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changes are accompanied by a general reduction in the relative number of observed anti interactions. Thus, the slight overall dominance of syn geometry arises from steric repulsion in the anti position. In the absence of steric hindrance, syn H-bonds are not significantly preferred.

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Supplementary Material Available: Listings of references to all crystal structures retrieved from the CSD, graphs showing the α(O$\cdots$H–D) distribution for the 876 H-bonds used in the survey, φ distributions for all carboxylate categories, and listings of H-bond geometries for interactions shown in Figure 4 (16 pages). Ordering information is given on any current masthead page.

Kinetics of Deprotonation of Arylnitromethanes by Benzoate Ions in Acetonitrile Solution. Effect of Equilibrium and Nonequilibrium Transition-State Solvation on Intrinsic Rate Constants of Proton Transfers

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Abstract: Second-order rate constants for benzoate ion promoted deprotonation reactions of (3-nitrophenyl)nitromethane, (4-nitrophenyl)nitromethane, and (3,5-dinitrophenyl)nitromethane have been determined in acetonitrile solution at 25 °C. These data were obtained at low benzoate buffer concentrations (<0.01 M), utilizing tetraethylammonium benzoate salts, and benzoate ion concentrations corrected for homoconjugation with data previously reported by Kolthoff and Chantooni. Acidity constants in acetonitrile have also been determined: (3-nitrophenyl)nitromethane, $pK_a = 21.7$; (4-nitromethyl)nitromethane, $pK_a = 20.6$; and (3,5-dinitrophenyl)nitromethane, $pK_a = 19.8$. A Brønsted β_B value of 0.56 and an α_{CH} value of 0.79 have been calculated for the benzoate, 3-bromobenzoate, and 4-nitrobenzoate ion promoted reactions of (3,5-dinitrophenyl)nitromethane and for the benzoate ion promoted reactions of (3-nitrophenyl)nitromethane and (3,5-dinitrophenyl)nitromethane, respectively; (4-nitrophenyl)nitromethane deviates negatively from the Brønsted plot due to the resonance effect of the 4-nitro group. The logarithms of the ***intrinsic*** rate constants for benzoate promoted deprotonations of (3-nitrophenyl)nitromethane, (4-nitrophenyl)nitromethane, and (3,5-dinitrophenyl)nitromethane are 4.81, 4.58, and 5.27, respectively, and these values are 1.43, 1.70, and 1.30 log units, respectively, higher in acetonitrile than in dimethyl sulfoxide. Transfer activity coefficients from dimethyl sulfoxide (D) to acetonitrile (A) solution, log ${}^{D}\gamma^{A}$, for (3-nitrophenyl)nitromethyl anion (0.28), (4-nitrophenyl)nitromethyl anion (0.56), (3-nitrophenyl)nitromethane (0.18), and (4-nitrophenyl)nitromethane (0.16) have been calculated, and log ${}^{D}\gamma^{A}$ for benzoic acid (~1.9) and the benzoate ion (~0.25) have been estimated. The solvent effects on the intrinsic rate constants are analyzed within the framework of the Principle of Nonperfect Synchronization (PNS) in terms of contributions by late solvation of the arylnitromethyl anion, late solvation of the benzoic acid (produced as a product of the reaction), early desolvation of the benzoate ion and the arylnitromethane, and by a classical solvent effect. The results are also compared with predictions by a theoretical model recently proposed by Kurz. For the comparison of intrinsic rate constants in water and dimethyl sulfoxide there is good agreement between the Kurz model and the experimental results as well as the PNS analysis, but there is a discrepancy between the results and the predictions of the Kurz model for the comparison of intrinsic rate constants in dimethyl sulfoxide and acetonitrile solutions.

Studies of the effects of solvent on proton-transfer reactions of carbon acids have helped clarify the factors that contribute to the relatively high energy barriers in these reactions[2] compared to proton transfers of oxygen and nitrogen acids.[3] One important factor appears to be nonperfect synchronization,[4] or imbalance,[5] in the transition state with respect to the extent to which proton transfer, the delocalization of negative charge, and solvent reorganization have progressed. These imbalances can be described by structure–reactivity parameters, such as Brønsted β and α values, and differences in these parameters, which can provide a measure of the extent to which the various processes have developed in the transition state.

When discussing solvent effects on proton transfers, it is particularly useful to focus on the ***intrinsic*** rate constant, k_0 (rate constant for the reaction when $\Delta G° = 0$), so as to clearly separate the kinetic from thermodynamic effects.[4] There is growing experimental evidence that the lag in the solvation of developing ions behind charge transfer (or desolvation of disappearing ions being ahead of charge transfer) increases the barrier of the reaction and hence lowers k_0. This increase in the barrier can be understood as the result of nonequilibrium solvation of the transition state caused by the asynchrony or imbalance between charge transfer and the reorganization of the solvation of that charge.[6]

The extent to which k_0 is decreased by nonequilibrium transition-state solvation depends on the solvent.[4,7] In order to further

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explore this phenomenon, we have studied benzoate ion promoted deprotonation reactions of several arylnitromethanes in acetonitrile solution. We were also interested in evaluating a recently proposed theoretical model of these reactions in which charged solutes were treated as charges inside spherical or ellipsoidal cavities within a dielectric continuum.[6a] This model predicts that for proton transfer between a neutral carbon acid and an anionic base, for which solvation of the transition is in disequilibrium, intrinsic rate constants should be larger in dimethyl sulfoxide (Me_2SO) than in acetonitrile (MeCN) solution. On the other hand, a formalism based on the Principle of Nonperfect Synchronization (PNS)[4] predicts k_0 to be larger in acetonitrile than in dimethyl sulfoxide.

Experimental Section

Melting points (uncorrected) were measured on a Thomas-Hoover melting point apparatus. ^1H NMR spectra were recorded on a Varian EM 360L or a Brucker 250-MHz spectrometer. Kinetic experiments were carried out in a Durrum-Gibson stopped-flow apparatus, and UV-vis spectra were obtained on a Perkin-Elmer Lambda-2 spectrophotometer.

Materials. MeCN was purified by fractional distillation, first from P_2O_5 and then from CaH_2, as described by Coetzee and Padmanabhan[8] (Method B). Me_2SO was purified by distillation from CaH_2 and stored over 4-Å molecular sieves. Tetraethylammonium benzoate, 3-bromobenzoate, and 4-nitrobenzoate were prepared as described by Kolthoff and Chantooni,[9] these salts were dried at 65 °C over P_2O_5 in vacuo for 24 h and then stored over P_2O_5 in a desiccator. The purity of the benzoate salts (98.4%, 98.0%, and 99.4% for benzoate, 3-bromobenzoate, and 4-nitrobenzoate, respectively) was determined by potentiometric titration against 0.0600 M HCl in 90 vol % Me_2SO in water. Two of the substrates employed in this work, (4-nitrophenyl)nitromethane and (3-nitrophenyl)nitromethane, were available from previous studies in this laboratory,[10] whereas (3,5-dinitrophenyl)nitromethane was synthesized from 3,5-dinitrobenzyl bromide as described below.

3,5-Dinitrobenzyl Bromide. This compound was synthesized by adding 0.050 mol of 3,5-dinitrobenzyl alcohol to 0.13 mol of $ZnBr_2$ dissolved in 50 mL of 48% HBr. After the alcohol had dissolved, HBr was bubbled through the solution until the product precipitated out (ca. 7 h). The product was recrystallized from ethanol: mp 92–93.5 °C (lit.[11] 65–66 °C); ^1H NMR ($CDCl_3$) δ 4.50 (s, 2 H), 8.38 (s, 2 H), 8.73 (br s, 1 H).

(3,5-Dinitrophenyl)nitromethane. This compound was made from 3,5-dinitrobenzyl bromide following the procedure described by Kornblum et al.[12] for the preparation of (4-nitrophenyl)nitromethane. The product was purified by column chromatography on silica using methylene chloride as the eluting solvent: mp 128–130 °C (lit.[13] mp 132 °C); ^1H NMR (acetone-d_6) δ 6.12 (s, 2 H), 8.93 (s, 2 H), 9.04 (s, 1 H).

