

Solvent Effects on Proton Transfer Reactions: Benzoate Ion Promoted Deprotonation Reactions of Arylnitromethanes in Methanol Solution

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Second-order rate constants and equilibrium constants have been determined for the benzoate ion promoted deprotonation reactions of (*m*-nitrophenyl)nitromethane, (*p*-nitrophenyl)nitromethane, and (3,5-dinitrophenyl)nitromethane in methanol solution. The pK_a values for the aryl nitromethanes in methanol are the following: $pK_a = 10.9, 10.5,$ and 9.86 for (*m*-nitrophenyl)nitromethane, (*p*-nitrophenyl)nitromethane, and (3,5-dinitrophenyl)nitromethane, respectively, relative to benzoic acid ($pK_a = 9.4$). A Bronsted β_B value of 0.50 and α_{CH} value of 1.31 have been calculated for the 3,4-dimethylbenzoate, benzoate, *m*-bromobenzoate, and 3,4-dichlorobenzoate ion promoted reactions of (3,5-dinitrophenyl)nitromethane, and for the benzoate ion promoted reactions of (*m*-nitrophenyl)nitromethane, (*p*-nitrophenyl)nitromethane, and (3,5-dinitrophenyl)nitromethane, respectively. The log of the intrinsic rate constants for benzoate ion promoted deprotonations of (*m*-nitrophenyl)nitromethane, (*p*-nitrophenyl)nitromethane, and (3,5-dinitrophenyl)nitromethane are 0.0212, 0.270, and 0.877, respectively. These values are $6.3 \times 10^4, 2.0 \times 10^4,$ and 2.5×10^4 times lower than for the same reactions in acetonitrile solution. The transfer activity coefficient from methanol to acetonitrile solution, $\log M_{\gamma}^{AN}$, for (*m*-nitrophenyl)nitromethyl anion (3.6) and (*m*-nitrophenyl)nitromethane (-1.0) have been calculated. The solvent effect on these reactions in methanol and acetonitrile, two solvents with similar dielectric constants, are analyzed within the framework of the Principle of Nonperfect Synchronization. The results suggest that the observed solvent effect is a result of an imbalanced transition state (*i.e.*, PNS effects), and a stronger transition state hydrogen bond between the carbon acid and benzoate ion in acetonitrile than in methanol solution.

Studies of solvent effects on proton-transfer reactions of carbon acids have helped understand the factors that are responsible for the relatively high energy barriers in these reactions¹ compared to proton transfer reactions of oxygen and nitrogen acids.² These factors include the inability of carbon acids to form strong hydrogen bonds³ and transition state imbalance.⁴ Transition state imbalance (embodied in The Principle of Nonperfect Synchronization (PNS)⁵) corresponds to a lack of synchronization between concurrent reaction events and can strongly influence the stability of transition states and the rates of chemical reactions.

Intrinsic rate constants for reactions, k_0 , provide a means for comparing the inherent reactivities of related reactions⁵ (*e.g.* proton transfers, nucleophilic additions, electron transfer, *etc.*). The intrinsic rate constant is the rate constant for a reaction for which $\Delta G^\ddagger = 0$ ($K = 1$). The concept of intrinsic rate constants was first introduced by Marcus in his theory of electron transfer reactions.⁶

Solvent effects on the rates of proton transfer reactions from aryl nitromethanes are large, with intrinsic rate constants for the oxyanion (benzoate or acetate ion)-promoted reactions that are 10^6 times greater in aceto-

nitrile than in water.⁷ Large but slightly smaller rate accelerations (*ca.* 10^4 – 10^5 fold relative to water) have also been observed in Me_2SO solution.⁸ The origin of these large solvent effects is not entirely clear. An analysis of the solvent effect on the benzoate ion promoted deprotonation reaction of aryl nitromethanes in Me_2SO and acetonitrile solutions⁷ suggests that most of the 27 fold increase in the intrinsic rate constant (the reaction is faster in acetonitrile) is a result of a classical (Hughes–Ingold) solvent effect⁹ (*i.e.*, the Hughes–Ingold Rules⁹ of solvent effects are based on electrostatic effects resulting from polar interactions between the solvent and the reactants and transition state). Similarly, it has been estimated that both a classical solvent effect and transition state imbalance (late solvation of the developing nitronate ion), contribute almost equally to the 10^4 difference in intrinsic rate constants for the acetate ion promoted deprotonation reactions of aryl nitromethanes in water and 90% Me_2SO -10% water (there is also a smaller but significant contribution to the observed solvent effect from early desolvation of the acetate ion).¹⁰

We report here a study of the benzoate ion deprotonation reactions of aryl nitromethanes in methanol solution and compare these results with results previously reported for the same reaction in acetonitrile.⁷ Since methanol and acetonitrile have dielectric constants that

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are almost the same (32.6¹¹ and 36,¹¹ respectively, at 25 °C), for the deprotonation reactions carried out in these solvents, the contribution from a classical solvent effect to the observed solvent effect is expected to be small.¹¹ The change in the intrinsic rate constant for the reaction carried out in these solvents should therefore be a more direct measure of the solvent effect that can be attributed to transition state imbalances (PNS effects). The analysis of the solvent effect reported here (a 10⁴–10⁵ increase in the intrinsic rate constant for reaction in acetonitrile compared to methanol) is consistent with a solvent effect that results from transition state imbalance (PNS effects), and a transition state hydrogen bond between the carbon acid and base that is stronger in acetonitrile than in methanol solution.

