JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
J. Am. Chem. Soc., 1996, 118(46), 11446-11453, DOI:10.1021/ja961837q

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SUPPORTING INFORMATION

C. F. Bernasconi and P. J. Wenzel, "Kinetics of Proton Transfer from 2-Nitro-4-X-phenylacetonitriles to Piperidine and Morpholine in Aqueous Me_2SO. Solvent and Substituent Effects on Intrinsic Rate Constants. Transition State Imbalances."

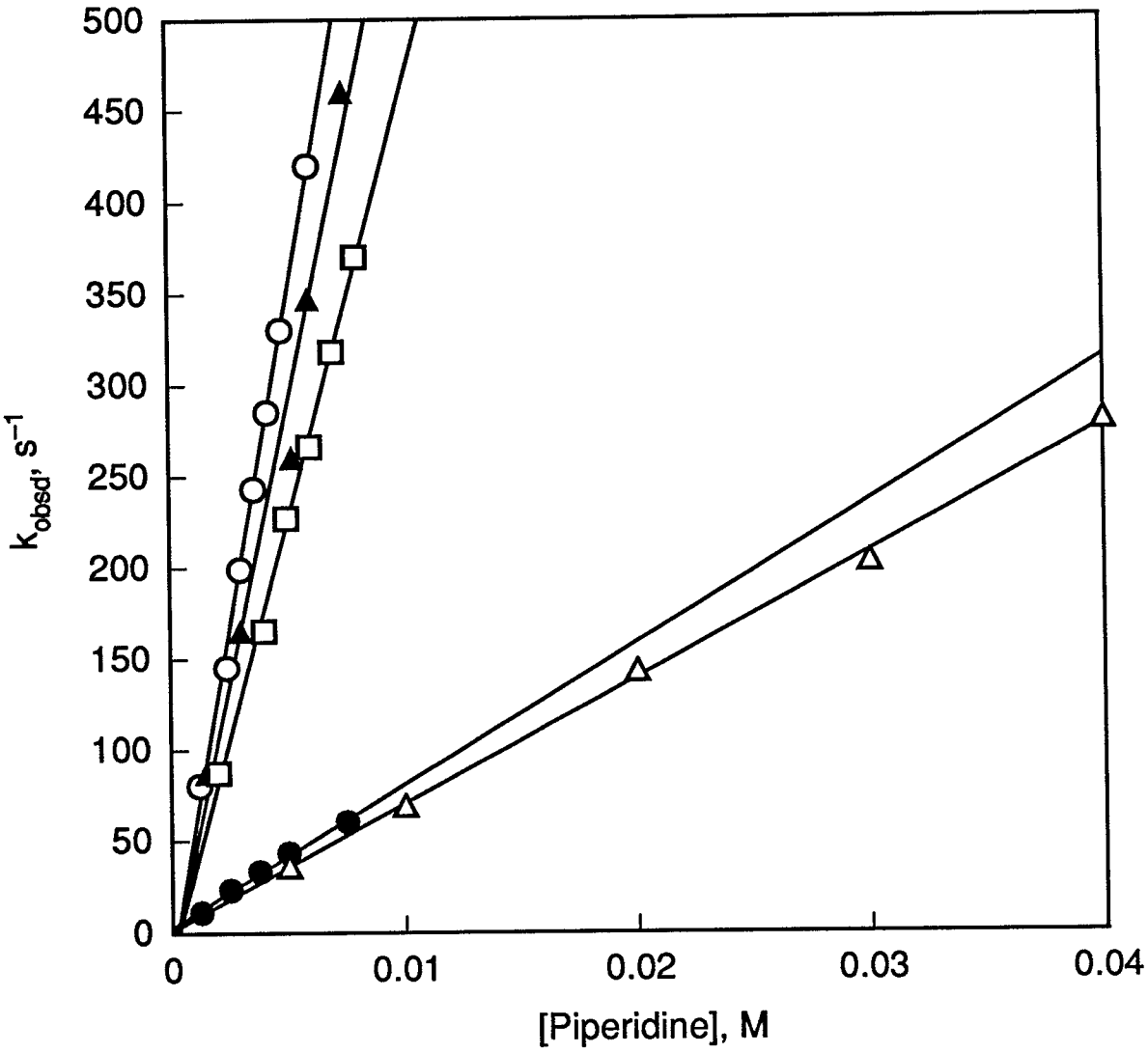

Figure S1: Plots of k_{obsd} versus amine concentration for the reaction of **2-Cl** with piperidine in 90% Me_2SO. O: pH 10.02; ▲: pH 10.12; □: pH 10.21; ●: pH 11.44; Δ: pH 11.74.

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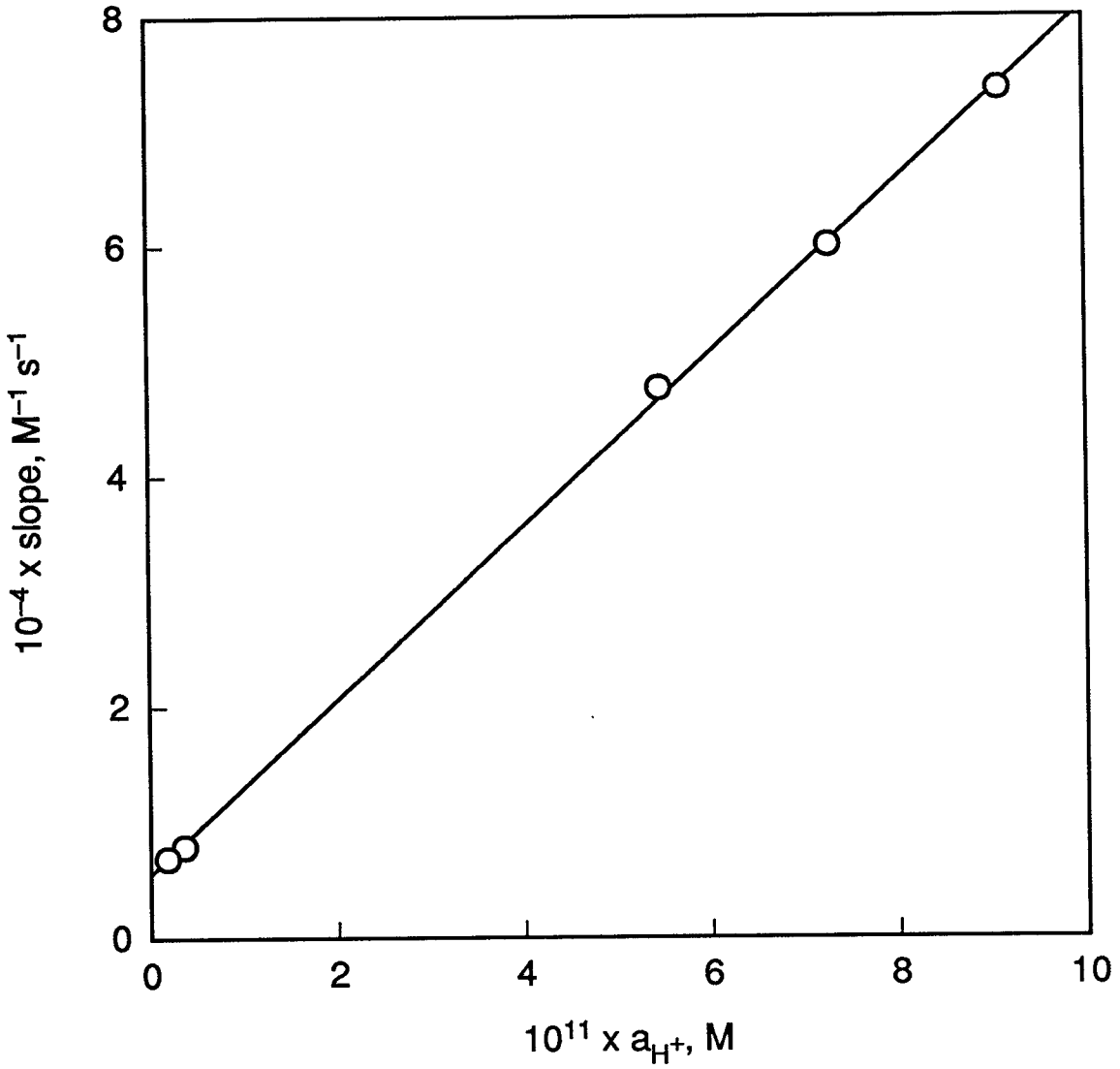

