low solute concentrations minimizes complications arising from aggregation phenomena frequently encountered in such solvents. Although this paper only describes results with picrate salts, the method can, and is being extended to include other anions, e.g., carboxylates. It is anticipated that the data obtained for different ionic solutes as a function of solvent and network variables will be helpful in rationalizing phenomena encountered when immobilized crown ethers, cryptands, or glymes are utilized in phase transfer, chromatography, or other applications.

Acknowledgment. The authors gratefully acknowledge the financial support of this research by the National Science Foundation under grant No. CHE 8205881.

Registry No. Sodium picrate, 3324-58-1; potassium picrate, 573-83-1.

Rates of Deprotonation of (4-Nitrophenyl)acetonitrile and (2,4-Dinitrophenyl)acetonitrile in 50% Me_2SO–50% Water

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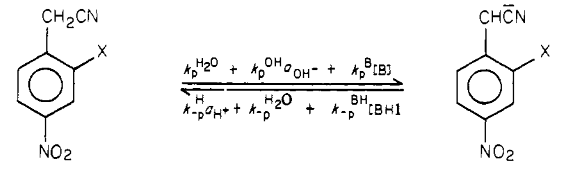
Contribution from the Thimann Laboratories of the University of California, Santa Cruz, California 95064. Received November 8, 1982

Abstract: Rates of reversible deprotonation of (2,4-dinitrophenyl)acetonitrile (**2**-$(NO_2)_2$) by OH^-, water, piperidine, morpholine, cacodylate, acetate, formate, and chloroacetate ion and of (4-nitrophenyl)acetonitrile (**2**-NO_2) by OH^-, piperidine, morpholine, *n*-butylamine, and 2-methoxyethylamine in 50% Me_2SO–50% water at 20 °C are reported. The intrinsic rate constant (in the Marcus sense) for the dinitro derivative is about 10-fold lower than that for the mononitro compound. This is consistent with the stronger charge delocalization in the anion of the dinitro compound, which leads to greater structural/electronic/solvational reorganization during the reaction. Brønsted β_B values (variation of base) for the deprotonation by piperidine and morpholine are 0.50 for **2**-$(NO_2)_2$ and 0.74 for **2**-NO_2, respectively. Brønsted α_{CH} values (variation of C–H acid) are 0.47 for deprotonation by morpholine and 0.35 for deprotonation by piperidine. The α_{CH} and β_B values indicate a charge imbalance ($I = \beta_B - \alpha_{CH} > 0$) in the transition state in the sense that positive charge development on the amine nitrogen seems to be ahead of negative charge development on the C–H acid. This imbalance is of opposite sign from that reported for the deprotonation of nitroalkanes and carbonyl compounds ($I < 0$) but must nevertheless have the same origin, namely, a lag in structural/electronic/solvational reorganization behind proton transfer in the transition state. The opposite sign is a consequence of having the substituent at a different location within the molecule. The dependence of β_B on the C–H acidity and the dependence of α_{CH} on amine basicity are related by the cross-correlation coefficient $p_{xy} = 0.053$. The change in transition-state structure, which is implied by these changes in β_B and α_{CH}, can be rationalized on the basis of a More O'Ferrall–Jencks diagram, which has separate axes for proton transfer and for electronic/structural/solvational organization.

This paper reports a kinetic study of the reactions shown in eq 1 in 50% Me_2SO–50% water at 20 °C. $k_p^{H_2O}$, k_p^{OH}, and k_p^{B} are



2-NO_2, X = H[1]
2-$(NO_2)_2$, X = NO_2[1]

2-NO_2^-, X = H[1]
2-$(NO_2)_2^-$, X = NO_2[1]

(1)

the rate constants for deprotonation by water, OH^-, and buffer bases, respectively, while k_{-p}^{H}, $k_{-p}^{H_2O}$, and k_{-p}^{BH} refer to the microscopic reverse of the k_p's.

The rate of deprotonation of **2**-NO_2 has first been studied in Caldin's laboratory in mixtures of ethanol and ether at −77 °C. Detritiation rates of **2**-NO_2 (tritium on benzylic carbon) by a variety of bases in aqueous solution have been reported by Hibbert and Long[4] while Walters[5] has studied the deprotonation of **2**-NO_2 in various Me_2SO–water mixtures. On the other hand, no reports on the kinetics of the proton-transfer reactions involving **2**-$(NO_2)_2$ could be found in the literature.

The reactions of eq 1 are of interest in the context of structure–reactivity relations in proton transfer involving C–H acids.[6] A question of particular interest is whether the second nitro group in **2**-$(NO_2)_2$, whose effect on the pK_a is quite dramatic (pK_a^{CH} (**2**-NO_2) = 12.62 and pK_a^{CH} (**2**-$(NO_2)_2$) = 8.06 in 50% Me_2SO–50% water), leads to an increase in the intrinsic barrier (in the Marcus[7,8] sense) for proton transfer. Such an effect might be expected because the added nitro group leads to a more effective delocalization of the negative charge in the anion (**2**-$(NO_2)_2^-$), a factor that is known to increase intrinsic barriers for proton transfers.[6,8,9] Thus, a study of **2**-NO_2 and **2**-$(NO_2)_2$ under identical conditions seemed desirable.

An additional motivation for such a study is related to our ongoing interest in structure–reactivity relationships of nucleophilic additions to activated olefins.[9] Of particular relevance is our recent investigation of the addition of amines to α-cyano-4-nitrostilbene

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(1) We use the symbols **2**-NO_2, etc., rather than **1**-NO_2, etc., for consistency and easier comparison with the symbols used in the following paper.[2]

(2) Bernasconi, C. F.; Murray, C. J.; Fox, J. P.; Carrē, D. J. *J. Am. Chem. Soc.* **1983**, following article in this issue.