Experimental Section

Materials. Methanol was purified by distillation using a 2 ft fractionating column. Potassium benzoate, 3-bromobenzoate, 3,4-dimethylbenzoate, and 3,4-dichlorobenzoate were prepared following the general procedure described by Kolthoff and Chantooni.¹² These salts were dried by several azeotropic distillations with toluene as cosolvent and then in vacuo over P₂O₅. The purity of the benzoate salts were determined by potentiometric titration against 0.0600 M HCl in 90 volume percent DMSO in water. The purities determined in this way for potassium benzoate, *m*-bromobenzoate, 3,4-dimethylbenzoate, and 3,4-dichlorobenzoate were 103%, 97%, 98%, and 98%, respectively.

(3,5-Dinitrophenyl)benzyl Bromide.¹³ In a 250 mL three-necked flask, under nitrogen, was dissolved 7.5 g of 3,5-dinitrobenzyl alcohol in 75 mL of CHCl₃. To this solution was added dropwise, over a 30 min period, 10.25 g of PBr₃ dissolved in 15 mL of CHCl₃. After the addition was complete, the solution was heated at reflux for an additional 2 h and then left overnight at room temperature. After workup, the final product was recrystallized from ethanol to yield 7.2 g of yellow crystals, mp 97–98 °C (lit. mp¹³ 65–66 °C and mp¹⁴ 97–99 °C). ¹H NMR (CDCl₃) δ 4.63 (2H, s), 8.63 (2H, s), 9.10 (1H, s).

(3,5-Dinitrophenyl)benzyl Iodide.¹⁴ With a Na vapor lamp as the only light source, 3.5 g of 3,5-dinitrobenzyl bromide was dissolved in dry acetone. This solution was slowly added, with stirring, to 90 mL of a 10% w/w solution of NaI in acetone. The resulting reaction was instantaneous. After workup the product (3.72 g) was recrystallized from ethanol, mp 89–90.5 °C (lit.¹⁴ mp 91.5–93 °C). ¹H NMR (CDCl₃) δ 4.63 (2H, s), 8.63 (2H, s), 8.95 (1H, s).

(3,5-Dinitrophenyl)nitromethane.¹⁵ In dry ether, 3.7 g of 3,5-dinitrobenzyl iodide was added over a 1 h period to a slurry of 4.7 g of AgNO₂ in ether. The mixture was continuously stirred and kept at 1 °C for 12 h. After evaporation of the ether, the crude product was recrystallized from ethanol (0.2 g yield), mp 128–129 °C (lit.¹⁶ mp 129–130 °C). ¹H NMR (CDCl₃) δ 5.68 (2H, s), 8.72 (2H, s), 9.18 (1H, s).

Kinetics. Kinetics were carried out by following spectrophotometrically the appearance of the arylnitromethane anions at the λ_{max} of the anions: 312 nm (ε 2.19 × 10⁴ M⁻¹ cm⁻¹), 394 nm (ε 1.80 × 10⁴ M⁻¹ cm⁻¹), and 305 nm (ε 1.55 × 10⁴ M⁻¹ cm⁻¹) for the anions of (3-nitrophenyl)nitromethane, (4-nitrophenyl)nitromethane, and (3,5-dinitrophenyl)nitromethane, respectively. Reactions were carried out at 25.0 °C in methanol under pseudo-first-order conditions, in the presence of excess buffer base and acid. Plots of ln(A_∞ - A) against time (using the program Enzfitter) obeyed pseudo-first-order kinetics and were monitored for at least two to three half-lives.

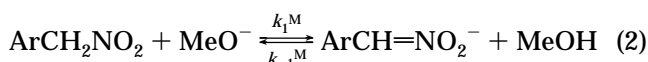
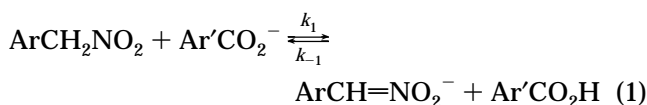
Buffer solutions were prepared by dissolving the buffer acid and its potassium salt in methanol.