Figure S2. Plot of slope (from Fig. 1S) vs. a_{H+}.

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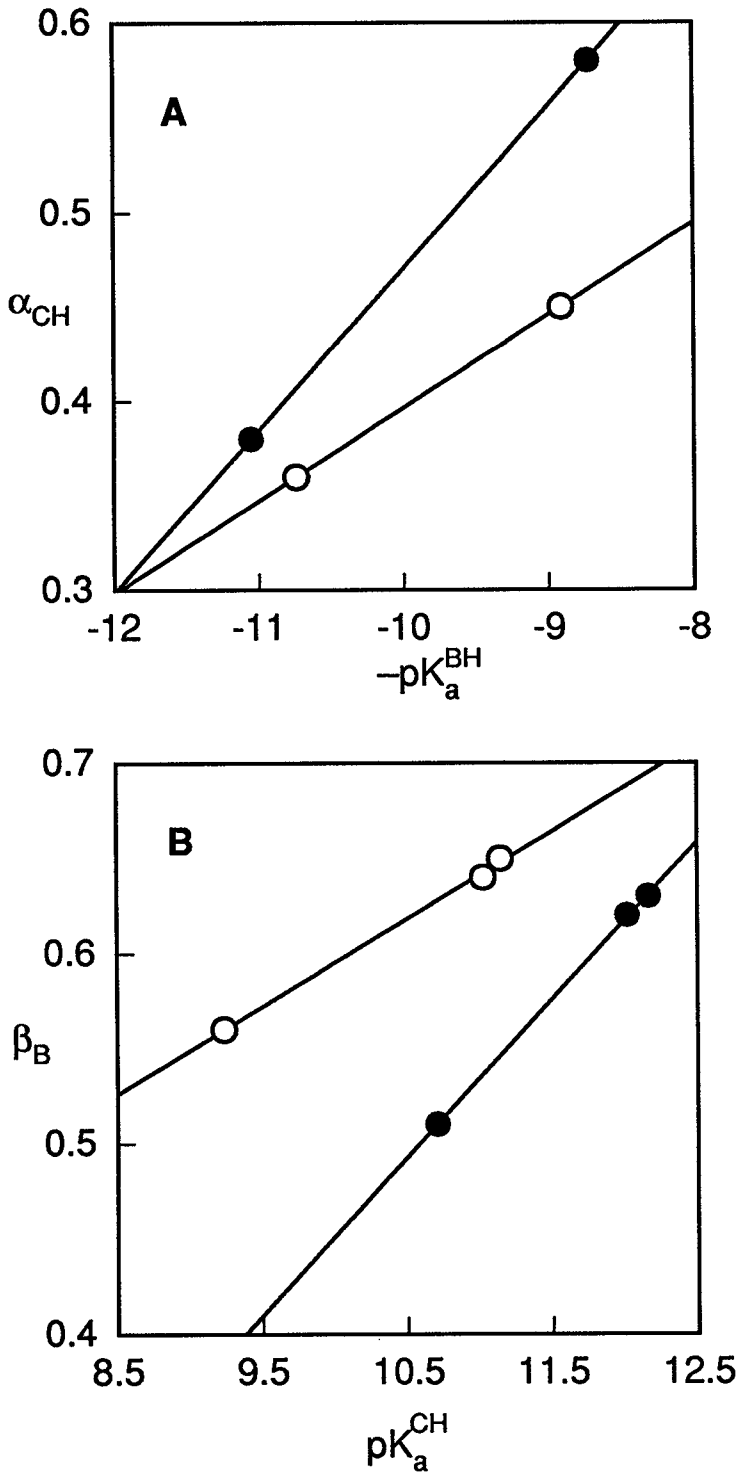

