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Proton Transfer from Carbon Acids to Carbanions. 1. Reactions of Various Carbon Acids with the Anions of Substituted Benzylmalononitriles in 90% Me$_2$SO–10% Water. Determination of Intrinsic Barriers of Identity Reactions from the Marcus Relationship

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Abstract: A kinetic study of the reversible deprotonation of 9-cyanofluorene (**2**), 1,3-indandione (**3**), 4-nitrophenylacetonitrile (**4**), (3-nitrophenyl)nitromethane (**5**), and (4-nitrophenyl)nitromethane (**6**) by the anions of substituted benzylmalononitrile (**1-X$^-$**) in 90% Me$_2$SO–10% water (v/v) at 20 °C is reported. Intrinsic rate constants and intrinsic barriers of these reactions have been determined by extrapolation or interpolation of Brønsted plots whose slopes (β) are all close to 0.5. Intrinsic barriers of the identity reactions CH + C$^-$ $\rightleftarrows$ C$^-$ + CH (CH = **2**, **3**, **4**, and phenylnitromethane) have been estimated on the basis of the Marcus equation, coupled with either a plausible value for the identity barrier of the reaction AH$^+$ + A $\rightleftarrows$ A + AH$^+$ (A = piperidine or morpholine) ("amine method") or a plausible value for the identity barrier of the reaction **2** + **2$^-$** $\rightleftarrows$ **2$^-$** + **2** ("9-cyanofluorene method"). There are discrepancies in the identity barriers for CH + C$^-$ $\rightleftarrows$ C$^-$ + CH (CH = **2**, **3**, **4**, and phenylnitromethane) calculated by the two methods. Possible reasons for these discrepancies and the significance of the results in terms of the validity and scope of the Marcus equation are discussed.

Proton transfer is one of the most important elementary reactions in chemistry and, not surprisingly, it is also one of the most thoroughly studied processes. Numerous reviews that deal mainly with proton transfers in solution have appeared over the years.[1–10] There has also been a growing interest in the study of proton transfers in the gas phase[11–16] and in the quantum chemical calculations of these processes.[17–22]

The focus of this paper is on proton transfer from carbon acids to carbanions in solution. In hydroxylic solvents, it is virtually impossible to measure the kinetics of such reactions because their rates are too slow to compete with the proton transfer to or from the solvent, the lyate, and the lyonium ion. Even with HCN, a carbon acid that comes very close to behaving like a normal acid, only an upper limit for its deprotonation rate constant by CN$^-$ could be obtained in aqueous solution.[23]

In nonhydroxylic solvents, the proton transfer between a carbon acid and a carbanion is, in principle, easily measured, but the number of reports of such measurements is surprisingly small. Ritchie[24] determined the rate constants for the reversible proton transfer between aromatic hydrocarbons and anions of such hydrocarbons in Me$_2$SO, e.g., fluorene with 9-methylfluorenyl anion, 9-cyanofluorene with carbomethoxyfluorenyl anion, etc. Wong and Smid[25] reported data on the former reaction in THF, tetrahydropyran, and 1,2-dimethoxyethane in the presence of crown ether. Bordwell et al.[26] measured rates for the deprotonation of 3-butenenitrile by a variety of carbanions, mainly substituted fluorenyl ions, in Me$_2$SO. Murdoch et al.[27] determined the proton-transfer kinetics between 9-alkylfluorenes and (9-alkylfluorenyl)lithium in ether and attempted to interpret their results within the framework of Marcus[28,29] theory. However,

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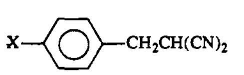
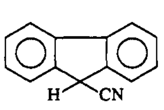
ion-pairing effects in this very nonpolar solvent play a major role which seems to grossly distort the intrinsic barriers[28,29] compared to what one would expect for the reaction of free ions.

The present paper reports a study of the reversible proton-transfer kinetics between the anions of phenyl-substituted benzylmalononitriles (**1-X**) and various carbon acids such as 9-cyanofluorene (**2**), 1,3-indandione (**3**), 4-nitrophenylacetonitrile (**4**), (3-nitrophenyl)nitromethane (**5**), and (4-nitrophenyl)nitromethane (**6**) in 90% Me_2SO–10% water (v/v) at 20 °C. Our main objective was to determine intrinsic rate constants or intrinsic barriers of these reactions, to correlate them with those for the reaction of the same carbon acids with "normal" (oxygen or nitrogen) bases, and to test for possible adherence to Marcus[28,29] rate theory. For the purposes of this paper, the intrinsic rate constant k_o, for reaction 1 is defined as $k_1/q = k_{-1}/p$ when $pK_a^{BH} - pK_a^{CH} + \log p/q = 0$ where CH is the carbon acid, B^- is the buffer base (may also be a carbanion), q is number of equivalent basic sites on B^- and p is number of equivalent protons on BH; the intrinsic barrier, $\Delta G_0^\ddagger$ is defined as the free energy of activation corresponding to k_o.



1-X



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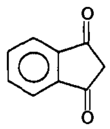

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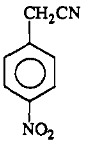

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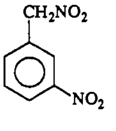

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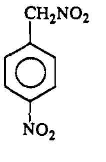

6

$$\mathrm{CH} + \mathrm{B}^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{C}^- + \mathrm{BH} \tag{1}$$

A determination of the proton-transfer kinetics between **4** and the secondary cyclic amines piperidine and morpholine in 90% Me_2SO–10% water is also reported. These experiments serve to fill a gap in our data base on reactions of carbon acids with nitrogen bases.

Results

When studying the kinetics of the reaction of carbon acids with normal bases such as oxyanions or amines, the most convenient method is to use a mixture of the normal base and its conjugate acid (buffer) in large excess over the C-H acid (substrate) and monitor the reaction spectrophotometrically. The same method was applied here with the benzylmalononitriles being assigned the role of the buffer. The reaction scheme may then be described by eq 2.

$$\mathrm{CH} \underset{k_{-1}^{\mathrm{H}}a_{\mathrm{H}^+} + k_{-1}^{\mathrm{H_2O}} + k_{-1}^{\mathrm{BH}}[\mathrm{BH}]}{\overset{k_1^{\mathrm{H_2O}} + k_1^{\mathrm{OH}}a_{\mathrm{OH}^-} + k_1^{\mathrm{B}}[\mathrm{B}^-]}{\rightleftarrows}} \mathrm{C}^- \tag{2}$$

The reciprocal relaxation time for reaction 2 is given by

$$\frac{1}{\tau} = k_1^{\mathrm{H_2O}} + k_1^{\mathrm{OH}}a_{\mathrm{OH}^-} + k_{-1}^{\mathrm{H}}a_{\mathrm{H}^+} + k_{-1}^{\mathrm{H_2O}} + k_1^{\mathrm{B}}[\mathrm{B}^-] + k_{-1}^{\mathrm{BH}}[\mathrm{BH}] \tag{3}$$

The choice of solvent for this study, 90% Me_2SO–10% water (v/v), was dictated by several considerations. The first was to minimize the terms involving reaction with water, H^+, and OH^-. The second was to be able to do pH measurements in a convenient manner. The third was the availability of a data base for reactions of our substrates with normal bases[8,30-32] with which we could compare our results.