Equilibrium Constants. Acidity constants for the arylnitromethanes in methanol were determined spectrophotometrically relative to benzoic acid (pK_a = 9.4).² Equilibrium acidity constants were determined in benzoate buffer solutions with buffer ratios (PhCOOH/PhCOO⁻) ranging from 0.0758 to 0.152 for (4-nitrophenyl)nitromethane, from 0.0710 to 0.155 for (3-nitrophenyl)nitromethane, and from 0.100 to 0.590 for (3,5-dinitrophenyl)nitromethane. The pK_a values of the substrates were evaluated using the equation $K_{CH} = K_a \{ [C^-] / [CH] \} \{ [BH] / [B] \}$, where K_{CH} is the acid dissociation constant of the arylnitromethane, K_a is the acid dissociation constant of benzoic acid in methanol ($K_a = 1.98 \times 10^{-10}$ M),¹¹ $\{ [C^-] / [CH] \}$ is the arylnitromethyl anion/arylnitromethane ratio, and $\{ [BH] / [B] \}$ is the benzoic acid/benzoate ion buffer ratio.

Transfer Activity Coefficients. The transfer activity coefficient from methanol to acetonitrile solution of the (3-nitrophenyl)nitromethyl anion was calculated using the expression, $\log M_{\gamma}^{AN}(C^-) = M_{\Delta}^{AN} pK_{CH} - \log M_{\gamma}^{AN}(H^+) + \log M_{\gamma}^{AN}(CH)$, where $M_{\Delta}^{AN} pK_{CH}$ is the difference in pK_a of the arylnitromethane in methanol relative to acetonitrile and M_{γ}^{AN} is the transfer activity coefficient of the arylnitromethyl anion (C⁻), the lyonium ion (H⁺), and the arylnitromethane (CH), respectively. The transfer activity coefficients are equal to $\Delta G^\circ / 2.303RT$, where ΔG° is the standard free-energy of transfer of a molecule or ion from methanol to acetonitrile solution. The transfer activity coefficient of (3-nitrophenyl)nitromethane was determined from solubility measurements as described by Kolthoff.¹⁷ The solubility was measured by saturating 1.00 mL of methanol with (3-nitrophenyl)nitromethane. This solution was made 0.001 M in HCl to suppress ionization of the substrate. The saturated solution of the substrate was kept in a shaker bath at 25.1 °C for 24 h. A 1 or 2 μL amount of this solution was then injected into 3.00 mL of acetonitrile, and the absorbance values of the resulting solutions were determined at 258 nm. At 258 nm, in acetonitrile solution, (3-nitrophenyl)nitromethane has a molar absorptivity constant of 0.770×10^4 M⁻¹ cm⁻¹.⁷ The solubility of (3-nitrophenyl)nitromethane determined in this way was 0.219 M.

Results

The deprotonation of an arylnitromethane by benzoate ions in methanol solution can be described by eqs 1 and 2, where eqs 1 and 2 represent the deprotonation (reprotonation) reactions promoted by benzoate ion (and benzoic acid) and methoxide ion (and methanol), respectively.



Under pseudo-first-order conditions, k_{obsd} is given by eq 3.

$$k_{\text{obsd}} = k_1[\text{Ar}'\text{CO}_2^-] + k_{-1}[\text{Ar}'\text{CO}_2\text{H}] + k_1^M[\text{MeO}^-] + k_{-1}^M \quad (3)$$

Equation 3 may be rearranged to eq 4, where $r = [\text{BH}] / [\text{B}]$, the benzoate buffer ratio, and $K_{\text{eq}} = k_1 / k_{-1}$.

$$k_{\text{obsd}} / (1 + r / K_{\text{eq}}) = k_1[\text{Ar}'\text{CO}_2^-] + \{ k_1^M[\text{MeO}^-] + k_{-1}^M \} / (1 + r / K_{\text{eq}}) \quad (4)$$

Figure 1 shows a plot of $k_{\text{obsd}} / (1 + r / K_{\text{eq}})$ against benzoate ion concentration for the deprotonation reac-

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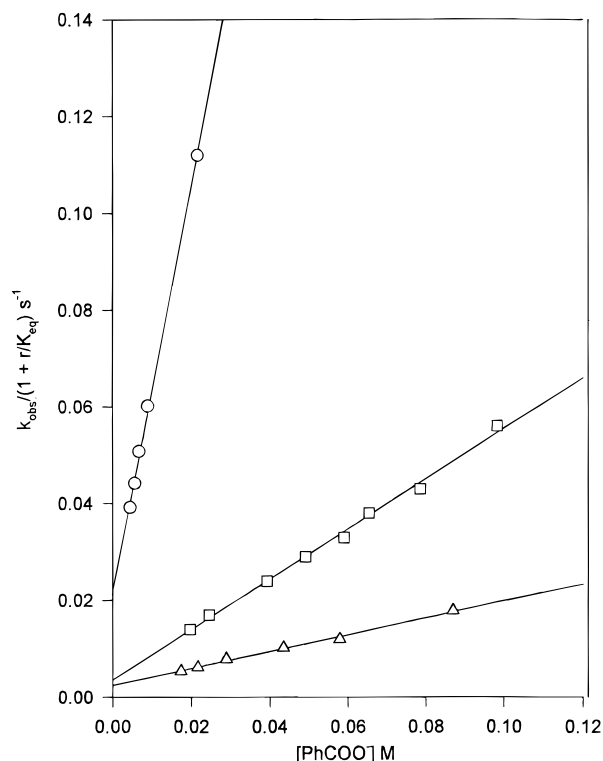


