_a^{\pm} + a_{H^+})$ was obtained as $\tau_1^{-1} - k_1[R_2NH]$. The results are included in Table S2.[7]

From an inversion plot (not shown) according to

$$\tau_1([R_2NH] = 0) = \frac{1}{k_{-1}} + \frac{K_a^{\pm}}{k_{-1}a_{H^+}} \tag{5}$$

which includes data from the experiments at single amine concentrations as well as the intercepts of Figure 1, one obtains $k_{-1} = 1.15 \pm 0.4 \times 10^4$ s^{-1} and $K_a^{\pm} = 1.75 \pm 0.75 \times 10^{-11}$ M (pK_a = 10.76 ± 0.24). The agreement between p$K_a^{\pm}$ determined from equilibrium measurements (10.28 ± 0.14) and from kinetics is only fair; part of the discrepancy may be due to some difficulties in the temperature control of the temperature-jump experiments. In our subsequent discussion we will use the value of 10.28 obtained from the equilibrium data. On the other hand, k_{-1} calculated as $k_1/K_1 = 1.20 \times 10^5$ s^{-1} agrees well with $k_{-1} = 1.15 \times 10^5$ obtained via eq 5.

The experiments at pH 13.92 were performed because the $k_{-1}a_{H^+}/(K_a^{\pm} + a_{H^+})$ term of eq 4 becomes very small at high pH, which reduces τ_1^{-1} to a level which makes it measurable in the more accurate stopped-flow mode. The results are also in Table S2.[7] The plot (not shown) of τ_1^{-1} vs. piperidine concentration yields a slope of $k_1 = 2.1 \pm 0.2 \times 10^5$ M^{-1} s^{-1}, which agrees very well with the value obtained in the temperature-jump mode.

The kinetics of the cleavage reaction was studied in the stopped-flow mode at 310 nm. τ_2^{-1} was measured under pseudo-first-order conditions as a function of piperidine concentration at pH 9.72, 10.00, and 10.38. Excellent first-order plots were obtained as long as the substrate concentration was very low ($\leq 2.6 \times 10^{-6}$ M); at higher substrate concentrations there was a deviation from first-order behavior in the sense of an apparent rate decrease with time. Reasons for this behavior will be discussed below; the results which are summarized in Table S3[7] were all obtained under conditions where the first-order rate law was strictly followed.

The data are consistent with the mechanism of Scheme II

Scheme II

$$S + R_2NH \overset{K_1}{\rightleftharpoons} T^{\pm} \underset{H^+}{\overset{K_a^{\pm}}{\rightleftharpoons}} T^- \underset{K_a^0}{\overset{H^+}{\rightleftharpoons}} T^0$$

$$\underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} PhCH{=}\overset{+}{N}R_2 + \overline{C}H(CN)_2$$

$$PhCH{=}\overset{+}{N}R_2 \xrightarrow{k_5^{H_2O} + k_5^{OH}a_{OH^-}} \rightarrow \rightarrow PhCH{=}O + R_2NH$$

where the first three steps are in rapid equilibrium and the k_4 step is rate limiting. τ_2^{-1} is given by[8]

$$\tau_2^{-1} = k_4 \frac{\frac{K_1K_a^{\pm}}{K_a^0}[R_2NH]}{1 + \left(K_1 + \frac{K_1K_a^{\pm}}{a_{H^+}}\right)[R_2NH]} \tag{6}$$

Rearranging of eq 6 affords

$$\tau_2^{-1}\left\{1 + \left(K_1 + \frac{K_1K_a^{\pm}}{a_{H^+}}\right)[R_2NH]\right\} = k_4\frac{K_1K_a^{\pm}}{K_a^0}[R_2NH] \tag{7}$$

A plot of the left side of eq 7 vs. piperidine concentration is shown in Figure 2. From the slope one obtains $k_4/K_a^0 = 1.76 \times 10^{10}$ M s^{-1}. If one assumes that K_a^0 is the same as for the morpholine adduct, which was determined to be 3.75×10^{-9} (see below), one obtains $k_4 = 66$ s^{-1}.