Kinetics. The kinetics were studied by spectrophotometrically following the appearance of the arylnitromethyl anions: 491 nm (ϵ 2.69 × 10^4), 349 nm (ϵ 2.19 × 10^4), and 343 nm (ϵ 1.77 × 10^4) for the anions of (4-nitrophenyl)nitromethane, (3-nitrophenyl)nitromethane, and (3,5-dinitrophenyl)nitromethane, respectively. Reactions were carried out at 25.0 °C in MeCN under pseudo-first-order conditions with excess buffer base. Plots of ln ($A_\infty - A$) against time obeyed first-order kinetics and were monitored for 2 or 3 half-lives. Buffer solutions were prepared by dissolving the buffer acid and its tetraethylammonium salt in MeCN. Because benzoate ions and their conjugate acids form homoconjugate pairs in MeCN solution[14] (eq 1), the amount of free benzoate ion in solution is calculated from reported equilibrium constants for homoconjugate pair formation[9] (4000 M^{-1} for benzoate ion and benzoic acid, 6000 M^{-1} for 3-bromobenzoate ion and 3-bromobenzoic acid, and 7000 M^{-1} for 4-nitrobenzoate ion and 4-nitrobenzoic acid). Because the fraction

$$\mathrm{Ar'COOH + Ar'COO^- \rightleftarrows Ar'COOH{-}^-OOCAr'} \qquad (1)$$

of free base in these solutions is large, the error in the calculated concentration of the benzoate ion due to errors in the magnitude of the homoconjugation constant is small and does not significantly change the second-order rate constants. All glassware was dried overnight in an oven at 120 °C and allowed to cool in desiccators. Initially, weighings and transfers were made under dry N_2 in a glove-bag. It was later determined, however, that working in a glove-bag was unnecessary; rate constants and equilibrium constants measured in this way agreed well with values measured when operations were made on the bench outside the glove-bag. In larger amounts, however, water has a significant effect on the rates of reaction. For example, for reactions of (4-nitrophenyl)nitromethane promoted by 0.000 616 M benzoate ion, k_{obsd} decreases from 70.5 (in the absence of added water) to 49.5 (0.10% added water) to 35.4 s^{-1} (0.2% added water). Similarly, k_{obsd} decreases from 163 to 97 to 76 s^{-1} for the reaction of (3-nitrophenyl)nitromethane promoted by 0.001 27 M benzoate ion in the absence of added water and in the presence of 0.17% and ca. 1.0% water, respectively.

Equilibrium Constants. Acidity constants for the arylnitromethanes in MeCN were determined spectrophotometrically relative to benzoic acid.[9] Neither the substrate nor the benzoate buffer absorbs at the wavelengths of maximum absorbance of the arylnitromethyl anions. Equilibrium acidity constants were determined in benzoate buffer solutions with buffer ratios ($PhCOOH/PhCOO^-$, corrected for homoconjugation) ranging from 4.76 to 0.455 for (4-nitrophenyl)nitromethane (pK_a^{CH} 20.6), from 0.547 to 0.0132 for (3-nitrophenyl)nitromethane (pK_a^{CH} 21.7), and from 31.5 to 2.37 for (3,5-dinitrophenyl)nitromethane (pK_a^{CH} 19.8). The pK_a^{CH} values were evaluated using the equation $K_a^{CH} = K_a^{BH}\{[C^-]/[CH]\}\{[BH]/[B^-]\}$, where K_a^{CH} is the acid dissociation constant of the arylnitromethane, K_a^{BH} is the acid dissociation constant of benzoic acid in MeCN (2.0×10^{-21}),[9] and $\{[C^-]/[CH]\}$ and $\{[BH]/[B^-]\}$ are the arylnitromethyl anion/arylnitromethane and benzoic acid/benzoate buffer ratios, respectively. The data are summarized in Tables S1–S3 of the supplementary material.[15] It was noted that the wavelengths of maximum absorbance of the arylnitromethyl anions were shifted to shorter wavelengths in the presence of added water. For example, for the (4-nitrophenyl)nitromethyl anion at low water concentrations (ca. <1%), $\lambda_{max} = \lambda_0 - 21.5W$, where λ_{max}, λ_0, and W are the wavelengths of maximum absorbance in the presence and absence of added water and the percentage of added water (w/w), respectively; this expression was not evaluated for water concentrations greater than 1%.

Transfer Activity Coefficients. The transfer activity coefficients of (3-nitrophenyl)nitromethyl and (4-nitrophenyl)nitromethyl anions from Me_2SO (D) to MeCN (A) solutions were calculated using the expression $\log {}^D\gamma^A_{C^-} = {}^D\Delta^A pK_a^{CH} - \log {}^D\gamma^A_{H^+} + \log {}^D\gamma^A_{CH}$, where ${}^D\Delta^A pK_a$ is the difference in pK_a^{CH} of the arylnitromethane in MeCN relative to Me_2SO and ${}^D\gamma^A$ is the transfer activity coefficient of the arylnitromethyl anion (C^-), the lyonium ion (H^+), and arylnitromethane (CH), respectively. The transfer activity coefficients of the arylnitromethanes were determined from the solubilities of the corresponding conjugate acids, as described by Kolthoff.[16] The solubilities were measured by saturating approximately 1 mL of MeCN or Me_2SO in a 1.00-mL volumetric flask with the arylnitromethane. The saturated solution was kept in a shaker bath at 25.0 °C for 24 h. This solution was then diluted twice: first 10 μL was added to 2.00 mL of MeCN, and then 10 μL of the diluted solution was added to 3.00 mL of MeCN in a cuvette. These dilutions resulted in a solution that gave rise to measurable absorbance values (for (4-nitrophenyl)nitromethane and (3-nitrophenyl)nitromethane in acetonitrile, λ_{max} = 261 and 258 nm and ϵ = 1.10 × 10^4 and 0.770 × 10^4, respectively). The solubilities were then calculated from the known molar absorptivity constants and dilution factors. For (3-nitrophenyl)nitromethane they are 2.36 and 3.56 M in MeCN and Me_2SO, respectively, and for (4-nitrophenyl)nitromethane 2.25 and 3.24 M in MeCN and Me_2SO, respectively.

Results

The deprotonation of an arylnitromethane by a benzoate ion can be described by eq 2:

$$\mathrm{ArCH_2NO_2 + Ar'COO^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ArCH{=}NO_2^- + ArCOOH} \qquad (2)$$

Under pseudo-first-order conditions (with $ArCH_2NO_2$ being the minor component), k_{obsd} is given by

$$k_{obsd} = k_1[B^-] + k_{-1}[BH] \qquad (3)$$

with $B^- = Ar'COO^-$ and $BH = Ar'COOH$. k_{obsd} values determined as a function of $[B^-]$ at various $[BH]/[B^-]$ ratios are

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Table I. Rate and Equilibrium Constants for Proton Transfer between Arylnitromethanes and Benzoate Ions in Acetonitrile Solution at 25 °C

CH (pK_a^{CH})[a]	B^- (pK_a^{BH})[b]	K_1	10^{-4} k_1, M^{-1} s^{-1}	$10^{-4}k_{-1}$, M^{-1} s^{-1}
$3\text{-}NO_2C_6H_4CH_2NO_2$ (21.7)	$C_6H_5COO^-$ (20.7)	0.10	2.40	24.0
$4\text{-}NO_2C_6H_4CH_2NO_2$ (20.6)	$C_6H_5COO^-$ (20.7)	1.26	9.60	7.62
$3,5\text{-}(NO_2)_2C_6H_3CH_2NO_2$ (19.8)	$C_6H_5COO^-$ (20.7)	7.94	77.0	9.70
$3,5\text{-}(NO_2)_2C_6H_3CH_2NO_2$ (19.8)	$3\text{-}BrC_6H_4COO^-$ (19.5)	0.50	19.2	38.4
$3,5\text{-}(NO_2)_2C_6H_3CH_2NO_2$ (19.8)	$4\text{-}NO_2C_6H_4COO^-$ (18.7)	0.079	5.90	74.3

[a] The pK_a^{CH} values were evaluated using the equation, $K_a^{CH} = K_a^{BH}\{[C^-]/[CH]\}\{[BH]/[B^-]\}$, where K_a^{CH} is the acid dissociation constant of the arylnitromethane, K_a^{BH} is the acid dissociation constant of benzoic acid (2×10^{-21}) (ref 8), and $\{[C^-]/[CH]\}$ and $\{[BH]/[B^-]\}$ are the arylnitromethyl anion/arylnitromethane and benzoic acid/benzoate ion buffer ratios, respectively. [b] Reference 9.