Figure 1. Plot of $k_{\text{obs}}/(1 + r/K_{\text{eq}})$ against benzoate ion concentration, where r is the benzoic acid/benzoate ion buffer ratio, and K_{eq} is the equilibrium constant for deprotonation of the aryl nitromethane by benzoate ion, for the deprotonation reaction of (3-nitrophenyl)nitromethane (Δ), (4-nitrophenyl)nitromethane (\square), and (3,5-dinitrophenyl)nitromethane (\circ) in methanol solution at 25 °C.

Table 1. Second-Order Rate Constants for Benzoate Ion Deprotonation Reactions of Arylnitromethanes^a

substrate	XPhCO ₂ ⁻	K _{eq} ^b	k ₁ , M ⁻¹ s ⁻¹	k ₋₁ , M ⁻¹ s ⁻¹
3-NO ₂ C ₆ H ₄ CH ₂ NO ₂	PhCO ₂ ⁻	0.030	0.181	6.08
4-NO ₂ C ₆ H ₄ CH ₂ NO ₂	PhCO ₂ ⁻	0.084	0.536	6.41
3,5-(NO ₂) ₂ C ₆ H ₃ NO ₂	PhCO ₂ ⁻	0.345	4.48	13.1
3,5-(NO ₂) ₂ C ₆ H ₃ NO ₂	3,4-Me ₂ PhCO ₂ ⁻	0.680	6.29	9.25
3,5-(NO ₂) ₂ C ₆ H ₃ NO ₂	PhCO ₂ ⁻	0.345	4.48	13.1
3,5-(NO ₂) ₂ C ₆ H ₃ NO ₂	<i>m</i> -BrPhCO ₂ ⁻	0.091	2.13	23.4
3,5-(NO ₂) ₂ C ₆ H ₃ NO ₂	3,4-Cl ₂ PhCO ₂ ⁻	0.048	1.69	35.2

^a In methanol solution at 25.0 °C. ^b $K_{\text{eq}} = [\text{C}^-][\text{BH}]/[\text{CH}][\text{B}]$, where CH, C⁻, BH, and B⁻ are the aryl nitromethane, the aryl nitromethane anion, benzoic acid, and the benzoate ion, respectively.

tions of (*m*-nitrophenyl)nitromethane, (*p*-nitrophenyl)nitromethane, and (3,5-dinitrophenyl)nitromethane. From the slopes of these plots, second-order rate constants for the benzoate ion promoted reactions (k_1) were calculated. These rate constants are summarized in Table 1 along with second-order rate constants, obtained in analogous fashion, for the *m*-bromobenzoate, 3,4-dichlorobenzoate, and 3,4-dimethylbenzoate ion promoted reactions of (3,5-dinitrophenyl)nitromethane. The plots of $k_{\text{obs}}/(1 + r/K_{\text{eq}})$ against benzoate ion concentration give rise to significant intercept values at zero benzoate ion concentration. These intercepts represent the solvent-catalyzed reactions: the deprotonation of the substrate by the methoxide ion and the reprotonation of the nitronate ion by methanol. Rate constants for the solvent-catalyzed reactions were calculated from the slope and intercept of plots of $I(1 + r/K_{\text{eq}})$ against the methoxide ion concentration, where I are the intercept values at various r values (buffer ratios). From the slope and intercept values of

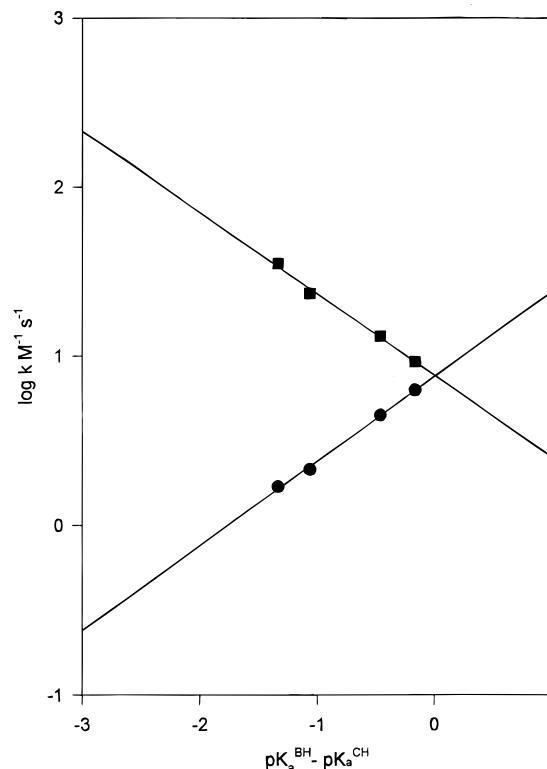


Figure 2. Bronsted plots for the reaction of (3,5-dinitrophenyl)nitromethane with the benzoate, *m*-bromobenzoate, and 3,4-dichlorobenzoate ions in methanol solution at 25 °C.