(3) (a) Caldin, E. F.; Harbron, E. *J. Chem. Soc.* **1962**, 2314. (b) Caldin, E. F.; Kasparian, M.; Tomalin, G. *Trans. Faraday Soc.* **1968**, *64*, 2802.

(4) Hibbert, F.; Long, F. A. *J. Am. Chem. Soc.* **1972**, *94*, 2647.

(5) Walters, E. A. *J. Phys. Chem.* **1977**, *81*, 1995. (b) *ibid.* **1978**, *82*, 1219.

(6) For recent reviews, see: (a) Bell, R. P. "The Proton in Chemistry"; 2nd ed.; Cornell University Press: Ithaca, NY, 1973. (b) Hibbert, F. *Compr. Chem. Kinet.* **1977**, *8*, 97. (c) Crooks, J. E. In "Proton Transfer Reactions"; Caldin, E. F., Gold, V., Eds.; Wiley: New York, 1975; p 153.

(7) (a) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891. (b) Cohen, A. O.; Marcus, R. A. *Ibid.* **1968**, *72*, 4249.

(8) Hine, J. *Adv. Phys. Org. Chem.* **1977**, *15*, 1.

(9) For a recent review, see: Bernasconi, C. F. *Pure Appl. Chem.* **1982**, *54*, 2335.

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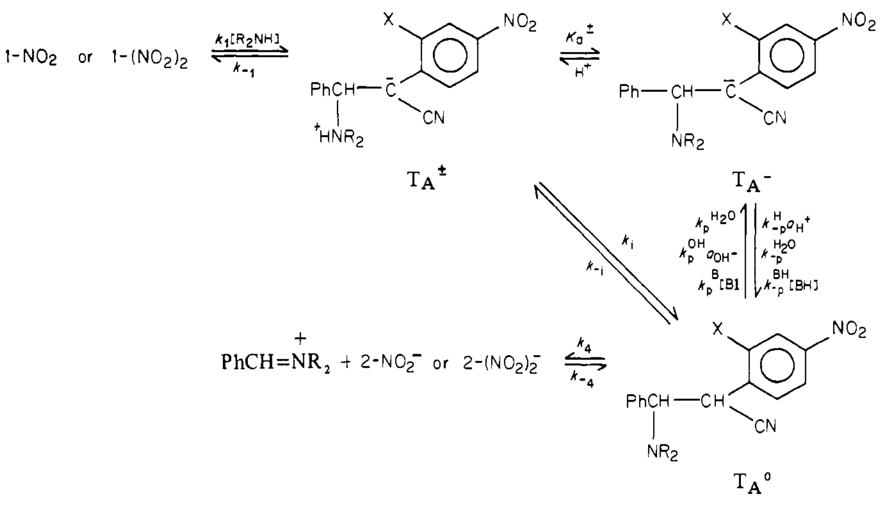
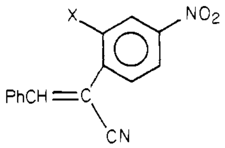
Scheme I



(1-NO_2) and α-cyano-2,4-dinitrostilbene (1-$(NO_2)_2$).[2,10] Scheme I summarizes the various processes that occur in these systems.



1-NO_2, X = H
1-$(NO_2)_2$, X = NO_2

The close analogy between the reaction $T_A^- \rightleftharpoons T_A^0$ in Scheme I and eq 1 is obvious. A question of particular interest is whether the intramolecular proton switch (k_i,k_{-i} steps in Scheme I) is a significant pathway or not.[10,11] By measuring k_{-p}^H in reaction 1, we hoped to obtain estimates for k_{-p}^H for the protonation of T_A^- by H_3O^+. Such estimates would help in deciding whether the *observed* rate constants, k_H, for hydronium ion catalyzed conversion of T_A^- to T_A^0 (Scheme I) are equivalent to k_{-p}^H or whether they include a significant, or even dominant, contribution by a $k_i/K_a^{\pm}$ term arising from the intramolecular proton switch.

In a more indirect way, eq 1 also provides a model for the nucleophilic addition step (k_1, k_{-1}) in Scheme I. We have shown that there is a strong qualitative similarity in how intrinsic barriers for nucleophilic additions to olefins and for proton transfers depend on the activating substituent(s).[2,9] Thus, it is of interest to see whether this similarity extends to the present systems.

Results

General Features. Rates and pK_a values were measured in buffer solutions or in dilute KOH, always under pseudo-first-order conditions. The ionic strength was kept constant at 0.5 M with KCl. The rates were measured in a stopped-flow spectrophotometer by monitoring the carbanion at or near its λ_{max} (515 nm (ϵ 43 500) for 2-NO_2^-, 444 nm (ϵ 26 500) for 2-$(NO_2)_2^-$). At pH > pK_a^{CH} the equilibrium was approached from left to right by mixing a slightly acidic solution of the C–H acid with the appropriate buffer or KOH solution; at pH < pK_a^{CH} the equilibrium was approached from right to left by mixing a basic solution of the carbanion with the appropriate buffer. The pseudo-first-order rate constant for equilibrium approach is given by

$$k_{obsd} = k_p^{H_2O} + k_p^{OH}a_{OH^-} + k_p^B[B] + k_{-p}^H a_{H^+} + k_{-p}^{H_2O} + k_{-p}^{BH}[BH] \quad (2)$$