Table II. Transfer Activity Coefficients for (3-Nitrophenyl)nitromethane and (4-Nitrophenyl)nitromethane and Their Anions at 25 °C[a]

	$\log {}^D\gamma^A(CH)$	$\log {}^D\gamma^A(C^-)$
$3\text{-}NO_2C_6H_4CH_2NO_2$	0.18	0.28
$4\text{-}NO_2C_6H_4CH_2NO_2$	0.16	0.56

[a] D = dimethyl sulfoxide, A = acetonitrile.

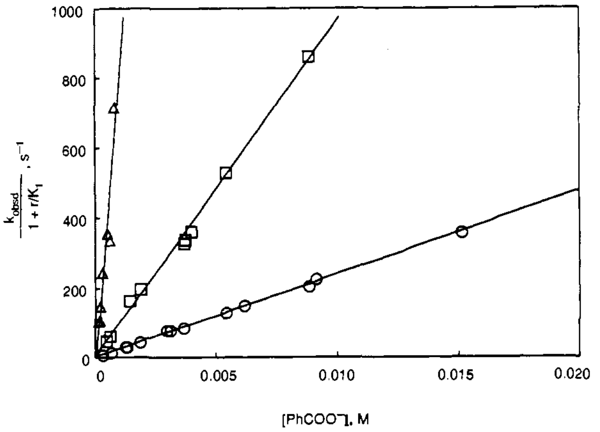

Figure 1. Plots according to eq 4 versus free benzoate ion concentration for the deprotonation of (3-nitrophenyl)nitromethane (○), (4-nitrophenyl)nitromethane (□), and (3,5-dinitrophenyl)nitromethane (△) in acetonitrile solution at 25 °C.

reported in Tables S4–S8 of the supplementary material.[15] Equation 3 may be rearranged to

$$\frac{k_{obsd}}{(1 + r/K_1)} = k_1[B^-] \tag{4}$$

where $r = [BH]/[B^-]$ and $K_1 = k_1/k_{-1} = K_a^{CH}/K_a^{BH}$. A plot of the left-hand side of eq 4 should provide a straight line of slope k_1.

Figure 1 shows plots according to eq 4 for the deprotonation of (3-nitrophenyl)nitromethane, (4-nitrophenyl)nitromethane, and (3,5-dinitrophenyl)nitromethane by benzoate ion. Similar plots, not shown, were obtained for the reactions of (3,5-dinitrophenyl)nitromethane with the 3-bromobenzoate and 4-nitrobenzoate ions. The rate constants, k_1 and k_{-1}, as well as the pK_a^{CH}, pK_a^{BH}, and K_1 values are summarized in Table I.

Transfer activity coefficients for (3-nitrophenyl)nitromethane and (4-nitrophenyl)nitromethane and their respective anions are reported in Table II. Note that a positive value $\log {}^D\gamma^A$ means that the species is less solvated in MeCN than in Me_2SO, and a negative value means the opposite. The transfer activity coefficients for the nitronate ions were calculated as described in the Experimental Section, using values of $\log {}^D\gamma_{H^+}^A = 11.4$,[17] ${}^D\Delta^A pK_a^{CH} = 11.5$[18] for (3-nitrophenyl)nitromethane and 11.8[18] for (4-nitrophenyl)nitromethane; ${}^D\gamma_{CH}^A$ values for the nitroalkanes were determined from solubility measurements as described in the Experimental Section.

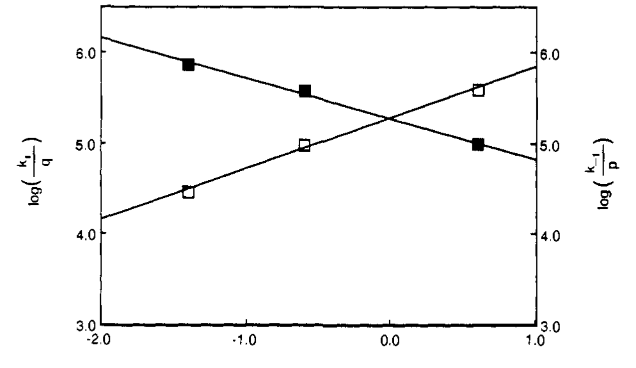

Figure 2. Brønsted type plots for the reaction of (3,5-dinitrophenyl)nitromethane with the benzoate, 3-nitrobenzoate, and 4-nitrobenzoate ions in acetonitrile solution at 25 °C: □, k_1/q; ■, k_{-1}/p.

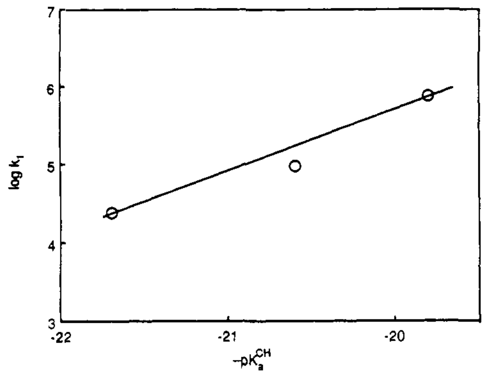

Figure 3. Brønsted plot for the deprotonation of arylnitromethanes by benzoate ion in acetonitrile solution at 25 °C.

Discussion

Qualitative Considerations. Figure 2 shows a Brønsted type plot of $\log(k_1/q)$ and $\log(k_{-1}/p)$ vs $pK_a^{BH} - pK_a^{CH} + \log(p/q)$ for the reactions of (3,5-dinitrophenyl)nitromethane with the benzoate, 3-bromobenzoate, and 4-nitrobenzoate ions; p and q are the usual statistical factors.[20] The slopes yield $\beta_B = 0.56 \pm 0.03$ and $\alpha_{BH} = 0.44 \pm 0.03$, respectively, while the point of intersection at $pK_a^{BH} - pK_a^{CH} + \log(p/q) = 0$ affords $\log k_0 = 5.27 \pm 0.03$ for the intrinsic rate constant (k_0 in units of M^{-1} s^{-1}). Figure 3 shows a Brønsted plot in which the acidity of the substrate is varied rather than that of the base. The plot represents data for the benzoate ion promoted deprotonations of (3-nitrophenyl)nitromethane, (4-nitrophenyl)nitromethane, and (3,5-dinitrophenyl)nitromethane. The plot is not very linear, and a least-squares line through the three points (not shown) yields a slope, α_{CH}, of 0.78 ± 0.16.

The most reasonable interpretation of the nonlinearity is that the point for (4-nitrophenyl)nitromethane deviates negatively by about 0.3 log unit from the line defined by the other two points, the slope of which (0.79) will be taken as α_{CH}. Similar or larger negative deviations of the 4-nitro derivative from Brønsted plots have been reported for the deprotonation of arylnitromethanes

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Table III. Brønsted Coefficients and Intrinsic Rate Constants for Deprotonation Reactions of Arylnitromethanes in Water, Dimethyl Sulfoxide, and Acetonitrile Solutions at 25 °C

reaction	β_B	α_{CH}	$\log k_0$ (Ar)[k]
	Water		
$ArCH_2NO_2 + RCOO^-$ [a,b]	0.54[c]		−2.10 (C_6H_5)
$ArCH_2NO_2 + R_2NH$ [d,e]	0.55[f]	1.29	−1.22 (C_6H_5)[a,b]
$ArCH_2NO_2 + OH^-$ [d]		1.54	
	Me_2SO		
$ArCH_2NO_2 + Ar'COO^-$ [g]	0.55[c,h]	0.92	2.66 (C_6H_5) 3.38 (3-$NO_2C_6H_4$) 2.88 (4-$NO_2C_6H_4$) 3.97 (3,5-$(NO_2)_2C_6H_3$)
	CH_3CN		
$ArCH_2NO_2 + Ar'COO^-$ [i]	0.56[i,j]	0.79	~4.35 (C_6H_5)[l] 4.81 (3-$NO_2C_6H_4$) 4.58 (4-$NO_2C_6H_4$) 5.27 (3,5-$(NO_2)_2C_6H_3$)