this plot (not shown) k_1^{M} and k_{-1}^{M} were determined to be $4.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and 0.013 s^{-1} , respectively.^{18a} Also included in Table 1 are the equilibrium constants, K_{eq} , for the reactions of the aryl nitromethanes with benzoate ions. These values were calculated as described in the Experimental Section.

Figure 2 shows a Bronsted plot for general base and acid catalysis of the deprotonation reactions of (3,5-dinitrophenyl)nitromethane by benzoate, *m*-bromobenzoate, 3,4-dichlorobenzoate, and 3,4-dimethylbenzoate ions. The slopes of this plot are the Bronsted β_{B} (0.50) and α_{BH} (0.50) values. The rate constant corresponding to the point of intersection of the two lines (where $k_1 = k_{-1}$) is the intrinsic rate constant for the deprotonation reaction ($\log k_0 = 0.877$ for (3,5-dinitrophenyl)nitromethane). The rate constants for the reaction promoted by methoxide ion (forward direction) and methanol (reverse direction) fall on the Bronsted lines (points not shown) of Figure 2:^{18b} there is no negative deviation for the solvent-promoted reactions from the Bronsted lines based on benzoate ions. Table 3 summarizes the intrinsic rate constants for the benzoate ion promoted reactions of aryl nitromethanes in three solvents: Me₂SO, acetonitrile, and methanol (this work). Also included in Table 3 is the data for the acetate ion promoted reactions in aqueous solution.

Figure 3 shows a Bronsted-type plot in which the acidity of the substrate is varied, rather than that of the base. This plot represents data for the benzoate ion promoted reactions of (*m*-nitrophenyl)nitromethane, (*p*-

(18) (a) The methoxide ion concentration was calculated based on a pK_{a} value for methanol of 16.92^{18c} and the pH of the benzoate buffer solution. (b) For the Bronsted plot, the pK_{a} of methanol was taken to be 16.92.^{18c} (c) Cox, J. P.; Crampton, M. R.; Wright, P. *J. Chem. Soc., Perkin Trans. 2* **1988**, 25.

Table 2. Acidity Constants for Arylnitromethanes and Benzoic Acids in Methanol Solution^a

substrate/PhCOOH	p <i>K</i> _a
3-NO ₂ C ₆ H ₄ CH ₂ NO ₂	10.9
4-NO ₂ C ₆ H ₄ CH ₂ NO ₂	10.5
3,5-(NO ₂) ₂ C ₆ H ₃ NO ₂	9.86
3,4-(Me) ₂ PhCOO ⁻	9.7 ^b
PhCOOH	9.4 ^b
<i>m</i> -BrPhCOOH	8.8 ^b
3,4-(Cl) ₂ PhCOOH	8.53 ^b

^a At 25.0 °C. ^b Reference 19.

Table 3. Bronsted Coefficients and Intrinsic Rate Constants for Deprotonation Reactions of Arylnitromethanes in Methanol, Acetonitrile, and Dimethyl Sulfoxide Solutions

reaction	β _B	α _{CH}	log <i>k</i> ₀ (Ar)
Water			
ArCH ₂ NO ₂ + RCO ₂ ⁻ ^a	0.54		-2.10 (Ph)
	0.59 ^b		-1.61 (Ph)
Methanol			
ArCH ₂ NO ₂ + Ar'CO ₂ ⁻ ^c	0.50	1.31	0.021 (3-NO ₂ Ph)
			0.270 (4-NO ₂ Ph)
			0.877 (3,5-(NO ₂) ₂ Ph)
Dimethyl Sulfoxide			
ArCH ₂ NO ₂ + Ar'CO ₂ ⁻ ^d	0.55	0.92	2.66 (Ph)
			3.88 (3-NO ₂ Ph)
			2.88 (4-NO ₂ Ph)
			3.97 (3,5-(NO ₂) ₂ Ph)
Acetonitrile			
ArCH ₂ NO ₂ + Ar'CO ₂ ⁻ ^e	0.56	0.79	4.35 ^f (Ph)
			4.81 (3-NO ₂ Ph)
			4.58 (4-NO ₂ Ph)
			5.27 (3,5-(NO ₂) ₂ Ph)

^a Reference 22. ^b For the reaction of phenylnitromethane with a variety of substituted acetate ions.²⁷ ^c This work. ^d Reference 8. ^e Reference 7. ^f Calculated value, see reference 7.

nitrophenyl)nitromethane, and (3,5-dinitrophenyl)nitromethane. The slope of this plot, α_{CH}, is 1.31.