(2,4-Dinitrophenyl)acetonitrile. Rates were determined in chloroacetate, formate, acetate, cacodylate, 2-methoxyethylamine, n-butylamine, morpholine, and piperidine buffers, and in KOH solutions. Typically, buffer ratios of 1:1, 1:2, or 2:1 were employed. At any given pH k_{obsd} was determined at 5–7 different buffer concentrations, with the raw data being summarized in Table S1.[12] Excellent linear plots were obtained from which k_p^B or k_{-p}^{BH} could be evaluated in a similar manner as described elsewhere.[13]

Table I. Rate Constants for the Reaction 2-$(NO_2)_2$ + B $\rightleftharpoons$ 2-$(NO_2)_2^-$ + BH^a

B	pK_a^{BH}	k_p^B,[b] M^{-1} s^{-1}	k_{-p}^{BH},[b] M^{-1} s^{-1}	$\Delta pK = pK_a^{BH} - pK_a^{CH}$ [c]
OH^-	17.34	3.64×10^5	5.39×10^{-3}/ 27.6	9.27
piperidine	11.01	2.37×10^4	27.2	2.94
n-$BuNH_2$	10.65	5.14×10^3	12.6	2.59
$MeOCH_2CH_2NH_2$	9.60	1.15×10^3	33.9	1.54
morpholine	8.72	1.71×10^3	3.40×10^2	0.65
$Me_2AsO_2^-$	7.50	7.92×10^2	1.69×10^2	−0.57
AcO^-	5.78	2.38×10^1	4.64×10^3	−2.30
$HCOO^-$	4.46	3.93	1.64×10^4	−3.61
$ClCH_2COO^-$	3.72	1.51	3.38×10^4	−4.35
H_2O	−1.44	3.73×10^{-3}/ 27.6	4.39×10^5	−9.51

[a] In 50% Me_2SO–50% water, 20 °C, μ = 0.5 M; experimental error in rate constants ±7% or better. [b] k_p^B and k_{-p}^{BH} symbols include B = OH^- and B = H_2O. [c] pK_a^{CH} = 8.06.

In most buffers, either the $k_p^B[B]$ or the $k_{-p}^{BH}[BH]$ term was dominant, and thus the slope would provide k_p^B (or k_{-p}^{BH}) directly while k_{-p}^{BH} (or k_p^B) could be calculated from $pK_a^{CH} - pK_a^{BH}$. In the cacodylate and morpholine buffers, both $k_p^B[B]$ and $k_{-p}^{BH}[BH]$ contributed significantly. Here data were obtained at two different buffer ratios for each buffer, which allowed direct experimental determinations of both k_p^B and k_{-p}^{BH}. The ratio k_p^B/k_{-p}^{BH} = 5.03 for morpholine was found to be in excellent agreement with K_a^{CH}/K_a^{BH} = 4.47, whereas for cacodylate the agreement was not as good but still satisfactory: k_p^B/k_{-p}^{BH} = 0.47, K_a^{CH}/K_a^{BH} = 0.27; pK_a^{CH} was determined spectrophotometrically in morpholine buffers by standard procedures.

From the intercepts of the buffer plots in the most acidic buffers k_{-p}^H for hydronium ion catalysis could be obtained while k_p^{OH} was evaluated from data in KOH solutions. All rate constants are summarized in Table I.

It should be noted that in KOH and piperidine solutions we observed what appeared to be a second (slower) kinetic process in the time range of ≈10 s. The extremely small OD change (0.04 or less) associated with this process precluded an accurate determination of rate constants and even suggests that the process might be a machine artifact. Spectra taken in the stopped-flow apparatus at times $t \gg 1/k_{obsd}$(fast) but $t \ll 1/k_{obsd}$(slow) were very similar to the spectrum at $t \gg 1/k_{obsd}$(slow), which would

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(10) Bernasconi, C. F.; Murray, C. J., manuscript in preparation.

(11) Bernasconi, C. F.; Hibdon, S. A.; McMurry, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 3459.

Table II. Rate Constants for the Reaction $\mathbf{2}\text{-NO}_2 + \text{B} \rightleftharpoons \mathbf{2}\text{-NO}_2^- + \text{BH}^a$

B	pK_a^{BH}	k_p^B,^{b} $M^{-1}\ s^{-1}$	k_{-p}^{BH},^{b} $M^{-1}\ s^{-1}$	$\Delta pK = pK_a^{BH} - pK_a^{CH\ c}$
OH^-	17.34	2.55×10^4	13.4/27.6	4.72
piperidine	11.01	6.23×10^2	2.54×10^4	−1.61
n-BuNH$_2$	10.65	9.53×10^1	8.29×10^3	−1.97
$MeOCH_2CH_2NH_2$	9.60	1.88×10^1	1.97×10^4	−3.02
morpholine	8.72	1.22×10^1	6.96×10^4	−3.90

[a] In 50% Me_2SO-50% water, 20 °C, $\mu = 0.5$ M; experimental error in the rate constants ±7% or better. [b] k_p^B and k_{-p}^{BH} symbols include B = OH^-. [c] $pK_a^{CH} = 12.62$.

support the notion of an artifact. Another possible interpretation is that the slow process refers to the reaction of traces of a hydrolysis product of **2**-$(NO_2)_2$ (amide?). The phenomenon was not investigated further.