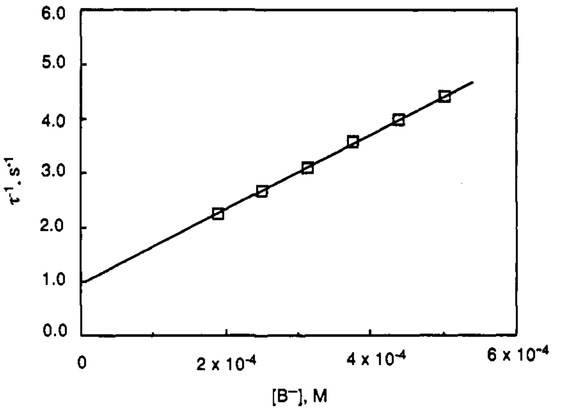

Figure 1. Buffer plot for the reaction of 1,3-indandione (**3**) with B^- = **1-OMe**$^-$ at pH 10.53.

In all cases, $k_1^B[B^-] + k_{-1}^{BH}[BH]$ was significant compared to the other terms in eq 3 and in several instances, these latter terms were actually virtually negligible, i.e., the intercepts of plots of τ^{-1} vs $[B^-]$ or [BH] were small or essentially zero. The slopes of these plots, given by eq 4 when plotting τ^{-1} vs $[B^-]$ or by eq 5 when plotting τ^{-1} vs [BH], were determined at several (usually four) buffer ratios. In a few situations, where the pK_a values of CH and BH were close, both k_1^B and k_{-1}^{BH} could be determined directly from the pH dependence of the slopes. However, the most common situation was that $pK_a^{BH} >(\gg)\ pK_s^{CH}$, so that eq 4 simplifies to slope = k_1^B. In these cases, k_{-1}^{BH} was obtained as $k_{-1}^{BH} = k_1^B K_a^{BH}/K_a^{CH}$.

$$\text{slope} = \left(k_1^{\mathrm{B}} + k_{-1}^{\mathrm{BH}}\frac{a_{\mathrm{H}^+}}{K_a^{\mathrm{BH}}}\right) \tag{4}$$

$$\text{slope} = \left(k_1^{\mathrm{B}}\frac{K_a^{\mathrm{BH}}}{a_{\mathrm{H}^+}} + k_{-1}^{\mathrm{BH}}\right) \tag{5}$$

The ionic strength was kept constant at 0.06 M with KCl in all experiments. In choosing a suitable range of buffer concentrations, a compromise had to be sought between maintaining pseudo-first-order conditions and avoiding high concentrations that would lead to buffer association. Such buffer association which is most likely due to the formation of homoconjugate pairs, $BH \cdot B^-$, manifested itself as downward curvature of plots of τ^{-1} vs $[B^-]$ or [BH]. Thus, total buffer concentration was typically varied between 4×10^{-4} and 3×10^{-3} M while the substrate concentration was 2-5 $\times 10^{-5}$ M. Under these conditions, plots of τ^{-1} vs $[B^-]$ or [BH] were strictly linear. Representative plots are shown in Figure 1 for the reaction of 1,3-indandione with *p*-(dimethylamino)benzylmalononitrile anion, in Figure 2 for the reaction of (*p*-nitrophenyl)nitromethane with benzylmalononitrile anion, and in Figure 3 for the reaction of *p*-nitrophenylacetonitrile with *p*-(dimethylamino)acetonitrile anions. The raw data are summarized elsewhere[33] while the rate constants are reported in Table I.

The procedures for determining the rates of the reactions of 4-nitrophenylacetonitrile with piperidine and morpholine were quite similar to those described for the benzylmalononitrile buffers. With each amine, the reaction was run at three different buffer

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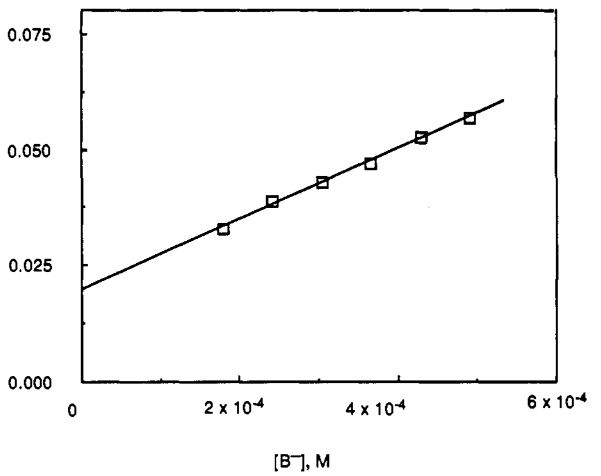

Figure 2. Buffer plot for the reaction of (4-nitrophenyl)nitromethane (**6**) with $B^- = \mathbf{1}\text{-}NMe_2^-$ at pH 11.30.