In view of our earlier observation that protonation of T$^-$ to form T^0 rather than the breakdown of T^0 is the rate-limiting step in the reactions of amines with 1,1-dinitro-2,2-diphenylethylene,[4] the question arises whether the present data might alternatively be consistent with such a rate-limiting proton transfer. In such a case τ_2^{-1} would be given by

$$\tau_2^{-1} = \frac{\frac{K_1K_a^{\pm}}{a_H^+}[R_2NH]}{1 + \left(K_1 + \frac{K_1K_a^{\pm}}{a_{H^+}}\right)[R_2NH]}k_p \tag{8}$$

with

$$k_p = k_p^W + k_p^H a_{H^+} + k_p^{AH}[R_2NH_2^+] \tag{9}$$

Table I. Summary of Rate and Equilibrium Constants for the Reactions of Benzylidenemalononitrile with Piperidine and Morpholine[a]

constant (method)	piperidine	morpholine
k_1, M^{-1} s^{-1} (TJ)	$1.85 \pm 0.20 \times 10^5$	$4.4 \pm 0.5 \times 10^4$
k_1, M^{-1} s^{-1} (SF)	$2.10 \pm 0.20 \times 10^5$	$5.9 \pm 0.5 \times 10^4$
k_{-1}, s^{-1} (TJ, eq 5)	$1.15 \pm 0.50 \times 10^4$	
k_{-1}, s^{-1} (K_1, k_1)	1.36×10^4	2.6×10^5
K_1, M^{-1} (spectr)	15.4 ± 2.5	0.23 ± 0.05
$pK_a^{\pm}$ (spectr)	10.28 ± 0.14	8.00 ± 0.14
$pK_a^{\pm}$ (TJ, eq 5)	10.76 ± 0.25	
pK_a^0 (spectr)	8.43 ± 0.20[b]	8.43 ± 0.20
$pK_a^{R_2NH_2^+}$	11.00[c]	8.72[c]
$pK_a^{CH_2(CN)_2}$	10.05	10.05
k_4, s^{-1}	66 ± 20	

[a] At 20 °C, μ = 0.5 M (KCl). [b] Assumed to be the same as for morpholine; see text. [c] Reference 4.

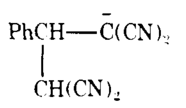
where k_p^H, k_p^W, and k_p^{AH} are the rate constants for protonation of T^- on carbon by the hydronium ion, water, and the piperidinium ion, respectively. The fit of the data to eq 8 (not shown) is about as good as the fit to eq 6; however, the value of ≤ 10 M^{-1} s^{-1} obtained for k_p^{AH} from such an analysis is inconsistent with an expected k_p^{AH} in the order of 10^5 M^{-1} s^{-1},[9] and excludes the hypothesis of a rate-limiting protonation of T^-.

Further evidence against rate-limiting protonation of T^- comes from the observation mentioned earlier that at high substrate concentration there is a deviation from first-order kinetics. Let us assume that the iminium ion $PhCH{=}N^+R_2$ in Scheme II is a steady-state intermediate; k_4 in eq 6 is then replaced by

$$\frac{k_4(k_5^{H_2O} + k_5^{OH}a_{OH^-})}{k_{-4}[\bar{C}H(CN)_2] + k_5^{H_2O} + k_5^{OH}a_{OH^-}}$$

When the initial substrate concentration is low, the $k_{-4}[\bar{C}H(CN)_2]$ term remains small during the entire reaction so that $k_5^{H_2O} + k_5^{OH}a_{OH^-} \gg k_{-4}[\bar{C}H(CN)_2]$ and eq 6 holds. When a high substrate concentration is used, the malononitrile anion builds up enough to make $k_{-4}[\bar{C}H(CN)_2]$ comparable to $k_5^{H_2O} + k_5^{OH}a_{OH^-}$ in the later stages of the reaction, thereby decreasing the rate and leading to a deviation in the first-order plots. This is a familiar phenomenon in S_N1 reactions.[11]