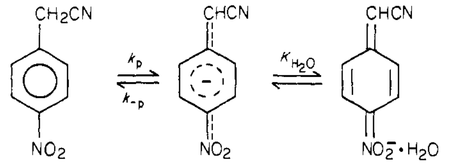
(4-Nitrophenyl)acetonitrile. With **2**-NO_2 the reaction could only be studied in relatively strongly basic buffers because the rates are too high for the stopped-flow method in more acidic buffers (high k_{-p}^{BH} due to high pK_a^{CH}). The bases used include KOH, piperidine, n-butylamine, morpholine, and 2-methoxyethylamine. The methodology was the same as for **2**-$(NO_2)_2$; the raw data are summarized in Table S2.[12]

In contrast to the situation with **2**-$(NO_2)_2$ the plot of k_{obsd} vs. a_{OH} for **2**-NO_2 not only yields $k_p^{OH} = 2.55 \times 10^4\ M^{-1}\ s^{-1}$ from the slope, but it has a measurable intercept, $k_{-p}^{H_2O} = 14.0\ s^{-1}$. K_a^{CH} calculated as $(k_p^{OH}/k_{-p}^{H_2O})K_w = 2.29 \times 10^{-13}$ is in excellent agreement with $K_a^{CH} = 2.40 \times 10^{-13}$ determined spectrophotometrically. The rate constants are summarized in Table II.

Just as in the reaction of **2**-$(NO_2)_2$ we observed a second (slower) kinetic process with a small amplitude. The amplitude tended to increase if the solution was incubated for an extended period of time in KOH solution. This strongly indicates that the process is probably due to the reaction of a hydrolysis product as mentioned above for **2**-$(NO_2)_2$.

Discussion

Mechanism for 2-NO$_2$. In the case of **2**-NO_2 there is evidence that the anion exists in two forms, one unspecifically solvated, the other hydrogen bonded to the nitro group as shown in eq 3.[5] It



(3)

2-NO_2^- **2**-$NO_2^-\cdot H_2O$

has been shown that the equilibrium between the two forms, which is rapidly established on the time scale of the proton transfer, depends strongly on the Me_2SO content of the solvent.[5] In pure water the hydrogen-bonded form predominates, but as the mole fraction of Me_2SO increases its importance decreases. In 50% Me_2SO–50% water (v/v) only about half of the carbanion is in the hydrogen-bonded form.

For simplicity we shall ignore this equilibrium; i.e., we consider the hydrogen-bonded and the non-hydrogen-bonded anion as one species. This means that our pK_a^{CH} value is an apparent pK_a, defined as $-\log\{([\mathbf{2}\text{-NO}_2^-] + [\mathbf{2}\text{-NO}_2^-\cdot H_2O])a_{H^+}/[\mathbf{2}\text{-NO}_2]\}$, while the rate constants for protonation of the anion are defined as

$$k_{-p} = \frac{k_{-p}(\mathbf{2}\text{-NO}_2^-) + K_{H_2O}k_{-p}(\mathbf{2}\text{-NO}_2^-\cdot H_2O)}{1 + K_{H_2O}} \tag{4}$$

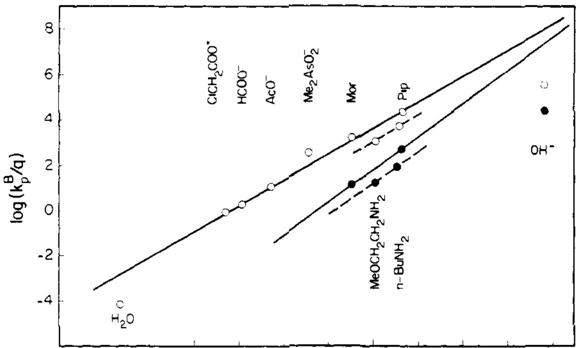


Figure 1. Brønsted plots for the deprotonation of (4-nitrophenyl)acetonitrile (**2**-NO_2, ●) and of (2,4-dinitrophenyl)acetonitrile (**2**-$(NO_2)_2$, ○).

Table III. β_B (α_{BH^+}) Values and $\log k_0$^{a}

	2-NO_2	**2**-$(NO_2)_2$
β_B	0.74	0.50 (0.58)^b
α_{BH^+}	0.26	0.50 (0.42)^b
$\log k_0$	3.70	2.70^c

[a] β_B (α_{BH^+}) and $\log k_0$ based on piperidine and morpholine. [b] Based on $ClCH_2COO^-$, $HCOO^-$, AcO^-, morpholine and piperidine. [c] A preliminary value of 3.0 was given in ref 9.

Since there is no way to obtain $k_{-p}(\mathbf{2}\text{-NO}_2^-)$ and $k_{-p}(\mathbf{2}\text{-NO}_2^-\cdot H_2O)$ separately, we shall not attempt any further analysis of eq 4.[14]

Rate Constants for Proton Transfer. The various rate constants are summarized in Tables I and II. For **2**-NO_2 our value for $k_p^{OH} = 2.55 \times 10^4\ M^{-1}\ s^{-1}$ compares well with that of Walters[5b] ($3.38 \times 10^4\ M^{-1}\ s^{-1}$) determined by the temperature-jump method in the same solvent at a slightly higher temperature (25 °C) and $\mu = 0.1$ M. Also, our $pK_a^{CH} = 12.62$ for **2**-NO_2 is in good agreement with $pK_a^{CH} = 12.75$[5a] at 25 °C.

Figure 1 shows statistically corrected Brønsted plots for base catalysis. In the case of **2**-$(NO_2)_2$ the points for the three carboxylic acids, for morpholine, and for piperidine define a fairly good straight line ($\beta = 0.59$) from which cacodylate ion deviates positively and 1-butylamine and 2-methoxyethylamine deviate negatively.

The negative deviation of the primary amines is also seen in the Brønsted plot for **2**-NO_2. The tendency of primary amines to be less effective proton-transfer catalysts than secondary amines of the same pK_a^{BH} is a common phenomenon[15] that is usually attributed to decreasing solvation in the order $RNH_3^+ > R_2NH_2^+$.