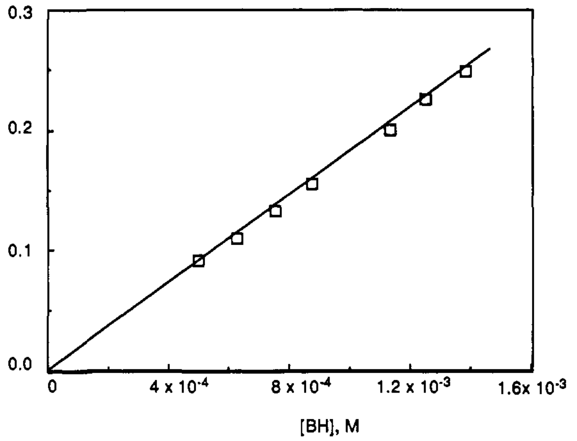

Figure 3. Buffer plot for the reaction of 4-nitrophenylacetonitrile anion ($\mathbf{4}^-$) with BH = **1**-NMe$_2$ at pH 11.30.

ratios (1:4, 1:1, 4:1). The rate constants are included in Table I, while the raw data are summarized elsewhere.[33]

The pK_a values of various benzylmalononitriles, (4-nitrophenyl)- and (3-nitrophenyl)nitromethane, and 4-nitrophenylacetonitrile were determined by standard spectrophotometric procedures using piperidine, *n*-butylamine, 2-methoxyethylamine, morpholine, acetate, and methoxyacetate buffers as appropriate. They are summarized in Table I. The pK_a^{CH} values of 1,3-indandione[30] and 9-cyanofluorene[31] were available from previous studies.

Discussion

With **3**, **5**, and **6**, rate constants were determined with four benzylmalononitrile buffers, allowing the construction of Brønsted plots. These plots are shown in Figure 4. The Brønsted β values which are summarized in Table II are all 0.5; the same is true for β calculated from two-point Brønsted plots for **2** and **4**. The Brønsted plots also allow the determination of the intrinsic rate constants or intrinsic barriers; log k_0 and $\Delta G_0^\ddagger$ values are reported in Table III. We shall discuss these latter first.

Intrinsic Rate Constants. Intrinsic rate constants and intrinsic barriers for some of the reactions of **2**-**6** with carboxylate ions and the piperidine/morpholine pair have been determined previously[8,30-32] and are included in Table III. Data for the reactions of **5** and **6** with these latter bases are not available, but log k_0 or $\Delta G_0^\ddagger$ for the reaction of the unsubstituted phenylnitromethane (**7**) are known. It would have been desirable to determine log k_0 or $\Delta G_0^\ddagger$ for the reaction of **7** with benzylmalononitrile anions, so as to have a better basis for comparison with

Table I. Summary of Rate Constants of Reactions of Various Carbon Acids with 4-X-$C_6H_4CH_2C(CN)_2^-$, and of 4-Nitrophenylacetonitrile with Piperidine and Morpholine, in 90% Me$_2$SO–10% Water (v/v) at 20 °C[a]

X	pK_a^{BH}	k_1^B (M^{-2} s^{-1})	k_{-1}^{BH} (M^{-1} s^{-1})
	9-Cyanofluorene, **2** (pK_a^{CH} = 8.01)		
Cl	10.37	7.60×10^3	33.2
Me$_2$N	11.30	2.24×10^4	11.5
	1,3-Indandione, **3** (pK_a^{CH} = 7.82)		
Cl	10.37	3.30×10^3	9.30
H	10.70	4.90×10^3	6.45
MeO	11.01	7.01×10^3	4.52
Me$_2$N	11.30	9.90×10^3	3.28
	4-Nitrophenylacetonitrile, **4** (pK_a^{CH} = 12.03)		
Cl	10.37	9.61	4.39×10^2
Me$_2$N	11.30	28.0	1.51×10^2
morpholine	8.91	1.03×10^2	1.36×10^5
piperidine	10.74	1.67×10^3	3.26×10^4
	(3-Nitrophenyl)nitromethane, **5** (pK_a^{CH} = 8.63)		
Cl	10.37	15.4	2.79×10^{-1}
H	10.70	22.7	1.93×10^{-1}
MeO	11.01	32.7	1.36×10^{-1}
Me$_2$N	11.30	45.0	9.62×10^{-2}
	(4-Nitrophenyl)nitromethane, **6** (pK_a^{CH} = 7.49)		
Cl	10.37	50.6	6.67×10^{-2}
H	10.70	73.8	4.55×10^{-2}
MeO	11.01	1.06×10	3.20×10^{-2}
Me$_2$N	11.30	1.49×10^2	2.31×10^{-2}

[a] μ = 0.06 M (KCl). Estimated errors in the pK_a^{CH} and pK_a^{BH} values ±0.03 or better; estimated error in the rate constant ±10% or better.

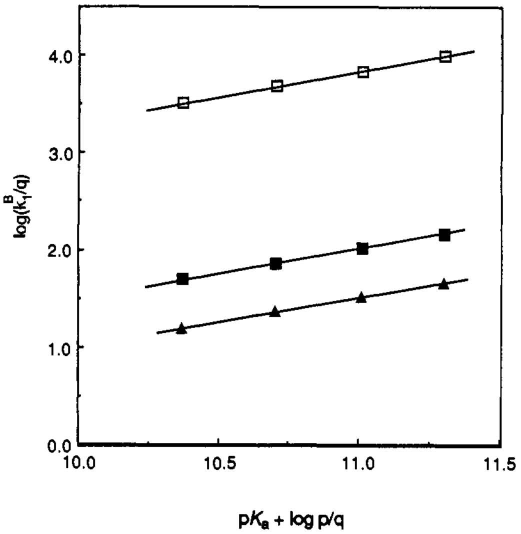

Figure 4. Brønsted plots for the reactions of 1,3-indandione (**3**), (3-nitrophenyl)nitromethane (**5**) and (4-nitrophenyl)nitromethane (**6**) with **1**-X$^-$ (X = H, Cl, OMe, NMe$_2$). Note that $p = q = 1$.

the reactions of **7** with carboxylate ions and the piperidine/morpholine pair. However, spectral overlap between the anion of **7** and the benzylmalononitrile anions precluded such experiments, and thus **5** and **6** were studied instead, based on the assumption that log k_0 and $\Delta G_0^\ddagger$ for **7** would be similar to the corresponding parameters for **5** and/or **6**, and could be estimated from these latter values (see below).