If the above analysis is correct, first-order behavior should be restored at high pH (large $k_5^{OH}a_{OH^-}$ term) even if a high substrate concentration is used. In fact, at pH 11.3 and 13.0 and $[\text{substrate}]_0 = 2.7 \times 10^{-5}$ M the first-order plots became almost perfect; the remaining small deviation is probably due to nucleophilic attack of malononitrile anion on the substrate, to form **1**. The rate constant for this latter reaction is 7.45×10^5 M^{-1} s^{-1}.[12]



$$\begin{array}{l} PhCH{-}\bar{C}(CN)_2 \\ \quad | \\ CH(CN)_2 \end{array}$$

1

In an attempt to quantify the above discussion we synthesized the *N*-benzylidene piperidinium salt ($PhCH{=}N^+R_2$) in order to measure $k_5^{H_2O}$, k_5^{OH}, and k_{-4}. However, its reactivity toward the solvent was too high for such measurements.

Reaction with Morpholine. Equilibrium measurements for adduct formation were carried out in the same way as for the piperidine reaction. The results are summarized in Table S4.[7] Evaluation of the data is by means of the equation

$$\frac{OD_0}{OD} - 1 = \left(K_1 + \frac{K_1K_a^{\pm}}{K_a^0} + \frac{K_1K_a^{\pm}}{a_{H^+}}\right)[R_2NH] \quad (10)$$

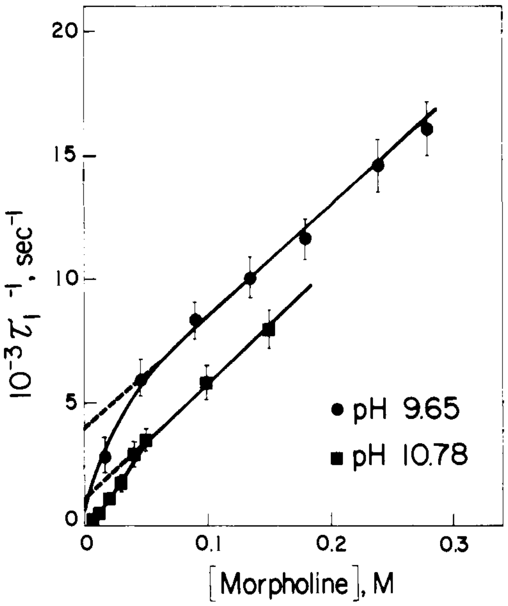


Figure 3. Reaction of benzylidenemalononitrile with morpholine. Kinetics of adduct formation, stopped-flow temperature-jump experiments.

which is analogous to eq 3 but includes a term for the T^0 form; it yields $K_1K_a^{\pm} = 2.26 \pm 0.30 \times 10^{-9}$ and $K_1(1 + (K_a^{\pm}/K_a^0)) = 0.83 \pm 0.15$ M^{-1}. K_1, $K_a^{\pm}$, and K_a^0 are obtained as follows. It is reasonable to assume that the difference between $pK_a^{\pm}$ and the pK_a of the parent $R_2NH_2^+$ is the same for both amines, i.e., $pK_a^{\pm}(\text{mor}) - pK_a(\text{morH}^+) = pK_a^{\pm}(\text{pip}) - pK_a(\text{pipH}^+)$. Thus one obtains $pK_a^{\pm}(\text{mor}) = 8.00$ and with it $K_1 = 0.23$ M^{-1} and $K_a^0 = 3.75 \times 10^{-9}$ M ($pK_a^0 = 8.43$). Since pK_a^0 should depend little on the amine, we assume the same pK_a^0 for the piperidine adduct. This then confirms our initial assumption that $pK_a^{\pm} \gg pK_a^0$ for piperidine but $pK_a^{\pm} < pK_a^0$ for morpholine[13] (see Table I for a summary of all rate and equilibrium constants).