The reason for the positive deviation of cacodylate ion is not entirely clear. As mentioned in the Results section the ratio k_p^B/k_{-p}^{BH} differs somewhat from the ratio K_a^{CH}/K_a^{BH}, which suggests some experimental problems although the deviation from the Brønsted line seems too large to be fully accounted for by experimental error. It is conceivable that (part of) the deviation reflects slight Marcus curvature.[7] Possibly the actual curvature is even stronger than is apparent from the plot in Figure 1 because it might be masked by the fact that catalysts of different charge types were employed. Such masking could come about because the amines are likely to be somewhat more effective catalysts, owing to an electrostatic stabilization of the transition state.[16] This means that k_p^B for hypothetical carboxylate ions of the same pK_a^{BH} as the amines would be lower than k_p^B for the amines, which would produce more pronounced curvature in the Brønsted plots.[16b]

The strong negative deviations for water (≈20-fold for **2**-$(NO_2)_2$) and for OH^- (≈400-fold for **2**-$(NO_2)_2$, ≈10^3-fold for

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[12] See paragraph concerning supplementary material at the end of this paper.

[13] Bernasconi, C. F.; Kanavarioti, A. *J. Org. Chem.* **1979**, *44*, 4829.

[14] Note that if $k_{-p}(\mathbf{2}\text{-NO}_2^-) = k_{-p}(\mathbf{2}\text{-NO}_2^-\cdot H_2O)$, then $k_{-p} = k_{-p}(\mathbf{2}\text{-NO}_2^-)$. Equation 4 in ref 5b implies this assumption.

[15] (a) Reference 6a, Chapter 10. (b) Spencer, T. A.; Kendall, M. C. R.; Reingold, I. D. *J. Am. Chem. Soc.* **1972**, *94*, 1250 and references cited therein.

[16] (a) Kresge, A. J.; Chiang, Y. *J. Am. Chem. Soc.* **1973**, *95*, 803. (b) Chwang, W. K.; Eliason, R.; Kresge, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 805.

Table IV. α_{CH} (β_{C^-}) Values[a]

	morpholine	piperidine	OH^-
α_{CH}	0.47	0.35	0.25
β_{C^-}	0.53	0.65	0.75

[a] Based on $pK_a^{CH} = 12.62$ for 2-NO_2 and $pK_a^{CH} = 8.06$ for 2-$(NO_2)_2$.

2-NO_2) are in the range typical for such reactions.[17]

Structure–Reactivity Parameters and Intrinsic Rate Constants. For the purpose of the following discussion we shall define Brønsted slopes on the basis of the reactions with piperidine and morpholine only. This definition avoids distortions by steric, electrostatic, and solvational factors or by the use of different central atoms. The Brønsted parameters are summarized in Table III. We use the symbols β_B (α_{BH^+}) to indicate that it is the pK_a of the buffer that is varied.

One can also define α_{CH} (β_{C^-}) on the basis of the variation of pK_a^{CH}. These latter parameters are summarized in Table IV. In principle, a steric effect by the *o*-nitro group could distort α_{CH} by reducing the rates for **2**-$(NO_2)_2$. If such a steric effect were to play a significant role, the catalytic advantage of the secondary over the primary amines seen for the unhindered **2**-NO_2 should be greatly reduced or disappear altogether for **2**-$(NO_2)_2$. However, inspection of Figure 1 shows that the reactivity difference between secondary and primary amines is virtually identical for the two substrates, indicating that steric effects play an insignificant role.

Table III includes values for log k_0 where k_0 is the "intrinsic" rate constant defined as k_p^B/q when $pK_a^{BH} + \log(p/q) - pK_a^{CH} = 0$, obtained by extrapolation from the piperidine/morpholine pair. The parameters in Tables III and IV permit us to draw the following conclusions:

(1) Introduction of a second nitro group into the benzene ring reduces k_0 as expected. The reduction amounts to about 1 order of magnitude. Since steric effects have already been excluded as a significant factor in these reactions, this reduction is best understood in terms of a greater structural/electronic/solvational reorganization in the reaction of the dinitro compound. The predominant factor is probably enhanced solvational reorganization because there are *two* nitro groups that need to be solvated in the anion **2**-$(NO_2)_2^-$. In support of this view we note that log k_0 for **2**-NO_2 in water, estimated at ≈ 3.0[9] on the basis of Hibbert and Long's[4] detritiation data, is considerably lower than our log k_0 = 3.7 in 50% Me_2SO–50% water. Such a solvent effect on k_0 is expected if solvent reorganization is a major contributor to the intrinsic barrier in the proton transfer.[9]

(2) The Brønsted β_B values, which are around 0.5 or higher, suggest that positive charge development on the amine nitrogen is half or more than half complete at the transition state. On the other hand, the α_{CH} values, which are lower than 0.5, suggest that negative charge development on the C–H acid is less than half complete at the transition state. Thus, a comparison of α_{CH} with β_B suggest that the transition state is imbalanced in the sense that charge development as seen by the amine base is ahead of charge development as seen by the substituent in the C–H acid. We shall quantify this imbalance in a crude manner by using average β_B (0.62) and α_{CH} (0.41) values and define $I = \beta_B(\text{av}) - \alpha_{CH}(\text{av}) = 0.21$.

Transition-state imbalances are a common phenomenon in many reactions,[18] including proton transfers involving most types of C–H acids.[9,19,20] The most dramatic case is the nitroalkane anomaly,[9,19] where α_{CH} is not only vastly different from β_B but lies outside the normal range of 0–1. In Table IV we have summarized α_{CH}, β_B, and I values for some representative proton-transfer reactions.