Figure S3. Plots of α_{CH} vs. $-pK_a^{BH}$ (A) and of β_B vs. pK_a^{CH} (B) used to determine p_{xy}. O 90% Me_2SO-10% water; ● 50% Me_2SO-50% water.

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Solvent Effects on Intrinsic Rate Constants: Semi-quantitative Treatment

In a discussion of solvent effects on log k_o, other factors besides delayed carbanion solvation and "classical" solvent effects need to be considered. They include delayed solvation of the developing ammonium ion (protonated amine) and desolvation of the amine and carbon acid that is ahead of proton transfer.[2a,2b] A recently proposed formalism[38] allows at least a semi-quantitative analysis of these factors. It is based on eq 1S. ${}^{I}\delta^{II} \log k_o^{II} = \log k_o(II) - \log k_o(I)$ is

$$ {}^{I}\delta^{II} \log k_o = \delta_{C^-} + \delta_{NH^+} + \delta_{CH} + \delta_N + \delta_{TS} \qquad (1S) $$

the solvent effect on log k_o for the change from solvent I to solvent II; δ_{C^-} is the contribution from the delayed carbanion solvation, δ_{NH^+} the contribution from delayed solvation of the developing ammonium ion, δ_{CH} and δ_N the contributions from desolvation of the carbon acid and amine, respectively, that are ahead of proton transfer; δ_{TS} accounts for all effects not related to late solvation/early desolvation of the various parts of the transition state and consists probably mainly of a "classical" solvent effect.[35]

δ_{C^-}, δ_{NH^+}, δ_{CH} and δ_N can be expressed by eqs S2-S5. $\lambda_{sol}^{C^-}$ is a parameter between 0

$$ \delta_{C^-} = \left(\lambda_{sol}^{C^-} - \beta_B\right)\left(-\log {}^{I}\gamma_{C^-}^{II}\right) \qquad (S2) $$

$$ \delta_{NH^+} = \left(\lambda_{sol}^{NH^+} - \beta_B\right)\left(-\log {}^{I}\gamma_{NH^+}^{II}\right) \qquad (S3) $$

$$ \delta_{CH} = \left(\lambda_{des}^{CH} - \beta_B\right)\log {}^{I}\gamma_{CH}^{II} \qquad (S4) $$

$$ \delta_N = \left(\lambda_{des}^{N} - \beta_B\right)\log {}^{I}\gamma_{N}^{II} \qquad (S5) $$

and 1 that measures the progress in the solvation of the carbanion at the transition state while $\lambda_{sol}^{NH^+}$ is similarly defined and measures the progress of ammonium ion solvation at the transition

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state; λ_{des}^{CH} and λ_{des}^{N} are measures of *de*solvation of the carbon acid and amine, respectively, at the transition state; ${}^{I}\gamma_{N}^{II}$ and ${}^{I}\gamma_{NH^+}^{II}$ are the transfer activity coefficients of the amine and protonated amine, respectively; they are defined in a similar way as ${}^{I}\gamma_{C^-}^{II}$ (eq 4).