The kinetics of adduct formation was studied by the stopped-flow temperature-jump method in a similar way as for the piperidine reaction. Measurements were made at pH 9.65, where morpholine acts as its own buffer, and at pH 10.78 in a borate buffer. Additional data were obtained in KOH solution at pH 13.41 by the stopped-flow method. The results are summarized in Table S5.[7]

At pH 13.41 a plot (not shown) of τ_1^{-1} vs. amine concentration yields a straight line of slope $5.9 \pm 0.5 \times 10^4$ M^{-1} s^{-1}. Plots of τ_1^{-1} vs. morpholine concentration at pH 9.65 and 10.78 (Figure 3) are curved at low amine concentration but merge into parallel straight lines at high concentration. The straight portion of the plots at pH 9.65 and 10.78, as well as the straight line at pH 13.41, corresponds to rate-limiting nucleophilic attack just as in the piperidine reaction. The slope is k_1 as seen from eq 11, which is derived for Scheme I assuming that $T^{\pm}$, T^-, and T^0 are in a rapid equilibrium with each other.

$$\tau_1^{-1} = k_1[R_2NH] + k_{-1}\frac{a_{H^+}}{K_a^{\pm} + (1 + K_a^{\pm}/K_a^0)a_{H^+}} \quad (11)$$

The slight discrepancy between $k_1 = 4.1 \pm 0.5 \times 10^4$ M^{-1} s^{-1} obtained at pH 9.65 and 10.78 compared to that obtained at pH 13.41 is probably due to the use of two different techniques and a possible slight difference in the temperature.

Using $k_1 = 5.9 \times 10^4$ M^{-1} s^{-1} and $K_1 = 0.23$ M determined from equilibrium measurements one obtains $k_{-1} = 2.6 \times 10^5$ s^{-1}. From k_{-1}, $K_a^{\pm}$, and K_a^0 one can now calculate the second term on the right side of eq 11 and compare it with the intercepts of the extrapolated straight lines of Figure 3. At pH 9.65 one calculates 5.4×10^3, which is in excellent agreement with

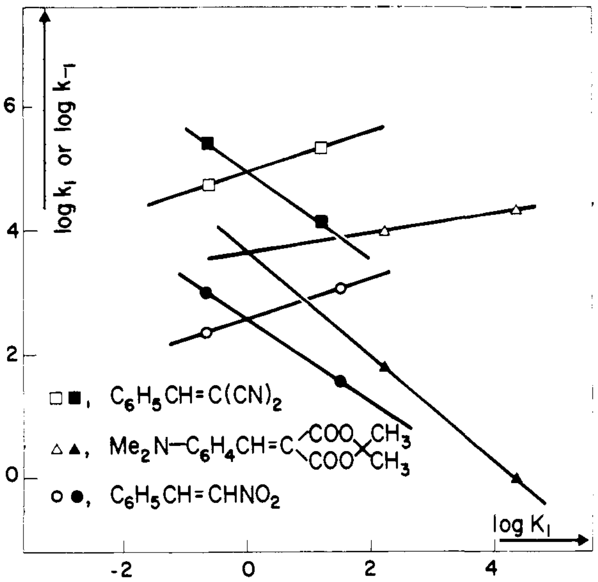


Figure 4. Log k_1 (open symbols) and log k_{-1} (closed symbols) vs. log K_1 for the reactions of piperidine and morpholine with benzylidenemalononitrile, *N,N*-dimethylaminobenzylidene Meldrum's acid, and *β*-nitrostyrene, respectively.