The most significant feature of the present results is that all log k_0 values for the reactions with **1**-X$^-$ are significantly lower (the $\Delta G_0^\ddagger$ values significantly higher) than those for the reactions with RCOO$^-$ or amines and that the rank order in log k_0 (**2** > **3** > **4** ≫ **5** ≃ **6**) is preserved. In fact, the differences between log k_0(pip/mor) and log(**1**-X$^-$) or between $\Delta G_0^\ddagger$(pip/mor) and $\Delta G_0^\ddagger$(**1**-X$^-$) are remarkably constant, as shown in the columns labeled Δlog k_0 and $\Delta\Delta G_0^\ddagger$, respectively (Table III), with an

Table II. Brønsted β Values for the Deprotonation of **2–6** by the Anions of Benzylmalononitriles and Other Bases in 90% Me_2SO–10% Water at 20 °C

substrate	β(**1-X**$^-$)[a]	β($RCOO^-$)	β(pip/mor)	β($1°RNH_2$)
9-cyanofluorene (**2**)	0.51 ± 0.03		≈0.54[c]	0.58 ± 0.04[c]
1,3-indandione (**3**)	0.51 ± 0.02	0.74 ± 0.01[b]	0.47 ± 0.03[b]	0.52 ± 0.02[b]
4-nitrophenylacetonitrile (**4**)	0.50 ± 0.03		0.66 ± 0.03[a]	
(3-nitrophenyl)nitromethane (**5**)	0.50 ± 0.02			
(4-nitrophenyl)nitromethane (**6**)	0.51 ± 0.02)			
phenylnitromethane (**7**)		0.75 ± 0.02[d]	0.69 ± 0.03[d]	0.65 ± 0.02[d]

[a] This work. [b] Reference 30. [c] Reference 31. [d] Reference 32.

Table III. Intrinsic Rate Constants (log k_0) and Intrinsic Barriers ($\Delta G_0^{\ddagger}$) for the Deprotonation of **2–6** by the Anions of Benzylmalononitriles (**1-X**$^-$) and Other Bases in 90% Me_2SO–10% Water at 20 °C

	1-X$^-$		$RCOO^-$		pip/mor			
substrate	log k_0	$\Delta G_0^{\ddagger}$ (kcal/mol)	log k_0	$\Delta G_0^{\ddagger}$ (kcal/mol)	log k_0	$\Delta G_0^{\ddagger}$ (kcal/mol)	Δlog k_0	$\Delta\Delta G_0^{\ddagger}$ (kcal/mol)
9-cyanofluorene (**2**)	2.70	13.46			~4.39	~11.21	~−1.69	~2.25
1,3-indandione (**3**)	2.21	14.12	4.53	11.02	3.85	11.92	−1.64	2.20
4-nitrophenylacetonitrile (**4**)	1.87	14.57			3.84	11.94	−1.97	2.63
(3-nitrophenyl)nitromethane (**5**)	0.32	16.63						
(4-nitrophenyl)nitromethane (**6**)	0.24	16.74						
$PhCH_2NO_2$ (**7**)	~−0.02[a]	~17.08[a]	1.88	14.55	1.75	14.72[a]	~−1.77	~2.36[a]

[a] Based on the assumption that Δlog k_0 = −1.77 ($\Delta\Delta G_0^{\ddagger}$ = 2.36 kcal/mol), which is the average for **2–4**, see text.

average Δlog k_o of −1.77 and a maximum variation of 0.33 log unit (average $\Delta\Delta G_0^{\ddagger}$ = 2.36 kcal/mol, maximum variation of 0.43 kcal/mol) for **2-4**.

In estimating log k_o for **7**, one may add the above calculated average Δlog k_o (−1.77) to log k_o for the reaction of **7** with the piperidine/morpholine pair, which yields log k_o = −0.02 ($\Delta G_0^{\ddagger}$ = 17.08 kcal/mol). The resulting estimate is qualitatively reasonable because log k_o for the nitrosubstituted phenylnitromethanes is expected to be somewhat higher than that for the unsubstituted one, due to the electron-withdrawing polar effect of the nitro groups;[8b,34] the slightly lower log k_o for the *p*-nitro compared to the *m*-nitro compound is attributable to a k_o-lowering resonance effect.[8b,34,35]

Correlation with Marcus Theory. As we will show, the fact that log k_o for the reactions of **2-7** with **1-X**$^-$ is lower ($\Delta G_0^{\ddagger}$ is higher) than that for the reactions with normal bases such as carboxylate ions or amines and that Δlog k_o or $\Delta\Delta G_0^{\ddagger}$ is approximately constant is a reasonable result that can be understood in the context of Marcus theory. Marcus theory was originally developed for outer-sphere electron transfers.[28] Subsequently, the rate-equilibrium *formalism*[36] of the Marcus theory was extended to proton,[28c,29,37] hydride,[28c,38] and methyl transfer[39] reactions. The extension of this formalism to hydride and methyl transfers has been remarkably successful, but in the case of proton transfers, the absence of systematic data has thus far precluded an assessment of the validity of Marcus theory for these reactions.

According to Marcus, the observed barrier of a proton transfer may be expressed as

$$\Delta G^{\ddagger}(\text{obsd}) = w_r + \left\{1 + \frac{\Delta G^{\circ}(\text{obsd}) - w_r + w_p}{4\Delta G_0^{\ddagger}}\right\}^2 \Delta G_0^{\ddagger} \quad (6)$$

where w_r and w_p are work terms for assembling the reactant and product precursor complexes, respectively (eq 7), ΔG° is the free energy of conversion of the reactant precursor complex into the product precursor complex, ΔG°(obsd) is the observed free energy of the reaction (ΔG°(obsd) = $\Delta G^{\circ} + w_r - w_p$), and $\Delta G_0^{\ddagger}$ is the intrinsic barrier for the interconversion of the two precursor complexes. For proton transfers at carbon, the work terms are

$$CH + B^- \overset{w_r}{\rightleftarrows} CH{\cdot}B^- \overset{\Delta G^{\circ}}{\rightleftarrows} C^-{\cdot}HB \underset{w_p}{\rightleftarrows} C^- + HB \quad (7)$$

frequently neglected[3,29b,37] (more on this below) which reduces eq 6 to

$$\Delta G^{\ddagger}(\text{obsd}) = \left(1 + \frac{\Delta G^{\circ}(\text{obsd})}{4\Delta G_0^{\ddagger}}\right)^2 \Delta G_0^{\ddagger} \quad (8)$$

Equation 6 or 8 may be used to calculate $\Delta G_0^{\ddagger}$ from observed $\Delta G^{\ddagger}$ and ΔG° values, but we generally prefer to calculate $\Delta G_0^{\ddagger}$ from log k_o obtained by interpolation or extrapolation of Brønsted plots.[8,30–32,34]

More pertinent to the present study is the Marcus relation (eq 9) between the intrinsic barrier of a reaction such as eq 7 and the intrinsic barriers of the corresponding identity reactions (eqs 10 and 11, precursor complexes not shown). We shall use the designation CH/C$^-$ for our substrates **2-7** and BH/B$^-$ for our benzylmalononitrile buffers (**1-X**).