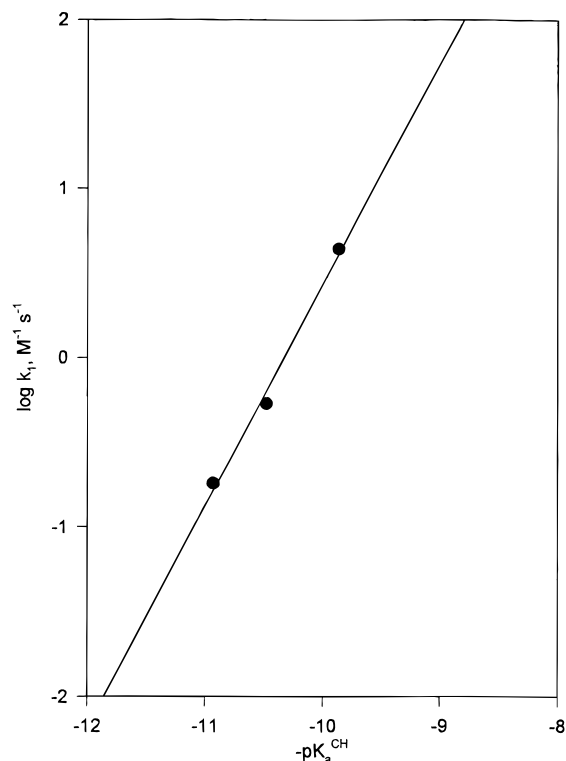
The transfer activity coefficient for (*m*-nitrophenyl)nitromethyl anion (3.6) was calculated as described in the Experimental Section, using values of log *M*_{γ^{AN}}(H⁺) = +6.2¹⁹, ^MΔ^{AN}p*K*_a = 10.8²⁰ for (*m*-nitrophenyl)nitromethane, and log *M*_{γ^{AN}}(CH) = -1.0 for (*m*-nitrophenyl)nitromethane. The values of the transfer activity coefficient of benzoic acid (-0.57) and the benzoate ion (5.7) are values previously reported by Kolthoff and Chantooni.²¹

Discussion

The data reported in the tables and figures show the following:

(1) Consistent with previous observations, Bronsted's β_B value varies only slightly with solvent, with values of 0.50, 0.54, 0.55, and 0.56 for the reaction carried out in methanol (this work), water (promoted by acetate ions),²² Me₂SO,⁸ and CH₃CN.⁷

(2) The value of α_{CH} in methanol solution is greater than 1 (α_{CH} = 1.31). This is consistent with an imbalanced transition state in which resonance delocalization of charge onto the nitro group (and the solvation of that

**Figure 3.** Bronsted plot for the deprotonation of aryl nitromethanes by benzoate ion in methanol solution at 25 °C.

charge) lags behind proton transfer. As a result, the aryl substituent more strongly interacts with the charge on the benzyl carbon in the transition state than in the nitronate ion. In the nitronate ion the charge is at a greater distance from the aryl group and requires less internal stabilization because of hydrogen bonding to the solvent. Values of α_{CH} greater than 1 have previously been reported for this reaction in aqueous solution promoted by thiolate ions,²² hydroxide ion,²³ and amines.²³

(3) There is a large increase in the intrinsic rate constant when the solvent is changed from methanol to acetonitrile or Me₂SO. For example, for the reaction of (3-nitrophenyl)nitromethane, *k*₀(CH₃CN)/*k*₀(CH₃OH) = 6.3 × 10⁴ and *k*₀(Me₂SO)/*k*₀(MeOH) = 2.3 × 10³. This increase can be understood in terms of the Principle of Non-Perfect Synchronization (PNS),⁵ because the nitronate ion is more strongly solvated in methanol solution than it is in dipolar aprotic solvents. In methanol there is a reduction in the intrinsic rate constant for the reaction (relative to the reaction in acetonitrile), because in methanol the transition state does not benefit much from charge delocalization into the nitro group, whereas the equilibrium acidity is strongly enhanced by this effect. This rate reduction can be described by eq 5,⁵ where δ log *k*₀^{sol}(C⁻) is the change in the intrinsic rate constant that can be attributed to this effect, (λ_{sol} - β_B) is a measure of the transition state imbalance (the degree of the lag in the delocalization of charge onto the nitro group and the concomitant solvation of that charge relative to proton transfer to the base), and δ log *K*₁^{sol}(C⁻) is a measure of stabilization of the nitronate ion brought about by solvation. Since δ log *K*₁^{sol}(C⁻) is larger in methanol than in acetonitrile or Me₂SO, and (λ_{sol} - β_B) is less than zero (resonance and solvation lag behind

(19) Kolthoff, I. M.; Chantooni, M. K. *J. Phys. Chem.* **1972**, *76*, 2024.
 (20) Based on p*K*_a values of 21.7 and 10.9 for (3-nitrophenyl)nitromethane in acetonitrile⁷ and methanol (this work) solutions, respectively.