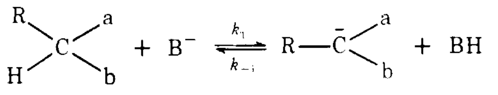
the experimental intercept of 4.0×10^3; at pH 10.78 the calculated and experimental values are 4.4×10^2 and 1.1×10^3, respectively, in fair agreement with each other.

Discussion

The various rate and equilibrium constants determined in this study are summarized in Table I.

Kinetic Barrier in Nucleophilic Addition. One of the most significant results of this work is that nucleophilic attack (k_1) as well as its reverse (k_{-1}) is very rapid compared to the analogous reactions with other olefins studied in our laboratory. Figure 4 shows a plot of log k_1 (log k_{-1}) vs. log K_1 for the addition of piperidine and morpholine to benzylidenemalononitrile, *β*-nitrostyrene,[3] and *p*-*N,N*-dimethylaminobenzylidene Meldrum's acid.[5] For a given equilibrium constant, the rate constants are seen to be highest for the cyano, intermediate for the alkoxycarbonyl, and lowest for the nitro activated olefin. Based on *rate* data alone, earlier workers have already suggested that leaving-group departure from cyano-stabilized carbanions might be intrinsically faster than that from nitro-stabilized carbanions;[14] the present work which includes *equilibrium* constants puts this hypothesis on firm ground.

If one defines the $k_1 = k_{-1} = k_0$ value at $K_1 = 1$ as the intrinsic rate constant of the reaction,[15] the differences between the olefins shown in Figure 4 can be put into quantitative terms: log $k_0 = 4.94$ for cyano, log $k_0 = 3.65$ for alkoxycarbonyl, and log $k_0 = 2.55$ for nitro. Alternatively, one may express these findings in energy terms by defining the intrinsic kinetic barrier as $\Delta G^{\ddagger}$ when $\Delta G^\circ = 0$.[16] The kinetic barrier is seen to increase in the order cyano < alkoxycarbonyl < nitro. It is significant that this is the same trend observed for the kinetic barrier of proton transfers involving carbon acids[19-26] activated by the same substituents, eq 12. For example, for the intrinsic rate constant in the deprotonation of cyano carbon acids log $k_0 \approx 7$;[10,22,26] for ketones, keto esters, and esters, which all seem to fit fairly well on a single Eigen plot, log $k_0 \approx 2.4$,[22] whereas for nitroalkanes log k_0 is close to zero or negative, e.g., ≈ -1.24 for nitroethane[27] and ≈ -1.5 for phenylnitromethane.[28]



(12)

Inasmuch as the structure of the anion formed by deprotonation of the carbon acid is very similar to that of $T^{\pm}$, we believe that the effect of the substituents a and b on the kinetic barrier of the two processes must have similar origins. The main factors which have been invoked in explaining the different kinetic barriers in proton transfers are structural and electronic reorganization (charge delocalization) which accompanies the interconversion between the acid and the anion[17d,19,22,25,26] and solvational changes[20,21,23,24,29] which occur as a consequence of electronic reorganization. This reorganization is particularly strong, and hence the kinetic barrier particularly high, when the negative charge is extensively delocalized; there exists independent evidence that delocalization in fact decreases in the order nitro > carbonyl > cyano.[17d,30,31]

Among the factors responsible for the high kinetic barrier in proton transfers, electronic reorganization[32] and concomitant solvational changes[34] should apply equally to the nucleophilic addition to olefins. On the other hand, there is a difference with respect to structural reorganization in the two types of reaction. In the deprotonation of the carbon acids there is a change in hybridization from sp^3 to something approaching sp^2, the sp^2 character increasing with the amount of charge delocalization,[17d,36] i.e., in the order $NO_2 > CO > CN$. Thus, rehybridization contributes increasingly to the kinetic barrier in the order $NO_2 > CO > CN$. In the olefin additions there is probably less rehybridization; what rehybridization there is is from sp^2 to something approaching sp^3 when the negative charge is not well delocalized, i.e., $CN > CO > NO_2$. Thus, here rehybridization may increase the kinetic barrier in the order $CN > CO > NO_2$, i.e., opposite to the order in the proton transfers. These opposing effects might be responsible for the much smaller *quantitative* differences in log k_0 for the olefin reactions (e.g., log k_0^{CN} − log $k_0^{NO_2} \approx 2.4$) compared to the proton-transfer reactions (e.g., log k_0^{CN} − log $k_0^{NO_2} \approx 8$). This interpretation would imply that, even though change in hybridization represents an important contribution to the kinetic barrier, the other factors are dominant.[37]