$$\Delta G_0^{\ddagger}(CH/B^-) = {}^1/_2\{\Delta G_0^{\ddagger}(CH/C^-) + \Delta G_0^{\ddagger}(BH/B^-)\} \quad (9)$$

$$CH + C^- \rightleftarrows C^- + CH \quad (10)$$

$$BH + B^- \rightleftarrows B^- + BH \quad (11)$$

In a similar way, one can write eqs 12 and 13 for the intrinsic barriers referring to reactions 14 and 15 where A is an amine (piperidine/morpholine) and $\Delta G_0^{\ddagger}(AH^+/A)$ is the intrinsic barrier for the identity reaction 16.

$$\Delta G_0^{\ddagger}(CH/A) = {}^1/_2\{\Delta G_0^{\ddagger}(CH/C^-) + \Delta G_0^{\ddagger}(AH^+/A)\} \quad (12)$$

$$\Delta G_0^{\ddagger}(BH/A) = {}^1/_2\{\Delta G_0^{\ddagger}(BH/B^-) + \Delta G_0^{\ddagger}(AH^+/A)\} \quad (13)$$

Since the proton transfer from nitrogen to nitrogen is generally very fast and much faster than proton transfers at carbon,[1–7] we have $\Delta G_0^{\ddagger}(AH^+/A) < \Delta G_0^{\ddagger}(BH/B^-)$ and $\Delta G_0^{\ddagger}(AH^+/A) < \Delta G_0^{\ddagger}(CH/C^-)$. Furthermore, one expects $\Delta G_0^{\ddagger}(CH/C^-)$ to be

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(34) (a) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301. (b) Bernasconi, C. F. *Adv. Phys. Org. Chem.* **1992**, *27*, 119.

(35) Keeffe, J. R.; Morey, J.; Palmer, C. A.; Lee, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1295.

(36) The actual Marcus *theory*[28] only applies to electron transfer.

(37) Keeffe, J. R.; Kresge, A. J. In *Investigation of Rates and Mechanisms of Reactions, Part I*; Bernasconi, C. F., Ed.; Wiley-Interscience: New York, 1986; p 747.

(38) (a) Kreevoy, M. M.; Lee, I.-S. *J. Am. Chem. Soc.* **1984**, *106*, 2550. (b) Kreevoy, M. M.; Ostović, D.; Lee, I.-S.; Binder, D. A.; King, G. *J. Am. Chem. Soc.* **1988**, *110*, 524.

(39) (a) Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978**, *16*, 87. (b) Lewis, E. S.; Hu, D. D. *J. Am. Chem. Soc.* **1984**, *106*, 3292.

$$\mathrm{CH + A \rightleftarrows C^- + AH^+} \tag{14}$$

$$\mathrm{BH + A \rightleftarrows B^- + AH^+} \tag{15}$$

$$\mathrm{AH^+ + A \rightleftarrows A + AH^+} \tag{16}$$

higher than $\Delta G_0^\ddagger(\mathrm{BH/B^-})$ because there is more resonance stabilization in $\mathrm{C^-}$ (anions of **2-7**) than in $\mathrm{B^-}$ (anions of **1-X**), a factor which is known to increase the intrinsic barrier of proton transfers.[8b,34] From $\Delta G_0^\ddagger(\mathrm{CH/C^-}) > \Delta G_0^\ddagger(\mathrm{BH/B^-})$, $\Delta G_0^\ddagger(\mathrm{CH/C^-}) > \Delta G_0^\ddagger(\mathrm{AH^+/A})$, and eqs 9 and 12, it follows immediately that $\Delta G_0^\ddagger(\mathrm{CH/B^-})$ is larger than $\Delta G_0^\ddagger(\mathrm{CH/A})$ and that $\Delta\Delta G_0^\ddagger$ in Table III is given by eq 17.

$$\Delta\Delta G_0^\ddagger = \Delta G_0^\ddagger(\mathrm{CH/B^-}) - \Delta G_0^\ddagger(\mathrm{CH/A}) = {}^1/_2\{\Delta G_0^\ddagger(\mathrm{BH/B^-}) - \Delta G_0^\ddagger(\mathrm{AH^+/A}\} \tag{17}$$

The Marcus equations (eqs 9, 12, 13) seem intuitively reasonable and are, at least in a qualitative sense, supported by our results. However, as mentioned above, there is a lack of data in the literature that probe their *quantitative* accuracy.[41] By determining the intrinsic barriers of a large number of reactions that are interrelated, one may be able to test the quantitative validity of these equations.

One possible approach is to estimate the intrinsic barrier of the identity reaction 16 from literature data which then allows calculation of the intrinsic barriers of all the other identity reactions. This will be referred to as the "amine method" (see Table IV). $\Delta G_0^\ddagger(\mathrm{AH^+/A})$ may be estimated on the basis of Grunwald's[43] study of the $\mathrm{(CH_3)_2NH_2^+/(CH_3)_2NH}$ system. In water, the direct proton transfer has a rate constant of $\sim 5 \times 10^7$ $\mathrm{M^{-1}\,s^{-1}}$, while the proton transfer involving a water bridge proceeds with a rate constant of 9.9×10^8 $\mathrm{M^{-1}\,s^{-1}}$. In the absence of data in 90% $\mathrm{Me_2SO}$–10% water, we shall assume that the first rate constant remains about the same while the second one decreases about 5-fold, to $\sim 2 \times 10^8$ $\mathrm{M^{-1}\,s^{-1}}$. It is not entirely clear whether $\Delta G_0^\ddagger(\mathrm{AH^+/A})$ should be calculated on the basis of the rate constant for the direct transfer or on the basis of the sum of the two rate constants. Inasmuch as proton transfers between carbon and oxygen or nitrogen are direct,[7,44–46] the former method of calculating $\Delta G_0^\ddagger(\mathrm{AH^+/A})$ seems more reasonable and will be adopted here. It provides $\Delta G_0^\ddagger(\mathrm{AH^+/A}) \approx 6.8$ kcal/mol, or $\log k_o(\mathrm{AH^+/A}) \approx 7.7$.

Inserting this value for $\Delta G_0^\ddagger(\mathrm{AH^+/A})$ into eq 17 and using the average value of 2.36 kcal/mol for $\Delta\Delta G_0^\ddagger$, based on the reactions of **2-4** with **1-X**$^-$, yields $\Delta G_0^\ddagger(\mathrm{BH/B^-}) = 11.5$ kcal/mol, or $\log k_o(\mathrm{BH/B^-}) = 4.16$. One may now also estimate $\Delta G_0^\ddagger(\mathrm{CH/C^-})$ for **2-7** by means of eq 9. These estimates are summarized in Table IV under "amine method."