Approximate values for δ_N and δ_{NH^+} based on literature data for ${}^{I}\gamma_{N}^{II}$ and ${}^{I}\gamma_{NH^+}^{II}$, and based on an estimated value of $\lambda_{des}^{CH} - \beta_B = -\left(\lambda_{sol}^{NH^+} - \beta_B\right) = 0.09$[2b] are reported in Table S1. They are independent of the specific reaction. Approximate δ_{CH} values can be obtained from $\log {}^{I}\gamma_{CH}^{II}$ determined in this work (Table 2) and using $\lambda_{des}^{CH} - \beta_B = 0.09$,[2b] while δ_{C^-} may be calculated from $-\log {}^{I}\gamma_{C^-}^{II}$ (Table 3) and $\lambda_{sol}^{C^-} - \beta_B \approx (\beta_B)^3 - \beta_B - 0.09$[42] for all reactions except for those of the diketones where $\lambda_{sol}^{C^-} - \beta_B \approx (\beta_B)^3 - \beta_B - 0.09$[42] appears to be a better approximation.[2b] δ_{TS} is then obtained from

$$\delta_{TS} = {}^{I}\delta^{II}\log k_o - \delta_{C^-} - \delta_{NH^+} - \delta_{CH} - \delta_N \qquad \text{(S6)}$$

Table S2 provides a breakdown of all ${}^{I}\delta^{II}\log k_o$ values into the various terms according to eq S1. In view of the fact that the most complete set was obtained for the change from 50% Me_2SO to 90% Me_2SO we shall focus the discussion on this set although the conclusions from the other sets are qualitatively the same.

The following points are noteworthy.

(1) For most reactions, the dominant contributions to the solvent effects come from the δ_{C^-} and δ_{TS} terms, whereas δ_{NH^+}, δ_{CH} and δ_N are of relatively minor importance.

(2) For all reactions except those of the two diketones, δ_{TS} is substantially positive, typically 1.1 ± 0.4 for the change from 50% Me_2SO to 90% Me_2SO, and 1.6 ± 0.8 for the change from water to 90% Me_2SO. The positive δ_{TS} is best understood in terms of preferential solvation of the polarizable transition state by the polarizable Me_2SO. Individual differences among the carbon acids are difficult to interpret; the very low δ_{TS} values for acetylacetone are suspect and might warrant a reinvestigation.

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(3) For all **2-X** as well as for 9-CN-Fl, $[(CO)_3C_6H_5]_2CHCN$ and 9-COOMe-Fl, δ_{C^-} is substantially negative, typically -0.9 ± 0.4 for 50% $Me_2SO \rightarrow$ 90% Me_2SO and -1.35 ± 0.55 for water $\rightarrow$ 90% Me_2SO. Thus the δ_{C^-} term essentially compensates for the δ_{TS} term in these reactions which leads to log k_o values that are rather insensitive to a solvent change.

(4) For the diketones and the nitroalkanes, δ_{C^-} is positive and, in the case of nitromethane, quite large. This, together with a positive δ_{TS} (except in the case of acetylacetone) leads to rather large increases in k_o with increasing Me_2SO content of the solvent, which clearly sets them apart from the first group.

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Table S1. Estimates for δ_N and δ_{NH^+}.[a]

Solvent change	δ_N	δ_{NH^+}
$H_2O \rightarrow 50\%\ Me_2SO$	–0.03	–0.16
$50\%\ Me_2SO \rightarrow 90\%\ Me_2SO$	0.02	—0.09
$H_2O \rightarrow 90\%\ Me_2SO$	–0.01	–0.25

[a]Based on Reference 2b.

Table S2. Breakdown of Solvent Effects on log k_o into Various Contributions According to Equation 9.