Another factor which would tend to reduce the range of k_0 for the olefin reactions is the damping of the electronic effect of the activating substituents by the stabilizing effect of the protonated nitrogen in $T^{\pm}$. However, this effect is relatively small[5] and hence cannot account for the entire reduction.

Rate-Limiting Proton Transfer. In the morpholine reaction the curvature in the plots of Figure 3 indicates that proton transfer is (partially) rate limiting at low amine concentrations. Since according to Scheme I there are three proton-transfer steps, $T^{\pm} \rightleftharpoons T^-$, $T^{\pm} \rightleftharpoons T^0$, and $T^- \rightleftharpoons T^0$, the question arises which of the three is responsible for the curved plots.

In principle the system of Scheme I is characterized by three relaxation times.[40] However, under the experimental conditions $K_a^{\pm}/a_{H^+} \gg 1$ and $K_a^0/a_{H^+} \gg 1$ so that $[T^{\pm}] \ll [T^-] \gg [T^0]$, which makes two of the three relaxation times undetectable in the temperature-jump experiments. The one which *is* detectable (τ_1) refers to the simplified scheme

$$S + R_2NH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} T^{\pm} \underset{k_{-2p,\,\text{acid}}}{\overset{k_{2p,\,\text{base}}}{\rightleftharpoons}} T^- \qquad (13)$$

with $T^{\pm}$ being a steady-state intermediate.[41] Thus, τ_1^{-1} is approximated by

$$\tau_1^{-1} = \frac{k_1 k_{2p}[R_2NH]}{k_{-1} + k_{2p}} + \frac{k_{-1}k_{-2p}}{k_{-1} + k_{2p}} \qquad (14)$$

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

$$k_{2p} = k_{2p}{}^{w} + k_{2p}{}^{OH}a_{OH^-} + k_{2p}{}^{A}[R_2NH] \qquad (15)$$

$$k_{-2p} = k_{-2p}{}^{H}a_{H^+} + k_{-2p}{}^{w} + k_{-2p}{}^{AH}[R_2NH_2{}^+] \qquad (16)$$

with k_{2p}^{w}, k_{2p}^{OH}, and k_{2p}^{A} being the rate coefficients for deprotonation of T$^{\pm}$ by the solvent, hydroxide ion, and the amine, respectively, and k_{-2p}^{H}, k_{-2p}^{w}, and k_{-2p}^{AH} being the rate coefficients for the protonation of T^{-} on nitrogen by the hydronium ion, the solvent, and $R_2NH_2^+$, respectively.

When the amine concentration approaches zero, we observe that τ_1^{-1} also approaches zero, which indicates that k_{2p} and k_{-2p} are dominated by the $k_{2p}^{A}[R_2NH]$ and $k_{-2p}^{AH}[R_2NH_2^+]$ terms, respectively.

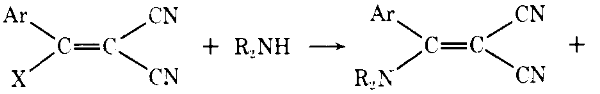
From Figure 3 we see that at a morpholine concentration ≥0.1 M the transition from rate-limiting proton transfer to rate-limiting nucleophilic attack is complete, i.e., $k_{2p} \gg k_{-1}$, which reduces eq 14 to

$$\tau_1^{-1} = k_1[R_2NH] + k_{-1}(a_{H^+}/K_a^{\pm}) \qquad (17)$$

This is the same as eq 11 for the special case $K_a^{\pm} \gg (1 + K_a^{\pm}/K_a^{0})a_{H^+}$, a condition which is fairly well approximated at the pH values of 9.65 and 10.78 used.