An alternative approach to the calculation of the intrinsic barriers and intrinsic rate constants of the various identity reactions can be based on the reaction of 9-cyanofluorene, **2**, with the anion of 9-carbomethoxyfluorene,[31] **8**, ($\log k_o(\mathbf{2}/\mathbf{8}^-) = 2.53$, $\Delta G_0^\ddagger(\mathbf{2}/\mathbf{8}^-) = 13.69$ kcal/mol), the reaction of **2** with primary aliphatic amines[31] ($\log k_o(\mathbf{2}/\mathrm{A}) = 3.57$, $\Delta G_0^\ddagger(\mathbf{2}/\mathrm{A}) = 12.30$ kcal/mol), and the reaction of **8** with the same primary aliphatic amines[31] ($\log k_o(\mathbf{8}/\mathrm{A}) = 3.09$, $\Delta G_0^\ddagger(\mathbf{8}/\mathrm{A}) = 12.94$ kcal/mol). It is easily shown[47] that $\Delta G_0^\ddagger(\mathbf{2}/\mathbf{2}^-)$ is given by eq 18, which yields $\Delta G_0^\ddagger(\mathbf{2}/\mathbf{2}^-) = 13.05$ kcal/mol and $\log k_o(\mathbf{2}/\mathbf{2}^-) = 3.00$. In a similar way, one obtains $\Delta G_0^\ddagger(\mathbf{8}/\mathbf{8}^-) = 14.33$ kcal/mol ($\log k_o(\mathbf{8}/\mathbf{8}^-) = 2.05$) and $\Delta G_0^\ddagger(\mathrm{AH^+/A}) = 11.55$ kcal/mol ($\log k_o(\mathrm{AH^+/A}) = 4.16$).

Table IV. Estimated Intrinsic Rate Constants and Intrinsic Barriers for Identity Reactions in 90% $\mathrm{Me_2SO}$–10% Water (v/v) at 20 °C

	amine method[a]		9-cyanofluorene method[b]	
acid	$\log k_0$	$\Delta G_0^\ddagger$ (kcal/mol)	$\log k_0$	$\Delta G_0^\ddagger$ (kcal/mol)
$\mathrm{R_2NH_2^+}$ ($\mathrm{pipH^+}$ or $\mathrm{morH^+}$)	7.70	6.8	5.76	9.37
benzylmalononitriles (**1–X**)	4.16	11.52	2.40	13.87
9-cyanofluorene (**2**)	1.24	15.40	3.00	13.05
1,3-indandione (**3**)	0.25	16.72	2.02	14.37
4-nitrophenylacetonitrile (**4**)	–0.42	17.62	1.42	15.17
(3-nitrophenyl)-nitromethane (**5**)	–3.50	21.74	–1.74	19.39
(4-nitrophenyl)-nitromethane (**6**)	–3.67	21.96	–1.91	19.61
phenylnitromethane (**7**)	–4.18	22.64	–2.33	20.17
9-carbomethoxyfluorene (**8**)			2.05	14.33

[a] Based on $\log k_0(\mathrm{AH^+/A}) \approx 7.7$ ($\Delta G_0^\ddagger(\mathrm{AH^+/A}) \approx 6.8$ kcal/mol) estimated from Grunwald's work, see text. [b] Based on $\log k_0(\mathbf{2}/\mathbf{2}^-) \approx 3.00$ ($\Delta G_0^\ddagger(\mathbf{2}/\mathbf{2}^-) = 13.05$ kcal/mol) calculated from eq 18, see text.

$$\Delta G_0^\ddagger(\mathbf{2}/\mathbf{2}^-) = \Delta G_0^\ddagger(\mathbf{2}/\mathbf{8}^-) + \Delta G_0^\ddagger(\mathbf{2}/\mathrm{A}) - \Delta G_0^\ddagger(\mathbf{8}/\mathrm{A}) \tag{18}$$

Using $\Delta G_0^\ddagger(\mathbf{2}/\mathbf{2}^-) = \Delta G_0^\ddagger(\mathrm{CH/C^-}) = 13.05$ kcal/mol in eq 9 yields a new value for $\Delta G_0^\ddagger(\mathrm{BH/B^-})$ (13.87 kcal/mol), which is then used to calculate $\Delta G_0^\ddagger(\mathrm{CH/C^-})$ for **3-7**, and $\Delta G_0^\ddagger(\mathrm{AH^+/A})$ for piperidine or morpholine is obtained from eq 12 using $\Delta G_0^\ddagger(\mathrm{CH/C^-}) = 13.05$ kcal/mol ("9-cyanofluorene method" in Table IV).

There is a significant difference between the two sets of calculated intrinsic barriers in Table IV. In the second set, $\Delta G_0^\ddagger$ for **2-6** is 2.35 kcal/mol smaller than in the first set (for **7** the respective difference is 2.47 kcal/mol) while $\Delta G_0^\ddagger$ for **1-X** in the second set is 2.35 kcal/mol *higher* than in the first. $\Delta G_0^\ddagger$ for piperidine/morpholine is also higher in the second set (2.57 kcal/mol).

Despite these differences, the dependence of $\log k_o$ and $\Delta G_0^\ddagger$ on the structure of the carbon acids **3-7** is qualitatively reasonable in both sets, i.e., there is a substantial decrease in $\log k_o$ (increase in $\Delta G_0^\ddagger$) with increasing resonance stabilization of the carbanion, as one would expect[8b,34] and as is the case for $\Delta G_0^\ddagger(\mathrm{CH/B^-})$ and $\Delta G_0^\ddagger(\mathrm{CH/A})$. This suggests that the Marcus treatment is, at least in a qualitative sense, reasonable. As to the reasons why the two sets of calculated intrinsic parameters for the identity reactions are so different, there are a number of possibilities.

(1) The Marcus relation between intrinsic barriers of cross reactions and identity reactions is at best qualitatively correct but, as a general proposition, fails in its quantitative application. This is probably too pessimistic a view.

(2) The Marcus relation may be valid as long as it is applied only to carbon acid/carbanion combinations but becomes problematic when carbon acid/amine combinations (and probably

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(40) Reference 5, p 275.