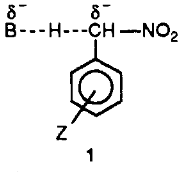
[a] Reference 7c. [b] 20 °C. [c] β_B determined for Ar = Ph. [d] Reference 23. [e] R_2NH = piperidine, morpholine, and piperazine. [f] β_B determined for $PhCH(CH_3)NO_2$. [g] Reference 19. [h] Keeffe, J. R. Personal communication. [i] This work. [j] β_B obtained for (3,5-dinitrophenyl)nitromethane. [k] $\log k_0$ was calculated as $\log (k_1/q) - \beta_B(pK_a^{BH} - pK_a^{CH} + \log (p/q))$. [l] Calculated from eq 6; see text.

by benzoate ion in Me_2SO[19] (−1.1 log units) and by HO^- in water (−0.4 log unit).[21] These negative deviations have been attributed to the resonance stabilization of the nitronate ion by the 4-nitro group, whose development lags behind proton transfer at the transition state, thereby lowering the intrinsic rate constant.[4,22]

It is instructive to compare the Brønsted parameters and the intrinsic rate constants determined in MeCN solution with the corresponding quantities in water and in Me_2SO solution (Table III). The following points are noteworthy.

(1) The β_B value for the deprotonation of $ArCH_2NO_2$ by carboxylate ions is the same in the three solvents. Even though the various β_B values are not strictly comparable since in MeCN β_B refers to the deprotonation of (3,5-dinitrophenyl)nitromethane while in water and Me_2SO it refers to the deprotonation of phenylnitromethane, Bordwell and Boyle[23] have shown that β_B is virtually independent of the phenyl substituent and, hence, the comparison of the β_B values is justified. The similarity of the β_B values even holds when the bases are changed from carboxylate ions to amines, at least in water.[7c]

(2) In contrast to β_B, the α_{CH} values display a strong solvent dependence. No α_{CH} value has been determined for the deprotonation of $ArCH_2NO_2$ by carboxylate ions in water but, on the basis of the α_{CH} values for the deprotonation of $ArCH_2NO_2$ by amines (1.29)[23] and by HO^- (1.54),[23] it is safe to assume that α_{CH} for carboxylate ions would also be >1 and probably somewhere between 1.29 and 1.54. These large α_{CH} values have been attributed to an imbalanced transition state (**1**) in which delocalization of the negative charge into the nitro group and concomitant solvation, two factors that provide major stabilization of the product ion (**2**), lag behind charge or proton transfer.[4,22-24] Note that for the reaction in the reverse direction such a transition state implies that the loss of solvation and resonance stabilization of **2** is ahead of charge or proton transfer.



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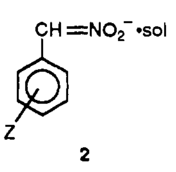

2

The imbalance, the extent of which is usually expressed in terms of $\alpha_{CH} - \beta_B$, is particularly large in aqueous solution because the hydrogen bonding solvation minimizes the need for internal stabilization of the nitronate ion and leads to a small substituent effect on the equilibrium acidity. This contrasts with the transition state whose charge is largely localized on carbon, relatively poorly solvated, and hence strongly dependent on internal stabilization, which results in a large substituent effect on the *rate* of deprotonation. The drastic reduction of α_{CH} and, with it, the reduction of the imbalance in the dipolar aprotic solvents are best understood if α_{CH} is expressed as the ratio of Hammett ρ values, i.e., $\alpha_{CH} = \rho(k_1)/\rho(K_1)$, and the solvent effect on $\rho(k_1)$ and $\rho(K_1)$ is evaluated separately. For the reaction of $ArCH_2NO_2$ with OH^- in water, $\rho(k_1) = 1.26$ and $\rho(K_1) = 0.83$.[23] For the reactions of $ArCH_2NO_2$ with $PhCOO^-$ in Me_2SO, $\rho(k_1) = 2.21$ and $\rho(K_1) = 2.40$,[25] whereas in MeCN $\rho(k_1) = 2.12$ and $\rho(K_1) = 2.68$ (based on 3-NO_2 and 3,5-$(NO_2)_2$). Both $\rho(k_1)$ and $\rho(K_1)$ are seen to increase significantly when changing from water to the dipolar aprotic solvents, but the increase in $\rho(K_1)$ is much larger than that for $\rho(k_1)$, which results in a lower α_{CH}. The large increase in $\rho(K_1)$ is largely a consequence of the loss of hydrogen bonding solvation of the nitronate ion, which strongly increases the need for internal stabilization and leads to a large substituent effect on K_1. On the other hand, since the transition state is relatively poorly solvated even in water, the change to a solvent with less solvating power has a relatively minor effect on transition-state stability and, hence, $\rho(k_1)$ increases less strongly than $\rho(K_1)$.

In comparing MeCN with Me_2SO, we note that the α_{CH} value in the former solvent (0.79) is somewhat lower than in the latter (0.92). This difference is consistent with MeCN solvating the nitronate ion somewhat less than Me_2SO, as shown by the positive values of $\log {}^{D}\gamma_{C^-}^{A}$ reported in Table II; the fact that $\rho(K_1)$ in MeCN (2.68) is slightly higher than in Me_2SO (2.40) is a further indication of this phenomenon.

(3) The intrinsic rate constant is enhanced dramatically when the solvent is changed from water to Me_2SO or MeCN. For the reaction of $PhCH_2NO_2$ with carboxylate ions, $\log k_0$ increases by 4.76 units from water to Me_2SO and by ~6.45 units from water to acetonitrile. These increases parallel the reduction in the imbalances and can be understood in the context of the PNS.[4,22] According to the PNS, a product stabilizing factor—in our example solvation of the nitronate ion—will lower k_0 if its development at the transition state lags behind charge transfer. This lowering of $\log k_0$ is proportional to the amount of product stabilization and the solvational disequilibrium or the lag, as formulated in eq 5. Product stabilization is expressed as $\delta \log K_1^{sol}(C^-)$, which represents the increase in $\log K_1$ brought about by the solvation of the nitronate ion, while the solvational disequilibrium is expressed as $\lambda_{sol}^{C^-} - \beta_B$, with $\lambda_{sol}^{C^-}$ being the progress in nitronate ion solvation and β_B taken to be a measure of charge transfer at the transition state.[5c,26,27] Since $\delta \log K_1^{sol}(C^-) > 0$, we have $\delta \log k_0^{sol}(C^-) < 0$ for solvation that lags behind charge transfer ($\lambda_{sol}^{C^-} - \beta_B < 0$). It thus follows from eq 5 that a change to a less solvating medium that reduces $\delta \log K_1^{sol}(C^-)$ will make $\delta \log k_0^{sol}(C^-)$ less negative and result in a higher k_0.

$$\delta \log k_0^{sol}(C^-) = (\lambda_{sol}^{C^-} - \beta_B)\delta \log K_1^{sol}(C^-) \tag{5}$$

The intrinsic rate constants are also seen to depend on the phenyl substituent, with $\log k_0$ showing an increase with increasing electron-withdrawing strength of the substituent. For Z substituents that do not contribute a resonance effect to the stabilization of the nitronate ion, the change in $\log k_0$ can be expressed as

$$\log k_0(Z) - \log k_0(H) = (\alpha_{CH} - \beta_B)(pK_a^{CH}(H) - pK_a^{CH}(Z)) \tag{6}$$

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(21) Analysis[22] of data by Bordwell and Boyle.[23]

(22) Bernasconi, C. F. *Adv. Phys. Org. Chem.* **1992**, *27*, 119.

(23) Bordwell, F. G.; Boyle, W. J., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 3907.

(24) Kresge, A. J. *Can. J. Chem.* **1974**, *52*, 1897.

(25) Based on data by Keeffe et al.[19] and omitting 4-NO_2 and 4-CN from the correlation.

(26) (a) Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*; Wiley: New York, 1963; p 156. (b) Kresge, A. J. In *Proton Transfer Reactions*; Caldin, E. F., Gold, V., Eds.; Wiley: New York, 1975; p 179.