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proton transfer), $\delta \log k_0^{\text{sol}}(\text{C}^-)$ is less than zero in methanol (rate reduction in methanol relative to acetonitrile).

$$\delta \log k_0^{\text{sol}}(\text{C}^-) = (\lambda_{\text{sol}} - \beta_{\text{B}}) \delta \log K_1^{\text{sol}}(\text{C}^-) \quad (5)$$

(4) The intrinsic rate constants are a function of the substituent on the benzene ring (Table 3). For example, $\log k_0$ is equal to 0.021, 0.27, and 0.88 for the benzoate ion promoted reactions of (*m*-nitrophenyl)nitromethane, (*p*-nitrophenyl)nitromethane, and (3,5-dinitrophenyl)nitromethane, respectively. The increase in the intrinsic rate constant as the phenyl substituent, Z or Z', is made more electron-withdrawing is described by eq 6.⁵ This effect is also a result of transition state imbalance, because electron-withdrawing substituents will stabilize the transition state proportionally more than they will stabilize the nitronate ion (a greater proportion of the negative charge is on the benzyl carbon in the transition state than in the nitronate ion). A plot of the left side of eq 6 for the reactions of (*m*-nitrophenyl)nitromethane, (*p*-nitrophenyl)nitromethane, and (3,5-dinitrophenyl)nitromethane against ($\text{p}K_{\text{a}}^{\text{CH}}(\text{Z}) - \text{p}K_{\text{a}}^{\text{CH}}(\text{Z}')$) (plot not shown) has a slope = $(\alpha_{\text{CH}} - \beta_{\text{B}}) = 0.81$.

$$\log k_0(\text{Z}'/\text{Z}) = (\alpha_{\text{CH}} - \beta_{\text{B}})(\text{p}K_{\text{a}}^{\text{CH}}(\text{H}) - \text{p}K_{\text{a}}^{\text{CH}}(\text{Z})) \quad (6)$$

PNS Analysis of the Solvent Effect on the Intrinsic Rate Constants. The change in the intrinsic rate constant upon a solvent change from methanol to acetonitrile can be described by eq 7,⁵ where $\delta_{\text{C}} + \delta_{\text{B}} + \delta_{\text{CH}} + \delta_{\text{BH}}$ are PNS effects (transition states imbalances): the contributions to the solvent effect from late development of resonance and solvation of the nitronate ion, early desolvation of the benzoate ion, late solvation of benzoic acid, and early desolvation of the aryl nitromethane. The $\delta_{\text{TS(B)}}$ term in eq 7 has been suggested to be a measure of the classical solvent effect²⁴ that reflects that part transition state solvation that is at equilibrium with its charge distribution (however, see below).

$${}^{\text{M}}\delta^{\text{AN}} \log k_0 = \delta_{\text{C}} + \delta_{\text{B}} + \delta_{\text{CH}} + \delta_{\text{BH}} + \delta_{\text{TS(B)}} \quad (7)$$

The terms in eq 7 are described by eq 8–11,⁵ where $\log {}^{\text{M}}\gamma_{\text{C}}^{\text{AN}}$, $\log {}^{\text{M}}\gamma_{\text{B}}^{\text{AN}}$, $\log {}^{\text{M}}\gamma_{\text{BH}}^{\text{AN}}$, and $\log {}^{\text{M}}\gamma_{\text{CH}}^{\text{AN}}$ are the solvent transfer activity coefficients of the nitronate ion (C), benzoate ion (B), aryl nitromethane (CH), and benzoic acid (BH), respectively. The terms $(\lambda_{\text{sol}}^{\text{C}} - \beta_{\text{B}})$, $(\lambda_{\text{des}}^{\text{B}} - \beta_{\text{B}})$, $(\lambda_{\text{des}}^{\text{CH}} - \beta_{\text{B}})$, and $(\lambda_{\text{sol}}^{\text{BH}} - \beta_{\text{B}})$ reflect transition state imbalances: the late development of solvation of the nitronate ion, the early desolvation of the benzoate ion and the aryl nitromethane, and the late development of solvation of benzoic acid, respectively.

$$\delta_{\text{C}} = (\lambda_{\text{sol}}^{\text{C}} - \beta_{\text{B}})(-\log {}^{\text{M}}\gamma_{\text{C}}^{\text{AN}}) \quad (8)$$

$$\delta_{\text{B}} = (\lambda_{\text{des}}^{\text{B}} - \beta_{\text{B}})(\log {}^{\text{M}}\gamma_{\text{B}}^{\text{AN}}) \quad (9)$$

$$\delta_{\text{CH}} = (\lambda_{\text{des}}^{\text{CH}} - \beta_{\text{B}})(\log {}^{\text{M}}\gamma_{\text{CH}}^{\text{AN}}) \quad (10)$$

$$\delta_{\text{BH}} = (\lambda_{\text{sol}}^{\text{BH}} - \beta_{\text{B}})(-\log {}^{\text{M}}\gamma_{\text{BH}}^{\text{AN}}) \quad (11)$$