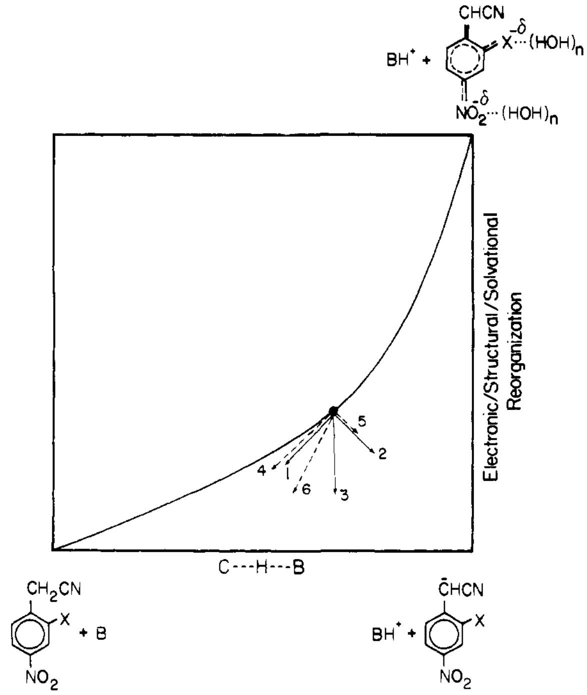
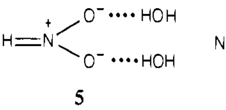


Figure 2. More O'Ferrall–Jencks diagram with separate axes for proton transfer and for electronic/structural/solvational reorganization for the deprotonation of **2**-NO_2 and **2**-$(NO_2)_2$ by amines. Curved reaction coordinate shows lag of reorganization behind proton transfer. Arrows show the effect of making the base stronger (arrows 1 and 2 with resulting arrow 3) and the effect of changing from **2**-NO_2 to **2**-$(NO_2)_2$ (arrows 4 and 5 with resulting arrow 6).

At first sight the **2**-NO_2/**2**-$(NO_2)_2$ pair appears to behave in a fundamentally different way from the other two examples because $I = \beta_B - \alpha_{CH}$ is positive. However, the underlying cause for the imbalance is probably the same in all cases, and the change in the sign of I is a consequence of a different location of the substituent within the molecule. Among the various explanations proposed for these imbalances[22] we favor one according to which solvent reorganization at the site where the bulk of the negative charge will ultimately reside (oxygen atoms of nitro or carbonyl groups) lags behind proton transfer.[9] In other words in the transition states (e.g., **3** or **4**), the negative charge remains relatively localized and unsolvated on carbon while in the product anions (e.g., **5** or **6**) it is delocalized and strongly solvated. This has the following consequences. For $ArCH_2NO_2$ and $ArCH_2CH(COMe)COOEt$ where the substituent is in the phenyl ring removed from the main activating group, the charge "seen" by the substituent appears enhanced in the transition state because it is closer to the substituent than it is in the product anion, and



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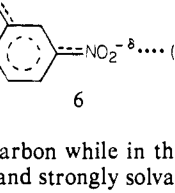

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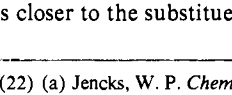

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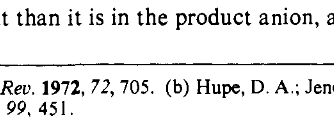

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[17] Kresge, A. J. *Chem. Soc. Rev.* **1973**, *2*, 475.

[18] See, e.g.: Bernasconi, C. F.; Leonarduzzi, G. D. *J. Am. Chem. Soc.* **1982**, *104*, 5133 and numerous references cited therein.

[19] (a) Bordwell, F. G.; Boyle, W. J., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 3907; **1975**, *97*, 3447. (b) Bordwell, F. G.; Bartmess, J. E.; Hautala, J. A. *J. Org. Chem.* **1978**, *43*, 3107.

[20] Bell, R. P.; Grainger, S. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1367.

[21] More O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 224.

[22] (a) Jencks, W. P. *Chem. Rev.* **1972**, *72*, 705. (b) Hupe, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 451.

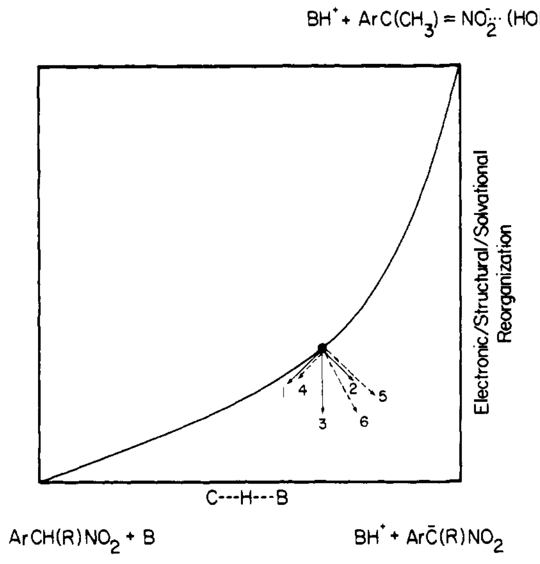


Figure 3. More O'Ferrall–Jencks diagram with separate axes for proton transfer and for electronic/structural/solvational reorganization for the deprotonation of $ArCH_2NO_2$ or $ArCH(CH_3)NO_2$ by amines. Curved reaction coordinate shows lag of reorganization behind proton transfer. Arrows show the effect of making the base stronger (arrows 1 and 2 with resulting arrow 3) and the effect of making the phenyl substituent more electron withdrawing (arrows 4 and 5 with resulting arrow 6).

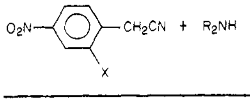
thus $I < 0$. For **2**-NO_2/**2**-$(NO_2)_2$ where the substituent is in the phenyl ring which is directly involved in the activation of the C–H acid, the charge "seen" by the substituent in the transition state appears to be reduced because it is further away than in the product anion, and thus $I > 0$.