(27) The notion that β_B is a measure of charge transfer has also been challenged: (a) Bordwell, F. G.; Hughes, D. L. *J. Am. Chem. Soc.* **1985**, *107*, 4737. (b) Pross, A.; Shaik, S. S. *New J. Chem.* **1989**, *13*, 427.

where H refers to the unsubstituted and Z to the substituted phenylnitromethane. As has been discussed elsewhere,[4,22] this substituent dependence of log k_0 does not reflect any special effect of the substituent but is a consequence of the imbalance, a phenomenon caused by the lag in resonance development in the α-nitro group and its concomitant solvation rather than by Z. The log k_0 value reported in Table III for the reaction of phenylnitromethane with benzoate ion was calculated from log k_0 for the reaction of (3-nitrophenyl)nitromethane with benzoate ion by means of eq 6.

For Z substituents that do contribute to the resonance stabilization of the nitronate ion (4-nitro), the increase in log k_0 that stems from the inductive effect (eq 6) is somewhat counteracted by the resonance effect, which leads to the negative deviation from the Brønsted plot (Figure 3) discussed earlier. As seen in Table III, log k_0 for (4-nitrophenyl)nitromethane (4.58) in MeCN is lower than for (3-nitrophenyl)nitromethane (4.81) but still higher than for the parent phenylnitromethane (~4.35); a similar situation is seen in Me_2SO solution.

Quantitative Analysis of Solvent Effects. A. PNS Approach. The contribution of nonequilibrium transition-state solvation to the solvent dependence of k_0 can be found from the difference in δ log $k_0^{\mathrm{sol}}(\mathrm{C}^-)$ (eq 5) for the two solvents. According to eq 5, this contribution, which we shall call δ_{C^-}, is given by

$$\delta_{\mathrm{C}^-} = \delta \log k_0^{\mathrm{sol}}(\mathrm{C}^-)_{\mathrm{II}} - \delta \log k_0^{\mathrm{sol}}(\mathrm{C}^-)_{\mathrm{I}} = (\lambda_{\mathrm{sol}}^{\mathrm{C}^-} - \beta_{\mathrm{B}})_{\mathrm{II}}\delta \log K_1^{\mathrm{sol}}(\mathrm{C}^-)_{\mathrm{II}} - (\lambda_{\mathrm{sol}}^{\mathrm{C}^-} - \beta_{\mathrm{B}})_{\mathrm{I}}\delta \log K_1^{\mathrm{sol}}(\mathrm{C}^-)_{\mathrm{I}} \quad (7)$$

where I and II refer to two different solvents, e.g., I = water, II = Me_2SO or acetonitrile. If we approximate $(\lambda_{\mathrm{sol}}^{\mathrm{C}^-} - \beta_{\mathrm{B}})_{\mathrm{I}} \approx (\lambda_{\mathrm{sol}}^{\mathrm{C}^-} - \beta_{\mathrm{B}})_{\mathrm{II}} \approx (\lambda_{\mathrm{sol}}^{\mathrm{C}^-} - \beta)$, eq 7 simplifies to

$$\delta_{\mathrm{C}^-} = (\lambda_{\mathrm{sol}}^{\mathrm{C}^-} - \beta_{\mathrm{B}})(-\log {}^{\mathrm{I}}\gamma_{\mathrm{C}^-}^{\mathrm{II}}) \quad (8)$$

where

$$-\log {}^{\mathrm{I}}\gamma_{\mathrm{C}^-}^{\mathrm{II}} = {}^{\mathrm{I}}\delta^{\mathrm{II}} \log K_1^{\mathrm{sol}}(\mathrm{C}^-) = \delta \log K_1^{\mathrm{sol}}(\mathrm{C}^-)_{\mathrm{II}} - \delta \log K_1^{\mathrm{sol}}(\mathrm{C}^-)_{\mathrm{I}} \quad (9)$$

with ${}^{\mathrm{I}}\gamma_{\mathrm{C}^-}^{\mathrm{II}}$ being the solvent activity coefficient for the transfer of C^- from I to II.

Even though δ_{C^-} is a major contributor to the solvent effect on k_0, it is not the only factor. PNS effects arising from late solvation of the carboxylic acid, δ_{BH}, from the early desolvation of the carboxylate ion, δ_{B^-}, and early desolvation of the carbon acid, δ_{CH}, also contribute to the solvent dependence of k_0. These terms are defined in a manner similar to δ_{C^-} and are given by eqs 10–12.[4,22]

$$\delta_{\mathrm{BH}} = (\lambda_{\mathrm{sol}}^{\mathrm{BH}} - \beta_{\mathrm{B}})(-\log {}^{\mathrm{I}}\gamma_{\mathrm{BH}}^{\mathrm{II}}) \quad (10)$$

$$\delta_{\mathrm{B}^-} = (\lambda_{\mathrm{des}}^{\mathrm{B}^-} - \beta_{\mathrm{B}}) \log {}^{\mathrm{I}}\gamma_{\mathrm{B}^-}^{\mathrm{II}} \quad (11)$$

$$\delta_{\mathrm{CH}} = (\lambda_{\mathrm{des}}^{\mathrm{CH}} - \beta_{\mathrm{B}}) \log {}^{\mathrm{I}}\gamma_{\mathrm{CH}}^{\mathrm{II}} \quad (12)$$

For the overall solvent effect on k_0, we may then write

$${}^{\mathrm{I}}\delta^{\mathrm{II}} \log k_0 = \delta_{\mathrm{C}^-} + \delta_{\mathrm{B}^-} + \delta_{\mathrm{CH}} + \delta_{\mathrm{BH}} + \delta_{\mathrm{TS(B)}} \quad (13)$$

Equation 13 contains an additional term, $\delta_{\mathrm{TS(B)}}$, which accounts for possible effects not related to the late solvation/early desolvation of the various parts of the transition state.[28] In earlier applications of eq 13,[7a,b] the $\delta_{\mathrm{TS(B)}}$ term, which was called δ_{SR} and included δ_{CH} and δ_{BH}, was believed to contain a significant contribution from a dynamic solvent effect.[6b,29] A more recent analysis[22] has led to the conclusion that $\delta_{\mathrm{TS(B)}}$ represents primarily and perhaps exclusively a "classical" solvent effect stemming from that part of the transition-state solvation that is in equilibrium with its charge distribution.[30]

Application of eq 13 requires that the various solvent activity coefficients be known and that $\lambda_{\mathrm{sol}}^{\mathrm{C}^-} - \beta_{\mathrm{B}}$, $\lambda_{\mathrm{sol}}^{\mathrm{BH}} - \beta_{\mathrm{B}}$, $\lambda_{\mathrm{des}}^{\mathrm{B}^-} - \beta_{\mathrm{B}}$, and $\lambda_{\mathrm{des}}^{\mathrm{CH}} - \beta_{\mathrm{B}}$ be estimated. An example for which this type of analysis has been feasible is the reaction of phenylnitromethane with acetate ion in water (I) and in 90% Me_2SO–10% water (II). The relevant transfer activity coefficients are log ${}^{\mathrm{I}}\gamma_{\mathrm{C}^-}^{\mathrm{II}} = 4.09$,[31] log ${}^{\mathrm{I}}\gamma_{\mathrm{CH}}^{\mathrm{II}} = -2.86$,[31] log ${}^{\mathrm{I}}\gamma_{\mathrm{B}^-}^{\mathrm{II}} = 6.50$,[32] and log ${}^{\mathrm{I}}\gamma_{\mathrm{BH}}^{\mathrm{II}} = -1.50$,[32] and the imbalances were estimated as −0.47 for $\lambda_{\mathrm{sol}}^{\mathrm{C}^-} - \beta_{\mathrm{B}}$,[22] −0.09 for $\lambda_{\mathrm{sol}}^{\mathrm{BH}} - \beta_{\mathrm{B}}$,[22] and 0.09 for $\lambda_{\mathrm{des}}^{\mathrm{B}^-} - \beta_{\mathrm{B}}$ and $\lambda_{\mathrm{des}}^{\mathrm{CH}} - \beta_{\mathrm{B}}$,[22] respectively. This leads to the following breakdown of the solvent effect: ${}^{\mathrm{I}}\delta^{\mathrm{II}}$ log $k_0 = 3.98$, $\delta_{\mathrm{C}^-} \approx 1.91$, $\delta_{\mathrm{CH}} \approx -0.26$, $\delta_{\mathrm{B}^-} \approx 0.59$, $\delta_{\mathrm{BH}} \approx -0.14$, and $\delta_{\mathrm{TS(B)}} \approx 1.88$. This analysis shows that the main contributors to the solvent effect are the PNS effects of late carbanion solvation and early carboxylate ion desolvation and the classical solvent effect ($\delta_{\mathrm{TS(B)}}$).