(41) Murdoch et al.[27] applied eq 9 to the reactions of 9-alkylfluorene with (9-alkylfluorenyl)lithium in ether but their results appear to be extremely distorted by ion-pairing effects as judged by rate constants for ergoneutral proton transfers in the range of 10^{-9} to 10^{-5} $\mathrm{M^{-1}\,s^{-1}}$, which are 7 to 11 orders of magnitude (!) lower than ours for 9-cyanofluorene. Norton et al.[42] used eq 9 in the context of proton transfers from hydrido transition-metal complexes in acetonitrile.

(42) (a) Eididin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945. (b) Kristjánsdóttir, S. S.; Norton, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 4366.

(43) Grunwald, E.; Ku, A. Y. *J. Am. Chem. Soc.* **1968**, *90*, 29. (b) Grunwald, E.; Ralph, E. K., III. *Acc. Chem. Res.* **1971**, *4*, 107.

(44) Albery, W. J., in ref 6, p 285.

(45) (a) Bednar, R. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1985**, *107*, 7126 and references cited therein. (b) Washabaugh, M. W.; Jencks, W. P. *Ibid.* **1989**, *111*, 674 and references cited therein.

(46) Keeffe, J. R.; Kresge, A. J. *Can. J. Chem.* **1988**, *66*, 2440.

(47) According to Marcus, we have $\Delta G_0^\ddagger(\mathbf{2}/\mathbf{8}^-) = {}^1/_2\{\Delta G_0^\ddagger(\mathbf{2}/\mathbf{2}^-) + \Delta G_0^\ddagger(\mathbf{8}/\mathbf{8}^-)\}$, $\Delta G_0^\ddagger(\mathbf{2}/\mathrm{A}) = {}^1/_2\{\Delta G_0^\ddagger(\mathbf{2}/\mathbf{2}^-) + \Delta G_0^\ddagger(\mathrm{AH^+/A})\}$, and $\Delta G_0^\ddagger(\mathbf{8}/\mathrm{A}) = {}^1/_2\{\Delta G_0^\ddagger(\mathbf{8}/\mathbf{8}^-) + \Delta G_0^\ddagger(\mathrm{AH^+/A})\}$, and hence, eq 18 immediately follows from these relationships.

also carbon acid/oxyanion combinations) are included. If this view is taken, the second set of intrinsic barriers reported in Table IV (9-cyanofluorene method) should be adopted except that the derived $\Delta G_0^\ddagger(\mathrm{AH^+/A})$ of 9.37 kcal/mol (log $k_o(\mathrm{AH/A}) = 5.76$) for the piperidine/morpholine pair would then constitute an overestimate (underestimate).

(3) The discrepancies may be a consequence of neglecting the work terms. Strictly speaking, the Marcus relation pertains to the intrinsic barriers for the conversion of a reactant precursor complex to a product precursor complex, e.g., $\mathrm{CH{\cdot}B^-}$ to $\mathrm{C^-{\cdot}HB}$ in eq 7. We shall use the symbol $\Delta G_0^\ddagger(\mathrm{M})$ to distinguish it from the *experimental* intrinsic barrier $\Delta G_0^\ddagger(\mathrm{obsd})$, which is what we have calculated from the experimental k_o values. The relationship between $\Delta G_0^\ddagger(\mathrm{obsd})$ and $\Delta G_0^\ddagger(\mathrm{M})$ is given by eq 19.

$$\Delta G_0^\ddagger(\mathrm{obsd}) = w_r + \Delta G_0^\ddagger(\mathrm{M}) \tag{19}$$

If eqs 9, 12, and 13 are applied to $\Delta G_0^\ddagger(\mathrm{M})$ rather than $\Delta G_0^\ddagger(\mathrm{obsd})$, we obtain, e.g., eqs 20 and 21.

$$\Delta G_0^\ddagger(\mathrm{CH/B^-}) - w_r(\mathrm{CH/B^-}) = {}^1/_2\{\Delta G_0^\ddagger(\mathrm{CH/C^-}) + \Delta G_0^\ddagger(\mathrm{BH/B^-})\} - {}^1/_2\{w_r(\mathrm{CH/C^-}) + w_r(\mathrm{BH/B^-})\} \tag{20}$$

$$\Delta G_0^\ddagger(\mathrm{CH/A}) - w_r(\mathrm{CH/A}) = {}^1/_2\{\Delta G_0^\ddagger(\mathrm{CH/C^-}) + \Delta G_0^\ddagger(\mathrm{AH^+/A})\} - {}^1/_2\{w_r(\mathrm{CH/C^-}) + w_r(\mathrm{AH^+/A})\} \tag{21}$$

For the work terms to be ignored, the relationships 22 and 23 need to hold. Since in eq 22 all terms refer to carbon acid/carbanion combinations, it is not unreasonable to expect this equation to hold, at least approximately.[48] On the other hand, the validity of eq 23 may be questionable because of carbon acid/amine and ammonium ion/amine terms. These considerations argue again in favor of the second set (9-cyanofluorene method) in Table IV.

$$w_r(\mathrm{CH/B^-}) = {}^1/_2\{w_r(\mathrm{CH/C^-}) + w_r(\mathrm{BH/B^-})\} \tag{22}$$

$$w_r(\mathrm{CH/A}) = {}^1/_2\{w_r(\mathrm{CH/C^-}) + w_r(\mathrm{AH^+/A})\} \tag{23}$$

(4) There may be no problems with either the Marcus relation or the validity of eqs 22 and 23, even when amines are combined with carbon acids. In this case, the reason for the inconsistency between the two sets in Table IV could be traced to our assumption that $\Delta G_0^\ddagger(\mathrm{AH^+/A})$ in 90% $\mathrm{Me_2SO}$–10% water is the same as that for $\mathrm{Me_2NH_2^+/Me_2NH}$ in water. Our second set suggests that in 90% $\mathrm{Me_2SO}$–10% water, $\Delta G_0^\ddagger(\mathrm{AH^+/A})$ should be 2.57 kcal/mol higher than that for $\mathrm{Me_2NH_2^+/Me_2NH}$ in water and have a log $k_o(\mathrm{AH^+/A})$ as low as 5.76. In view of Ritchie and Lu's recent report[50] of remarkably reduced rates of proton transfers between normal acids and bases in pure $\mathrm{Me_2SO}$, such a low log $k_o(\mathrm{AH^+/A})$ may not be unreasonable. For example, log $k_o(\mathrm{AH^+/A}) = 5.6$ at 20 °C for A = *N*,*N*-dimethylbenzylamine,[50] which is very close to our log $k_o(\mathrm{AH^+/A})$ value of 5.76 for piperidine and morpholine based on the 9-cyanofluorene method (Table IV).