A convenient way to schematically illustrate these imbalances is to place the reactions on More O'Ferrall–Jencks[21-23] diagram, which have separate axes for proton transfer and for electronic/structural/solvational reorganization. Such diagrams are shown in Figure 2 for the (nitrophenyl)acetonitriles and in Figure 3 for the arylnitroalkanes. The lag in electronic/structural/solvational reorganization is represented by the curved reaction coordinates, with the transition state being located near the hypothetical[24] intermediate whose charge is localized on carbon. These diagrams should of course not be taken too literally in terms of precise geometry, direction of reaction coordinate, location of the transition state, etc.,[25] but merely regarded as a helpful tool in visualizing the observed imbalances.

It is interesting to note that the transition-state imbalances and the effect of changing substituents on the intrinsic rate constants are related.[26] In the case of the **2**-NO_2/**2**-$(NO_2)_2$ pair there probably are two complementary aspects to this interrelationship. In the first one may understand the reason why α_{CH} is relatively small (and thus $I > 0$) by appreciating that the rate-enhancing effect of the second nitro group (which helps stabilize the developing negative charge in the transition state) is counteracted by the rate-retarding effect (lower k_0) caused by the greater need for solvent reorganization. The second aspect simply relates to the effects of the additional nitro group on the transition state (small stabilization) and the product anion (large stabilization). These effects lead to a disproportionally small increase in $k_p{}^B$ relative to the change in $pK_a{}^{CH}$, which manifests itself not only in a small α_{CH} value but also in an effective reduction of k_0.

In the cases where the substituent is on the other phenyl group ($ArCH_2NO_2$, $ArCH_2CH(COMe)COOEt$) the second aspect is likely to be dominant. Here the effect of a more electron-withdrawing substituent is seen to be disproportionately large on $k_p{}^B$ relative to $pK_a{}^{CH}$. This leads not only to an exalted α_{CH} value (and thus to $I < 0$) but should also bring about an increase in k_0. This is borne out by experimental data. For example, on the basis of the deprotonation of 1-phenylnitroethane by piperidine and morpholine[19a] one calculates log $k_0 = -2.45$ while for the deprotonation of 1-(*p*-nitrophenyl)nitroethane by the same amines[19a] one obtains log $k_0 = -2.00$.

Table V. Transition-State Imbalances in Proton Transfers

reaction	β_B	α_{CH}	$I = \beta_B - \alpha_{CH}$	source
$ArCH_2NO_2 + R_2NH$	0.65	1.29	−0.64	ref 19
$ArCH_2CH(COMe)COOEt + RCOO^-$	0.44	0.76	−0.32	ref 20
	0.62	0.41	+0.21	this work

Changes in Transition-State Structure. We note that β_B is substantially different for the two C–H acids (Table III) and that α_{CH} depends strongly on the identity of the base (Table IV). The dependence of β_B on the $pK_a{}^{CH}$ of the C–H acid and the dependence of α_{CH} on the $pK_a{}^{BH}$ of the two amines are related by the diagonal interaction coefficient p_{xy}[23]

$$p_{xy} = \frac{\partial \beta_B}{\partial pK_a{}^{CH}} = -\frac{\partial \alpha_{CH}}{\partial pK_a{}^{BH}} = 0.053 \qquad (5)$$

These changes in β_B and α_{CH} (positive p_{xy} coefficient) are consistent with the reactivity–selectivity principle (RSP)[27] or a simple Hammond effect.[28] However, in view of the controversy surrounding the RSP,[27,29] no fundamental importance can be attached to the fact that our reactions adhere to it. Furthermore, as discussed below, the substituent effect in the deprotonation of nitroalkanes seems to go in the opposite direction, violating the RSP. Hence an interpretation of p_{xy} based on an analysis of substituent-induced transition-state changes provides more insights. Such an analysis can be based on the diagram in Figure 2.

We shall make the common assumption that β_B is not only a measure of positive charge development on the base but also an approximate measure of progress along the horizontal axis (proton transfer). Unlike β_B, α_{CH}, which is a measure of negative charge development in the benzene ring, is not a measure of the degree of proton transfer, even though it must of course include a proton-transfer component. For simplicity we shall ignore this proton-transfer component and make the crude approximation that α_{CH} simply measures progress along the vertical axis, with α_{CH} increasing from bottom to top.

The following predictions can thus be made. An increase in amine basicity has the effect of stabilizing the right-hand edge of the diagram. This induces a parallel shift of the transition state toward the lower left corner (arrow 1) and a perpendicular shift toward the lower right corner (arrow 2). The net result (arrow 3) is a transition state with a closer resemblance to the intermediate in the lower right corner and thus α_{CH} should be reduced, as observed.

The change from **2**-NO_2 to **2**-$(NO_2)_2$ has the effect of strongly stabilizing the intermediate in the upper right corner and of somewhat stabilizing the one in the lower right corner. This generates the shifts of unequal magnitude indicated by arrows 4 and 5, with the net result shown by arrow 6. Thus, the transition state moves in the direction of less proton transfer, with a reduced β_B; this is consistent with experimental observation.[30]

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[23] Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7948.

[24] Bordwell[19] has suggested that for the nitroalkanes this is not a hypothetical but an actual intermediate.

[25] One of the problems with the diagrams of Figures 2 and 3 is that the upper left corner is undefined. We also cannot be sure whether there is a significant barrier along the right edge.

[26] For more on the substituent dependence of intrinsic barriers, see ref 18.

[27] For a recent review, see: Pross, A. *Adv. Phys. Org. Chem.* **1977**, *14*, 69.