At the present time, not all requisite transfer activity coefficients are available that would permit the same thorough analysis for the solvent change from water to pure Me_2SO or acetonitrile; furthermore, the fact that in water the kinetic data were obtained with acetate and substituted acetate ions, whereas in Me_2SO and acetonitrile they refer to benzoate ions, introduces another uncertainty. Nevertheless, the same qualitative picture is expected as for the change from water to 90% Me_2SO–10% water, i.e., large contributions by δ_{C^-} and $\delta_{\mathrm{TS(B)}}$, a smaller but significant contribution by δ_{B^-}, and relatively minor contributions by δ_{CH} and δ_{BH}. Inasmuch as ${}^{\mathrm{I}}\delta^{\mathrm{II}}$ log k_0 for II = Me_2SO and particularly for II = acetonitrile is larger than for II = 90% Me_2SO–10% water (Table III), some or all the terms that contribute positively to ${}^{\mathrm{I}}\delta^{\mathrm{II}}$ log k_0 (δ_{C^-}, δ_{B^-}, $\delta_{\mathrm{TS(B)}}$) should be larger than for II = 90% Me_2SO–10% water.

For the comparison of k_0 in Me_2SO and MeCN, the requisite transfer activity coefficients have been determined (log ${}^{\mathrm{D}}\gamma_{\mathrm{CH}}^{\mathrm{A}}$ and log ${}^{\mathrm{D}}\gamma_{\mathrm{C}^-}^{\mathrm{A}}$, Table II) or can be estimated (log ${}^{\mathrm{D}}\gamma_{\mathrm{BH}}^{\mathrm{A}}$, log ${}^{\mathrm{D}}\gamma_{\mathrm{B}^-}^{\mathrm{A}}$) as follows. For BH = benzoic acid, log ${}^{\mathrm{D}}\gamma_{\mathrm{BH}}^{\mathrm{A}} \approx 1.9$[33] is taken as the average of the values 1.5, 1.9, 2.1, 2.3, and 1.9 that have been reported for 3,4-dimethyl-, 4-(dimethylamino)-, 4-bromo-, 4-iodo-, and 3,4-dichlorobenzoic acid, respectively;[16] for the benzoate ion, log ${}^{\mathrm{D}}\gamma_{\mathrm{B}^-}^{\mathrm{A}} \approx -0.25$ is taken as the average of the values 0.1, −0.5, −0.5, and 0.1 reported for 3,4-dimethyl-, 4-(dimethylamino)-, 4-bromo-, and 3,4-dichlorobenzoate ion, respectively.[16] Using the same estimates for $\lambda_{\mathrm{sol}}^{\mathrm{C}^-} - \beta_{\mathrm{B}}$ (−0.47), $\lambda_{\mathrm{sol}}^{\mathrm{BH}} - \beta_{\mathrm{B}}$ (−0.09), $\lambda_{\mathrm{des}}^{\mathrm{B}^-} - \beta_{\mathrm{B}}$ (0.09), and $\lambda_{\mathrm{des}}^{\mathrm{CH}} - \beta_{\mathrm{B}}$ (0.09) as before, the value δ log ${}^{\mathrm{D}}k_0^{\mathrm{A}} = 1.43$ for the reaction of (3-nitrophenyl)nitromethane breaks down into $\delta_{\mathrm{C}^-} = 0.13$, $\delta_{\mathrm{CH}} = 0.02$, $\delta_{\mathrm{B}^-} = -0.02$, $\delta_{\mathrm{BH}} = 0.17$, and $\delta_{\mathrm{TS(B)}} = 1.13$, while the value δ log ${}^{\mathrm{D}}k_0^{\mathrm{A}} = 1.70$ for the reaction of (4-nitrophenyl)nitromethane breaks down into $\delta_{\mathrm{C}^-} = 0.26$, $\delta_{\mathrm{CH}} = 0.01$, $\delta_{\mathrm{B}^-} = -0.02$, $\delta_{\mathrm{BH}} = 0.17$, and $\delta_{\mathrm{TS(B)}} = 1.28$. The major conclusion from this analysis is that nonequilibrium transition-state solvation is quite similar in the two solvents and contributes relatively little to the increase in k_0 in acetonitrile, i.e., most of the enhancement in k_0 in acetonitrile reflects the classical solvent effect on a reaction with more charge dispersion in the transition state than in the reactants and conducted in a less polar solvent.

B. The Kurz Model. Just as in the PNS approach, a major premise of the Kurz[6a] model is that nonequilibrium solvation of the transition state makes a significant contribution to the solvent effect on k_0. In defining the intrinsic barrier of a reaction, Kurz follows Marcus[34] and separates the operational or "observed" intrinsic barrier, $\Delta G_0^{\ddagger}(\mathrm{obsd}) = 2.303RT(\log (k_{\mathrm{B}}T/h) - \log k_0)$, into a work ($w_{\mathrm{R}}$) term for bringing the reactants together to form a precursor complex and the "Marcus intrinsic barrier" ($\Delta G_0^{\ddagger}(\mathrm{M})$) for the conversion of the precursor complex into a successor complex (eq 14).

$$\Delta G_0^{\ddagger}(\mathrm{obsd}) = w_{\mathrm{R}} + \Delta G_0^{\ddagger}(\mathrm{M}) \quad (14)$$

By breaking down $\Delta G_0^{\ddagger}(\mathrm{M})$ into a component for "internal terms,"

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(28) For the deprotonation of a carbon acid by an amine, the solvent effect on k_0 is given by ${}^{\mathrm{I}}\delta^{\mathrm{II}} \log k_0 = \delta_{\mathrm{C}^-} + \delta_{\mathrm{NH}^+} + \delta_{\mathrm{CH}} + \delta_{\mathrm{N}} + \delta_{\mathrm{TS(N)}}$, with $\delta_{\mathrm{NH}^+} = (\lambda_{\mathrm{sol}}^{\mathrm{NH}^+} - \beta_{\mathrm{B}})(-\log {}^{\mathrm{I}}\gamma_{\mathrm{NH}^+}^{\mathrm{II}})$ referring to late solvation of the protonated amine, $\delta_{\mathrm{N}} = (\lambda_{\mathrm{des}}^{\mathrm{N}} - \beta_{\mathrm{B}}) \log {}^{\mathrm{I}}\gamma_{\mathrm{N}}^{\mathrm{II}}$ referring to the early desolvation of the amine, and $\delta_{\mathrm{TS(N)}}$ being the counterpart of $\delta_{\mathrm{TS(B)}}$ in eq 13.[22] $\delta_{\mathrm{TS(N)}}$ and $\delta_{\mathrm{TS(B)}}$ are numerically similar but not identical.[22]

(29) Hynes, J. T. *Annu. Rev. Phys. Chem.* **1985**, *36*, 573.

(30) In the earlier analysis, the δ_{C^-} term of eq 13 was underestimated while the $\delta_{\mathrm{TS(B)}}$ term was overestimated.[22]

(31) Bernasconi, C. F.; Bunnell, R. D. *J. Am. Chem. Soc.* **1988**, *110*, 2900.

(32) Wells, C. F. *Adv. Chem. Ser.* **1979**, *177*, 53.

(33) The large log ${}^{\mathrm{D}}\gamma_{\mathrm{BH}}^{\mathrm{A}}$ value reflects the loss of hydrogen bonding of the carboxylic acid to Me_2SO when transferred to MeCN.

(34) (a) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891. (b) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

Table IV. Solvent Effect Parameters for Most Likely Cavity Sizes of Precursor Complex and Transition State According to the Kurz Model

	H_2O	Me_2SO	CH_3CN
w_R, kcal/mol[a]	6.17–10.47	4.28–7.55	3.88–6.90
$\Delta G_0{}^\ddagger{}_{eq}(M)$, kcal/mol[a]	1.58	0.61	0.48
F_S, kcal/mol[b]	226.2	117.4	143.6

[a] Defined in eq 15. [b] Defined in eq 17.