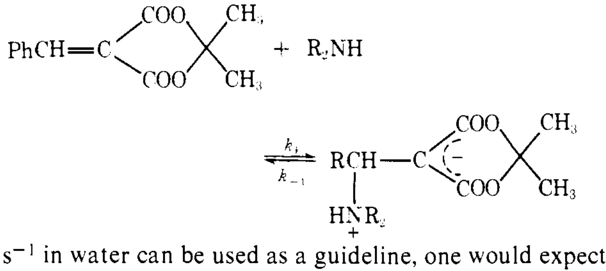
At a morpholine concentration of 0.025 M the changeover in rate-limiting step is about half complete, indicating $k_{-1} \approx k_{2p} \approx k_{2p}^{A}[R_2NH]$. From this we estimate $k_{2p}^{A} \approx 10^7$ M^{-1} s^{-1}. This value of k_{2p}^{A} is about 30–100 times smaller than expected for the deprotonation of a nitrogen acid by a nitrogen base with a similar pK_a difference as between T$^{\pm}$ and morpholine.[42,43] T$^{\pm}$ being a rather bulky tertiary ammonium ion, the rate reduction is probably due to a steric effect which, however, is much less severe than in the deprotonation of the corresponding T$^{\pm}$ adduct between 1,1-dinitro-2,2-diphenylethylene and morpholine ($k_{2p}^{A} = 3.8 \times 10^4$ M^{-1} s^{-1}).[4]

Our results are relevant to the problem of mechanism of base catalysis in nucleophilic vinylic substitutions by amines. Rappoport et al.[44,45] have shown that the reactions of various amines with dicyano activated vinylic substrates bearing a sluggish leaving group are base catalyzed in acetonitrile (eq 18). An earlier interpretation of such base catalysis has been in terms of a rapid equilibrium deprotonation of the T$^{\pm}$-like adduct followed by rate-limiting, general-acid-catalyzed leaving group departure from the T^{-}-like adduct.[44] More recently, Rappoport and Peled[45] have advocated a rate-limiting deprotonation of the T$^{\pm}$-like adduct.



(18)

Even though a comparison of our results with Rappoport's may not be fully warranted because of a difference in solvent and the replacement of the leaving group X by hydrogen, they nevertheless show that rate-limiting proton transfer in the formation of the T^{-}-like adduct in nucleophilic vinylic substitution is a real possibility. In fact, if the solvent effect on the reaction of benzylidene Meldrum's acid with morpholine (eq 19) for which $k_{-1} = 310$ s^{-1} in acetonitrile[46] and $k_{-1} = 2.0$ s^{-1} in water can be used as a guideline, one would expect an increased k_{-1} in acetonitrile, which enhances the chances for a rate-limiting proton transfer in that solvent. It needs to be pointed out, however, that proton transfer can only be rate limiting for the *overall* substitution reaction if leaving-group departure from the T^{-}-like intermediate is faster than the reversion of the T^{-}-like intermediate to the T$^{\pm}$-like intermediate.[47]



(19)

Acidity of T$^{\pm}$. The p$K_a^{\pm}$ values of T$^{\pm}$ are about 0.7 unit lower than those of the respective parent $R_2NH_2^+$, indicating that the anionic $\bar{C}(CN)_2$ moiety is somewhat electron withdrawing. In comparison, the T$^{\pm}$ adducts between β-nitrostyrene and piperidine or morpholine are about 2.7 pK units more acidic than the respective parent $R_2NH_2^+$,[3] indicating that the anionic $\bar{C}HNO_2$ moiety is substantially more electron withdrawing. This result is striking because the equilibrium constants K_1 for addition of the two amines to benzylidenemalononitrile and to β-nitrostyrene are almost identical,[3] indicating that for nucleophilic addition the activating effects of the $CHNO_2$ and of the $C(CN)_2$ moieties are about the same. It should be noted, however, that in the K_1 equilibrium the activating moieties are neutral[49] in the ground state while they are anionic in the ground state of the p$K_a^{\pm}$ equilibrium.