CH	β_B[a]	$\lambda_{sol}^{C^-} - \beta_B$[b]	δ_{C^-}	δ_{NH^+}	δ_{CH}	δ_N	δ_{TS}	${}^{I}\delta^{II}$ log k_o
				Water → 50% Me_2SO				
2-NO_2	0.44	–0.44	–0.17	–0.16	–0.04	–0.03	0.31	–0.09
2-SO_2CH_3	0.43	–0.44	–0.27	–0.16	–0.07	–0.03	0.53	0.00
2-CN	0.45	–0.45	–0.30	–0.16	–0.06	–0.03	0.50	–0.05
9-CN-Fl[d]	0.50	–0.47	–0.64	–0.16	–0.15	–0.03	1.12	0.14
1,3-indandione[d]	0.40	–0.33[c]	0.14	–0.16	–0.04	–0.03	0.25	0.16
$CH_2(COCH_3)_2$	0.40	–0.33[c]	0.78	–0.16	0.02	–0.03	–0.46	0.15
$PhCH_2NO_2$	0.50	–0.47	0.94	–0.16	–0.10	–0.03	0.32	0.97
CH_3NO_2	0.60	–0.47	1.36	–0.16	–0.03	–0.03	0.16	1.32
				50% Me_2SO → 90% Me_2SO				
2-NO_2	0.52	–0.47	–0.91	–0.09	–0.09	0.02	0.85	–0.22
2-SO_2CH_3	0.50	–0.47	–0.65	–0.09	–0.11	0.02	0.87	0.04
2-CN	0.49	–0.46	–0.51	–0.09	–0.05	0.02	0.72	0.09
2-CF_3	0.53	–0.47	–1.15	–0.09	–0.19	0.02	1.49	0.08
2-Br	0.63	–0.47	–0.86	–0.09	–0.18	0.02	1.30	0.19

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Table S2, continued

2-Cl	0.64	–0.47	–0.78	–0.09	–0.16	0.02	1.20	0.19
9-CN-Fl	0.53	–0.47	–1.25	–0.09	–0.20	0.02	1.33	–0.19
$[(CO)_3C_6H_5]_2CHCN$	0.68	–0.45	<–1.22	–0.09	<–0.23	0.02	>1.20	–0.32
9-COOMe-Fl	0.55	–0.47	–1.00	–0.09	–0.20	0.02	1.52	0.25
1,3-indandione	0.44	–0.34[c]	0.47	–0.09	–0.11	0.02	0.43	0.72
$CH_2(COCH_3)_2$	0.47	–0.34[c]	0.91	–0.09	–0.04	0.02	0.09	0.89
$PhCH_2NO_2$	0.61	–0.47	0.99	–0.09	–0.16	0.02	1.24	2.00
CH_3NO_2	0.66	–0.46	1.76	–0.09	–0.07	0.02	0.71	2.33
			Water → 90% Me_2SO					
2-NO_2	0.47	–0.46	–1.17	–0.25	–0.15	–0.01	1.27	–0.31
2-SO_2CH_3	0.47	–0.46	–0.92	–0.25	–0.19	–0.01	1.41	0.04
2-CN	0.48	–0.46	–0.82	–0.25	–0.05	–0.01	1.17	0.04
9-CN-Fl[e]	0.56	–0.47	–1.89	–0.25	–0.35	–0.01	2.45	–0.05
1,3-indandione[e]	0.44	–0.34[c]	0.61	–0.25	–0.15	–0.01	0.67	0.88
$CH_2(COCH_3)_2$	0.44	–0.34[c]	1.71	–0.25	–0.02	–0.01	–0.39	1.04
$PhCH_2NO_2$	0.59	–0.47	1.91	–0.25	–0.26	–0.01	1.57	2.97
CH_3NO_2	0.64	–0.47	3.15	–0.25	–0.08	–0.01	0.84	3.65

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Table S2, continued

[a]Average value for the two solvents. [b]$\lambda_{sol}^{C^-} - \beta_B = (\beta_B)^3 - 0.09 - \beta_B$, see text. [c]$\lambda_{sol}^{C^-} - \beta_B = (\beta_B)^2 - 0.09 - \beta_B$, see text. [d]10% Me_2SO → 50% Me_2SO. [e]10% Me_2SO → 90% Me_2SO.

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