$\Delta G_0{}^\ddagger{}_{int}(M)$, one for equilibrium solvation, $\Delta G_0{}^\ddagger{}_{eq}(M)$, and one for nonequilibrium solvation, $\Delta G_0{}^\ddagger{}_{noneq}(M)$, eq 14 becomes

$$\Delta G_0{}^\ddagger(\text{obsd}) = w_R + \Delta G_0{}^\ddagger{}_{int}(M) + \Delta G_0{}^\ddagger{}_{eq}(M) + \Delta G_0{}^\ddagger{}_{noneq}(M) \quad (15)$$

The relationship between the solvent effect on the intrinsic rate constant, ${}^1\delta^{11} \log k_0$, and the parameters in eq 15 is then given by eq 16; note that $\Delta G_0{}^\ddagger{}_{int}(M)$ is solvent-independent and hence cancels in eq 16.

$$-2.303RT{}^1\delta^{11} \log k_0 = {}^1\delta^{11}\Delta G_0{}^\ddagger(\text{obsd}) = {}^1\delta^{11}w_R + {}^1\delta^{11}\Delta G_0{}^\ddagger{}_{eq}(M) + {}^1\delta^{11}\Delta G_0{}^\ddagger{}_{noneq}(M) \quad (16)$$

To estimate w_R, $\Delta G_0{}^\ddagger{}_{eq}(M)$, and $\Delta G_0{}^\ddagger{}_{noneq}(M)$, Kurz modeled the reactants, precursor complex, and transition state as charges imbedded in spherical (reactants) or ellipsoidal cavities (precursor complex and transition state) in a dielectric continuum. w_R, $\Delta G_0{}^\ddagger{}_{eq}(M)$, and $\Delta G_0{}^\ddagger{}_{noneq}(M)$ depend on cavity size and the extent of solvational disequilibrium at the transition state. The dependence of $\Delta G_0{}^\ddagger{}_{noneq}(M)$ on this disequilibrium was formulated as the product of a Hooke's law force constant, F_S, and the square of the displacement from charge/solvation equilibrium, as shown in eqs 17 and 18. z_{TS}, assumed to be −0.5, is the fraction of an

$$\Delta G_0{}^\ddagger{}_{noneq}(M) = \frac{1}{2}F_S(m - z_{TS})^2 \quad (17)$$

$${}^1\delta^{11}\Delta G_0{}^\ddagger{}_{noneq}(M) = \frac{1}{2}(F_S^{11} - F_S^{1})(m - z_{TS})^2 \quad (18)$$

electronic charge that is located at each of the foci of the transition-state ellipsoid, while m is the value of the hypothetical fraction of the electronic charge at each focus that would be in equilibrium with the real, slowly relaxing component of the solvent polarization. The magnitude of the difference between the real and hypothetical charges, $|m - z_{TS}|$, thus measures the extent of charge/solvation disequilibrium.

The results of such model calculations for what Kurz considers the most likely cavity sizes of precursor complex and transition state are summarized in Table IV for water, Me_2SO, and MeCN, while Table V (Part C) reports the solvent effects on the various parameters according to eq 16. Thus, for I = H_2O → II = Me_2SO Kurz obtains ${}^1\delta^{11}w_R$ between −1.89 and −2.92 kcal/mol and ${}^1\delta^{11}\Delta G_0{}^\ddagger{}_{eq}(M) = -0.97$ kcal/mol, resulting in a total contribution of −2.86 to −3.89 kcal/mol by equilibrium solvation effects to ${}^1\delta^{11}\Delta G_0{}^\ddagger(\text{obsd})$. ${}^1\delta^{11}\Delta G_0{}^\ddagger{}_{noneq}(M)$ is given by $-54.4(m - z_{TS})^2$, which yields ${}^1\delta^{11}\Delta G_0{}^\ddagger{}_{noneq}(M) = -0.54$, −1.22, −2.18, −3.40, and −4.90 kcal/mol for $|m - z_{TS}| = 0.10$, 0.15, 0.20, 0.25, and 0.30, respectively.

How does the Kurz analysis compare with the one based on eq 13? Since in eq 13 $\delta_{TS(B)}$ represents the contribution from equilibrium solvation of reactants and transition state, it should correspond to ${}^1\delta^{11}w_R + {}^1\delta^{11}\Delta G_0{}^\ddagger{}_{eq}(M)$ in eq 16, while the sum of $\delta_{C^-} + \delta_{CH} + \delta_{B^-} + \delta_{BH}$ in eq 13 includes all nonequilibrium solvation/desolvation effects and should be the counterpart of ${}^1\delta^{11}\Delta G_0{}^\ddagger{}_{noneq}(M)$ in eq 16. Hence we set

$$-2.303RT\delta_{TS(B)} \approx {}^1\delta^{11}w_R + {}^1\delta^{11}\Delta G_0{}^\ddagger{}_{eq}(M) \quad (19)$$

$$-2.303RT(\delta_{C^-} + \delta_{CH} + \delta_{B^-} + \delta_{BH}) \approx {}^1\delta^{11}\Delta G_0{}^\ddagger{}_{noneq}(M) \quad (20)$$

The PNS analysis discussed above for the reaction of phenylnitromethane with acetate ion gives $\delta_{TS(B)} \approx 1.88$ and $\delta_{C^-} + \delta_{CH} + \delta_{B^-} + \delta_{BH} \approx 2.10$ for I = water → II = 90% Me_2SO–10% water (Table V, Part A). The former value translates into ${}^1\delta^{11}w_R + {}^1\delta^{11}\Delta G_0{}^\ddagger{}_{eq}(M) \approx -2.56$ kcal/mol (eq 19), which is close to the lower end of the range obtained by the Kurz model for I = water → II = Me_2SO. As argued earlier, $\delta_{TS(B)}$ for I = water → II = Me_2SO is likely to be somewhat larger than 1.88 (assumed to be ~2.3 in Table V); hence, ${}^1\delta^{11}w_R + {}^1\delta^{11}\Delta G_0{}^\ddagger{}_{eq}(M)$ calculated therefrom will be more negative than −2.56 kcal/mol (ca. −3.1 kcal/mol), which would bring it into even better agreement with the range predicted by Kurz. The value of 2.10 for $\delta_{C^-} + \delta_{CH} + \delta_{B^-} + \delta_{BH}$ corresponds to ${}^1\delta^{11}\Delta G_0{}^\ddagger{}_{noneq}(M) = -2.86$ kcal/mol, again with a somewhat more negative value expected for I = water → II = Me_2SO (ca. −3.4 kcal/mol). This result, too, is consistent with the Kurz model calculations, with a $|m - z_{TS}|$ value probably around 0.25. These sample calculations, which are summarized in Table V, Part B, thus show a remarkably good agreement between the two models for the case I = water and II = Me_2SO.

Table V. Solvent Effects Induced by the Transfer from Solvent I to Solvent II. Analysis by the PNS Approach and Predictions by the Kurz Model

	I = H_2O, II = 90% Me_2SO[a]	I = H_2O, II = Me_2SO[b]	I = Me_2SO, II = AN[c]
A. PNS Analysis of Experimental Data			
${}^1\delta^{11} \log k_0$	3.98	~4.8	1.43 (1.70)
$\delta_{TS(B)}$	1.88	~2.3	1.13 (1.28)
$\delta_{C^-} + \delta_{CH} + \delta_{B^-} + \delta_{BH}$	2.10	~2.5	0.30 (0.42)
B. Conversion of PNS Parameters into Kurz Parameters			
${}^1\delta^{11}\Delta G_0{}^\ddagger(\text{obsd})$, kcal/mol	−5.41	ca. −6.5	−1.94 (−2.31)
${}^1\delta^{11}w_R + {}^1\delta^{11}\Delta G_0{}^\ddagger{}_{eq}(M)$, kcal/mol[d]	−2.56	ca. −3.1	−1.54 (−1.74)
${}^1\delta^{11}\Delta G_0{}^\ddagger{}_{noneq}(M)$, kcal/mol[e]	−2.86	ca. −3.4	−0.41 (−0.57)
C. Predictions by Kurz Model			
${}^1\delta^{11}w_R$, kcal/mol		−1.89 to −2.92	−0.40 to −0.65
${}^1\delta^{11}\Delta G_0{}^\ddagger{}_{eq}(M)$, kcal/mol		−0.97	−0.13
${}^1\delta^{11}w_R + {}^1\delta^{11}\Delta G_0{}^\ddagger{}_{eq}(M)$, kcal/mol		−2.86 to −3.89	−0.53 to −0.78
${}^1\delta^{11}\Delta G_0{}^\ddagger{}_{noneq}(M)$, kcal/mol		ca. −3.4[f]	0.82[f]
${}^1\delta^{11}\Delta G_0{}^\ddagger(\text{obsd})$, kcal/mol		ca. −6.26 to −7.29[f]	0.04 to 0.29[f]

[a] Reaction of phenylnitromethane with acetate ion. [b] Estimated; see text. [c] Reaction of (3-nitrophenyl)nitromethane and (4-nitrophenyl)nitromethane (in parentheses) with benzoate ion. [d] From eq 19. [e] From eq 20. [f] Based on $|m - z_{TS}| = 0.25$; see text.