A possible cause for the change in relative electron-withdrawing strength when the $CHNO_2$ and $C(CN)_2$ groups become anionic is that the effect of the negative charge is weaker for the nitro compound due to stronger delocalization of the charge[30,31] which removes it out of the proximity of the amino nitrogen. In other words, the reasons for the different p$K_a^{\pm}$ values and for the different kinetic barriers in the nucleophilic addition seem to be related.

Cleavage Reaction. Our results were shown to be consistent with rate-limiting cleavage of T^{0} (k_4 step in Scheme II) rather than rate-limiting protonation of T^{-} as in previous cases.[4,5] This conclusion is reasonable since proton transfers involving cyano activated carbon acids are known to be very fast[10,22,26] and to approach the behavior of normal acids,[19] while the k_4 step has a rather small rate constant in the order of 66 s^{-1}.

Experimental Section

Materials. Benzylidenemalononitrile was synthesized according to Patai and Rappoport,[51] mp 83 °C (84 °C[51]). Benzylidenepiperidinium perchlorate was prepared by the method of Leonard and Paukstelis:[52] mp 129–131 °C; ^{1}H NMR ($CDCl_3$) δ 9.14 (s, 1, HC=), 7.9–7.4 (m, 5, aromatic), 4.3 (m, 4, $^+NCH_2$), 1.9 (m, 6, CH_2); IR (KBr) 1590 cm^{-1} (>C=N$^+$<); UV (CH_3CN) 272 nm (ε 5270). Morpholine and piperidine were purified and stored as described before.[4] Malononitrile was recrystallized from water and stored over P_2O_5, mp 31–32.5 °C. Reagent-grade Me_2SO was stored over 4A molecular sieves. All other materials were analytical-grade products which were used without further purification.

Kinetic and Equilibrium Measurements. Solutions were prepared by adding Me_2SO to amine buffer and inorganic salts and diluting the mixture to volume with water (50% Me_2SO–50% water, v/v). The olefin was stored in a Me_2SO stock solution and only added to kinetic solutions immediately prior to an experiment. The stopped-flow and stopped-flow temperature-jump experiments were performed in a Durrum D-115 apparatus; for the temperature-jump experiment jumps of 3.5 °C, from 16.5 to 20 °C, were used. The pH of the reaction solutions was determined in mock mixing experiments as described before.[4] Both equilibrium and kinetic measurements were performed at 310 nm.

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Supplementary Material Available: Equilibrium measurements of adduct formation (Table S1), kinetics of adduct formation (Table S2), and kinetics of cleavage reaction (Table S3) for the reaction of benzylidenemalononitrile with piperidine and equilibrium measurements of adduct formation (Table S4) and kinetics of adduct formation (Table S5) for the reaction of benzylidenemalononitrile with morpholine (5 pages). Ordering information is given on any current masthead page.

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(9) The rate constant for the protonation of bromomalononitrile anion by the morpholinium ion is 3×10^6 M^{-1} s^{-1} while $\Delta pK = pK_a(MorH^+) - pK_a(CHBr(CN)_2) = 0.85$.[10] Since the Brønsted α value for the protonation of cyanoalkane anions is ~1 in the thermodynamically unfavored direction[10] one can estimate that for the protonation of T^{-} by piperidinium ion for which $\Delta pK = pK(pipH^+) - pK_a(T^0) \sim 2.5$ the rate constant must be $\sim 10^5$ M^{-1} s^{-1}.

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