For the benzoate ion promoted deprotonation reactions of aryl nitromethanes in methanol, all the terms in eq 7

are known or can be estimated. The values for $\log {}^{\text{M}}\gamma_{\text{C}}^{\text{AN}}$, $\log {}^{\text{M}}\gamma_{\text{B}}^{\text{AN}}$, $\log {}^{\text{M}}\gamma_{\text{CH}}^{\text{AN}}$, and $\log {}^{\text{M}}\gamma_{\text{BH}}^{\text{AN}}$ are 3.6, 5.7, -1.0, and -0.57, respectively (see the Experimental Section). Values of -0.47, -0.09, 0.09, and 0.09 have been estimated²⁴ for $(\lambda_{\text{sol}}^{\text{C}} - \beta_{\text{B}})$, $(\lambda_{\text{sol}}^{\text{BH}} - \beta_{\text{B}})$, $(\lambda_{\text{des}}^{\text{B}} - \beta_{\text{B}})$, and $(\lambda_{\text{des}}^{\text{CH}} - \beta_{\text{B}})$, respectively. Substituting these values into eq 7 leads to the following breakdown of the solvent effect (${}^{\text{M}}\delta^{\text{AN}} \log k_0 = 4.79$) for the benzoate ion promoted reaction of (3-nitrophenyl)nitromethane: $\delta_{\text{C}} = 1.7$, $\delta_{\text{CH}} = -0.09$, $\delta_{\text{B}} = 0.51$, $\delta_{\text{BH}} = -0.051$, and $\delta_{\text{TS(B)}} = 2.7$. Although this analysis is crude, the results suggest roughly equal contributions to the solvent effect from PNS effects and the $\delta_{\text{TS(B)}}$ term. It has previously been suggested that the $\delta_{\text{TS(B)}}$ term may represent a classical solvent effect⁷ (for a reaction of this charge type, less polar solvents, should speed the reaction). The results presented here, however, are not consistent with this interpretation, because the dielectric constants of methanol and acetonitrile are almost the same, so that differences in electrostatic effects between these two solvents are expected to be small (we are referring here to the Hughes–Ingold classical solvent effect that is related to the overall polarity of the solvent).

Internal Stabilization of the Transition State. As a result of the nitronate ion being more strongly solvated in methanol than in acetonitrile, internal stabilization of the transition state by polar substituents (in the benzene ring) and by hydrogen bonding to the base is expected to be more important in acetonitrile solution. The larger sensitivity to substituent effects in dipolar aprotic solvents than in water (manifested by larger Hammett ρ values) on the deprotonation reaction of aryl nitromethanes (k_1) and on their equilibrium acidities (K_{eq} values) is illustrated by the following data: in acetonitrile⁷ ($\rho(k_1) = 2.12$, $\rho(K_{\text{eq}}) = 2.68$); in DMSO⁸ ($\rho(k_1) = 2.21$, $\rho(K_{\text{eq}}) = 2.40$), and in water²² ($\rho(k_1) = 1.26$, $\rho(K_{\text{eq}}) = 0.83$). Similarly, the strength of the transition state hydrogen bond between the aryl nitromethane and the benzoate ion is expected to be stronger in acetonitrile than in methanol (I). This effect will lower the intrinsic barrier for reaction in acetonitrile and increase the intrinsic rate constant. The importance of transition state hydrogen bonding on the rates of proton transfer reactions of carbon acids is demonstrated by the fact that thiolate ions are poorer bases than oxyanions (up to 200 fold) in the deprotonation reactions of HCN³ and 4-(4-nitrophenoxy)-2-butanone.²⁵ Furthermore, in the deprotonation reaction of HCN in aqueous solution,²⁶ the second-order rate constants at $\Delta \text{p}K_{\text{a}} = 0$ (corresponding to the intrinsic rate constants for reaction) decrease in the following order: phenols ($1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), amines ($3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$), thiols ($\leq 5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$), and cyanide ($< 10^5 \text{ M}^{-1} \text{ s}^{-1}$). This order is consistent with reduced rates of proton transfer that are at least partly a result of progressively weaker transition state hydrogen bonds. Variation in the strength of transition state hydrogen bonds has also been suggested to contribute to the observed changes in thiolate/oxyanion rate constant ratios in proton transfer reactions of carbon acids.²² These results suggest that the strength of transition state hydrogen bonds can be an important contributing factor in determining the magnitude of the solvent effects on

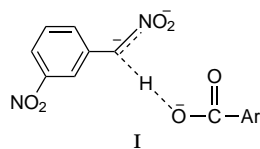
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intrinsic rate constants in proton transfer reactions of carbon acids.



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Supporting Information Available: Nine tables of kinetic data (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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