For the effect of changing from Me_2SO (I) to acetonitrile (II), the agreement is much less satisfactory. For ${}^1\delta^{11}w_R$, the Kurz model predicts −0.40 to −0.65 kcal/mol and ${}^1\delta^{11}\Delta G_0{}^\ddagger{}_{eq}(M) = -0.13$ kcal/mol, resulting in a total contribution of −0.53 to −0.78 kcal/mol to ${}^1\delta^{11}\Delta G_0{}^\ddagger(\text{obsd})$ by equilibrium solvation effects (Table V, Part C). For ${}^1\delta^{11}\Delta G_0{}^\ddagger{}_{noneq}(M)$ we have $13.1(m - z_{TS})^2$; taking $|m - z_{TS}| = 0.25$ as obtained above yields ${}^1\delta^{11}\Delta G_0{}^\ddagger{}_{noneq}(M) = 0.82$ kcal/mol (Table V, Part C). Hence, the Kurz model predicts that the equilibrium solvation effects should lead to a somewhat higher k_0 in acetonitrile but that this effect is offset by a rate-retarding nonequilibrium solvation effect, i.e., k_0 ($\Delta G_0{}^\ddagger(\text{obsd})$) is esssentially unaffected by the change of solvent or is even slightly lower (higher) in acetonitrile (${}^1\delta^{11}\Delta G_0{}^\ddagger(\text{obsd}) = 0.04$ to 0.29 kcal/mol, Table V, Part C). This contrasts with our finding that k_0 *increases* by 1.43 and 1.70 log units ($\Delta G_0{}^\ddagger(\text{obsd})$ decreases by 1.94 to 2.31 kcal/mol) for (3-nitrophenyl)nitromethane and (4-nitrophenyl)nitromethane, respectively (Table V, Parts A and B). It is also interesting to note that the prediction of a positive ${}^1\delta^{11}\Delta G_0{}^\ddagger{}_{noneq}(M)$ value by the Kurz model is contradicted by the PNS analysis, according to which this term is slightly negative (−0.41 kcal/mol for (3-nitrophenyl)nitromethane, −0.57 kcal/mol for (4-nitrophenyl)nitromethane, Table V, Part B).

Conclusions

The solvent effects on k_0 ($\Delta G_0{}^\ddagger(\text{obsd})$) for the deprotonation of arylnitroalkanes by carboxylate ions can be understood to arise from a combination of a classical solvent effect (equilibrium solvation of the transition state) and various PNS effects arising from nonequilibrium solvation of different parts of the transition state. For the comparison between water and Me_2SO, the PNS analysis suggests that the equilibrium and nonequilibrium solvation effects of the transition state contribute approximately equally to the large overall change in k_0 ($\Delta G_0^\ddagger$(obsd)). If $|m - z_{TS}|$ is assumed to be 0.25, which seems to be a reasonable value, the Kurz analysis leads to a similar breakdown into equilibrium and nonequilibrium solvation effects.

For the change from Me_2SO to MeCN, the PNS analysis suggests that the observed increase in k_0 (decrease in $\Delta G_0^\ddagger$(obsd)) is in large measure an equilibrium solvation effect, although there is a small contribution by a nonequilibrium solvation effect. The Kurz model also predicts an increase in k_0 (decrease in $\Delta G_0^\ddagger$(obsd)) from an equilibrium solvation effect but a rather small one. On the other hand, assuming $|m - z_{TS}| = 0.25$ as above, the Kurz model calls for a substantial decrease in k_0 (increase in $\Delta G_0^\ddagger$(obsd)) by nonequilibrium solvation, which completely offsets (or even overcompensates) the equilibrium solvation effect in contradiction with the experimental results.

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Registry No. (3-Nitrophenyl)nitromethane, 34063-52-0; (4-nitrophenyl)nitromethane, 1610-26-0; (3,5-dinitrophenyl)nitromethane, 70136-12-8; tetraethylammonium benzoate, 16909-22-1; tetraethylammonium 3-bromobenzoate, 68570-54-7; tetraethylammonium 4-bromobenzoate, 137570-74-2; benzoate, 766-76-7; 3-bromobenzoate, 16887-61-9; 4-bromobenzoate, 2906-29-8; (3-nitrophenyl)nitromethyl anion, 66291-20-1; (4-nitrophenyl)nitromethyl anion, 66291-19-8; 3,5-dinitrobenzyl bromide, 137570-75-3; 3,5-dinitrobenzyl alcohol, 71022-43-0.

Supplementary Material Available: Tables (S1–S8) of kinetic and equilibrium data for benzoic acid, the phenylnitromethanes, and their corresponding anions (8 pages). Ordering information is given on any current masthead page.

Structure and Thermodynamic and Kinetic Properties of Eosin–Bipyridinium Complexes

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Abstract: Eosin, Eo^{2-}, and *N,N'*-dimethyl-4,4'-bipyridinium, MV^{2+}, form a crystalline 1:1 complex [Eo^{2-}–MV^{2+}]. With *N,N'*-dibenzyl-4,4'-bipyridinium, BV^{2+}, the dye Eo^{2-} forms a crystalline complex where one BV^{2+} unit is intercalated between two Eo^{2-} units and the second BV^{2+} unit is positioned outside this sandwich structure [Eo^{2-}–BV^{2+}–Eo^{2-};BV^{2+}]. Electrostatic, charge-transfer, and π interactions stabilize these intermolecular assemblies. In solution, Eo^{2-} and MV^{2+} initially form the 1:1 intermolecular structure [Eo^{2-}–MV^{2+}]. The latter complex is transformed to the thermodynamically stable complex structure [Eo^{2-}–MV^{2+}–Eo^{2-};MV^{2+}] (in DMF, $k = 57.3$ M^{-1} s^{-1} at 331 K and $E_a = 25.3 \pm 0.5$ kcal mol^{-1}). The 1:1 complex [Eo^{2-}–MV^{2+}] shows thermal population of the charge-transfer band.

Attractive interactions between π-systems control the formation of diverse molecular complexes. Stabilization of the double helical structure of DNA[1], intercalation of drugs into DNA,[2,3] stacking of aromatic molecules in the crystal structure,[4] formation of host–guest complexes,[5,6] and aggregation of organic dyes[7] or porphyrins[8] originate from intermolecular π–π interactions. Theoretical studies have outlined the significance of π-interactions in controlling orientational effects and the structure of π-stacked systems.[9] Electron donor–acceptor interactions provide another route for the stabilization of molecular complexes.[10] Selective molecular complexation in biological systems[11,12] and formation of stable host–guest assemblies[13,14] have been attributed to stabilizing electron donor–acceptor interactions. The interactions in electron donor–acceptor complexes might originate from electrostatic interactions, polarization interactions, charge-transfer interactions, and dispersion energy. It has been emphasized[9] that π-interactions and electron donor–acceptor interactions are two different mechanisms leading to the stabilization of molecular complexes. While π–π interactions are controlled by the intermolecular contact of the components in the complex, electron donor–acceptor interactions are influenced by the oxidation and reduction potentials of the components. Nevertheless, the two modes can act cooperatively in the selective stabilization of defined molecular complexes.[15]

Xanthene dyes exhibit photophysical properties that allow their application as photosensitizers in photosynthetic systems.[16–18]

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