[28] Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

[29] See for example: (a) Johnson, C. D. *Chem. Rev.* **1975**, *75*, 755. (b) McLennan, D. J. *Tetrahedron* **1978**, *34*, 2331. (c) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 3288. (d) Buncel, E., Chuaqui, C.; Wilson, H. *J. Org. Chem.* **1980**, *45*, 3621. (e) Bordwell, F. G.; Hughes, D. L. *Ibid.* **1980**, *45*, 3314. (f) Arnett, E. M.; Reich, R. *J. Am. chem. Soc.* **1980**, *102*, 5892.

It is of interest to compare our results with those for the C–H acids in Table V. For $ArCH_2NO_2$ and $ArCH_2CH(COMe)COOEt$ not enough data suitable to calculate p_{xy} are available, but for $ArCH(CH_3)NO_2$ Bordwell et al.[19] report $\alpha_{CH} = 0.94 \pm 0.02$ with morpholine and $\alpha_{CH} = 0.99 \pm 0.03$ with piperidine as the base. Thus one calculates $p_{xy} = -\partial\alpha_{CH}/\partial pK_a^{BH} = -0.022 \pm 0.022$. The change in α_{CH} should be matched by a corresponding increase in β_B with increasing C–H acidity, but the experimental uncertainty in β_B is higher than the observed changes in β_B.[19]

The p_{xy} value of -0.022 ± 0.022 is seen to be smaller in absolute magnitude and probably of different sign (possibly $p_{xy} = 0$ within experimental error) than $p_{xy} = 0.053$ for the (nitrophenyl)acetonitriles. A change in sign may be qualitatively understandable in terms of Figure 3. We again assume that β_B is related to progress along the horizontal axis and α_{CH} to the progress along the vertical axis. However, here the effect of the substituent in the phenyl group is most strongly felt near the lower right corner of the diagram so that progress along the vertical axis toward the upper right corner must be associated with a *decrease* in α_{CH}. Hence, an increase in amine basicity will lead to the same shifts as in Figure 2 (arrow 1 for parallel, arrow 2 for perpendicular, and arrow 3 for overall shift), but the result is an *increase* in α_{CH}, as observed.

Introduction of a more electron-withdrawing phenyl substituent will have the effect of strongly stabilizing the lower right corner intermediate and of somewhat stabilizing the upper right corner one. This will produce a small parallel shift (arrow 4) and a large perpendicular shift (arrow 5), with the net motion (arrow 6) indicating more proton transfer in the transition state. As mentioned above, the experimental uncertainties in β_B do not allow confirmation of these expectations.[30]

Irrespective of the fine details it seems clear from the above considerations that, just as with the different signs in the imbalances (*I* values in Table V), the different signs for p_{xy} (or the drastically smaller value for $ArCH(CH_3)NO_2$ if $p_{xy} \approx 0$) are simply a consequence of the different locations of the substituents with respect to the site of negative charge development in the two types of C–H acids. The rather large absolute magnitude of p_{xy} for the (nitrophenyl)acetonitriles is probably related to the fact that the substituent is very close to the site of negative charge development in the product anion. Different curvatures of the respective energy surfaces[23] on which we have no information may be a contributing factor to the large p_{xy} value, as well as the fact that the representations in Figures 2 and 3 are oversimplifications of a much more complex situation.

Bell's Recent Central-Force Model. After submission of this paper we became aware of recent theoretical considerations by Bell[31] that relate to the observed inequalities between β_B and α_{CH}. According to his proposed "central-force model" β_B should always be smaller than α_{CH}, as is frequently observed (see, e.g., first two entries in Table V). Our observations with **2**-NO_2 and **2**-$(NO_2)_2$ show, however, that β_B can be larger than α_{CH}, indicating that Bell's model cannot be general.

Experimental Section

Materials. (4-Nitrophenyl)acetonitrile (**2**-NO_2) was available from Eastman, mp 151–152 °C after recrystallization from ethanol. (2,4-Dinitrophenyl)acetonitrile (**2**-$(NO_2)_2$ was prepared by the method of Fairbourne and Fawson,[32] mp 88–89 °C after recrystallization from carbon tetrachloride (lit.[32] mp 89 °C). The amines were purified as described previously.[33] Chloroacetic acid was recrystallized from hexane. Reagent grade Me_2SO was stored over 4-Å molecular sieves prior to use. All other chemicals were reagent grade and were used without further purification.

Rate, pH, and pK_a Measurements. We followed the procedures described earlier.[13]

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Registry No. 2-$(NO_2)_2$, 57746-44-8; **2**-NO_2, 555-21-5; OH^-, 14280-30-9; *n*-$BuNH_2$, 109·73-9; $MeOCH_2CH_2NH_2$, 109-85-3; $Me_2AsO_2^-$, 15132-04-4; AcO^-, 71-50-1; $HCOO^-$, 71-47-6; $ClCH_2COO^-$, 14526-03-5; H_2O, 7732-18-5; piperidine, 110-89-4; morpholine, 110-91-8.

Supplementary Material Available: Pseudo-first-order rate constants for ionization of **2**-$(NO_2)_2$ and **2**-NO_2, Tables S1 and S2 (3 pages). Ordering information is given on any current masthead page.

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(30) It needs to be stressed again that these diagrams should be taken with a grain of salt and that they only serve to qualitatively visualize the effect of substituent changes on the transition state. For example, the exact direction and degree of the shifts depend of course on the curvatures of the surface and the direction of the reaction coordinate, etc.[23]

(31) Bell, R. P. *J. Chem. Soc. Faraday Trans 1* **1982**, *78*, 2593.

(32) Fairbourne, A.; Fawson, H. R. *J. Chem. Soc.* **1927**, 46.

(33) Bernasconi, C. F.; Carré, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 2698.