On the basis of the foregoing discussion, the second set of $\Delta G_0^\ddagger$ and log k_o values in Table IV is to be preferred,[51] even though it leads to one rather puzzling conclusion, namely, that log k_o for **1-X**/**1-X**$^-$ is somewhat lower than that for **2**/**2**$^-$. This finding implies that in 90% $\mathrm{Me_2SO}$–10% water, log k_o for the reaction of amines with **1-X** is slightly lower than that for the reaction of amines with **2**,[52] which contrasts with the situation in water where the opposite is true.[53] log k_o for the reaction of **1-X**$^-$ with piperidine/morpholine in 90% $\mathrm{Me_2SO}$–10% water has not been determined experimentally because spectral overlap between $\mathrm{Me_2SO}$ and **1-X**$^-$ precludes kinetic measurements.

Brønsted Coefficients. Our Brønsted β values are summarized in Table II, along with Brønsted coefficients for deprotonation by carboxylate ions, the piperidine/morpholine pair, and primary aliphatic amines. $\beta(\mathrm{RCOO^-})$, β(pip/mor), and $\beta(1°\mathrm{RNH_2})$ are not known for **5** and **6**, but they are likely to be very similar to those for phenylnitromethane (**7**).[54]

The β(**1-X**$^-$) values are remarkably similar for all substrates, although the fact that they are virtually identical is probably fortuitous. The two $\beta(\mathrm{RCOO^-})$ are also very similar to each other but substantially higher than the β(**1-X**$^-$) values. With β(pip/mor) and $\beta(1°\mathrm{RNH_2})$, there is more variation and a trend toward larger values with decreasing reactivity of the carbon acid. It is difficult to draw unambiguous conclusions from these β values. Nevertheless, we offer the following comments.

(1) The β(**1-X**$^-$) values being close to 0.5 are consistent with predictions based on Marcus theory for proton transfers with relatively high intrinsic barriers and $\Delta G°$ values not grossly different from zero. This can be seen from eq 24 which is the Marcus expression for β. For the compound with the lowest intrinsic barrier, **2**, $\Delta G_0^\ddagger = 13.46$ kcal/mol and $\Delta G°$ [56] covers a range from −3.14 to −4.38 kcal/mol. From eq 24, one calculates $\beta = 0.47$ for $\Delta G° = -3.14$ kcal/mol and $\beta = 0.46$ for $\Delta G° = -4.38$ kcal/mol. For **3**, $\Delta G_0^\ddagger = 14.12$ kcal/mol and $\Delta G°$ covers a range from −3.39 to −4.63 kcal/mol; thus, eq 24 predicts $\beta = 0.47$ and 0.46, respectively. For **4**, we have $\Delta G_0^\ddagger = 14.57$ kcal/mol, $\Delta G° = 0.97$ and 1.68 kcal/mol, and β should be 0.51 for both $\Delta G°$ values. With **6** which has the highest intrinsic barrier ($\Delta G_0^\ddagger \approx 16.74$ kcal/mol) and where $\Delta G°$ covers a range from −3.83 to −5.07 kcal/mol, the Marcus β values range from 0.46 to 0.47.

$$\beta = 0.5 + \frac{\Delta G°}{8\Delta G_0^\ddagger} \tag{24}$$

All these calculated βs are seen to be very close to the experimental β values of 0.50–0.51, i.e., the reactions of **2**-**6** with **1-X**$^-$ conform quite well to the Marcus equation. The calculated β(**1-X**$^-$) values for any given substrate are also seen to be virtually independent of $\Delta G°$, which is consistent with the strict linearity of the Brønsted plots (Figure 4).

(2) In comparing β(**1-X**$^-$) with other β values, the comparison with $\beta(\mathrm{RCOO^-})$ which refers to bases of the same charge type seems the most pertinent. The $\beta(\mathrm{RCOO^-})$ values are significantly larger than β(**1-X**$^-$) even though eq 24 predicts $\beta(\mathrm{RCOO^-})$ to be

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(48) A word of caution is called for her. It has recently been suggested that w_r may not have a necessary relationship to a precursor complex; if rate constants computationally generated from potential surfaces are fitted to Marcus theory, substantial values of w_r are sometimes obtained in the complete absence of metastable intermediates or even inflection points on the minimum energy path.[49]

(49) (a) Kreevoy, M. M.; Ostović, D.; Truhlar, D. G.; Garrett, B. C. *J. Phys. Chem.* **1986**, *90*, 3766. (b) Kim, Y.; Truhlar, D. G.; Kreevoy, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 7837.

(50) Ritchie, C. D.; Lu, S. *J. Am. Chem. Soc.* **1989**, *111*, 8542; **1990**, *112*, 7748.

(51) Whether the calculated $\Delta G_0^\ddagger(\mathrm{AH^+/A})$ value for piperidine/morpholine in the second set reflects the true value of the intrinsic barrier or whether it is too high because of a breakdown of the Marcus relation when reactions of carbon acids with carbanions are intermixed with reactions involving amines, and/or because the work terms do not cancel, cannot be unambiguously decided at this point. Further work is planned aimed at answering this question.

(52) From eq 12, one calculates $\Delta G_0^\ddagger = 11.62$ kcal/mol and log $k_o = 4.08$ for the reaction of piperidine/morpholine with **1-X** while we have $\Delta G_0^\ddagger = 11.21$ kcal/mol and log $k_o = 4.39$ for the reaction of the same amines with **2** (Table III).

(53) In water, log k_o for the reaction of malononitrile derivatives with piperidine/morpholine is ≈7.0[7] while log k_o for the reaction of **2** with the same amines is ≈4.5[31] (10% $\mathrm{Me_2SO}$–90% water).

(54) In water, β for the deprotonation of a series of 1-arylnitroethanes is constant.[55]

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

(56) $\Delta G°$ is calculated from $\mathrm{p}K_a^{\mathrm{BH}} - \mathrm{p}K_a^{\mathrm{CH}} + \log p/q$; in our systems $q = p = 1$.

close to $\beta(\mathbf{1\text{-}X}^-)$. For example, for **2**, we have $\Delta G_0^\ddagger = 11.21$ kcal/mol and $\Delta G°$ ranges from 2.49 to 4.57 kcal/mol. This should yield $\beta = 0.53$ for $\Delta G° = 2.49$ kcal/mol, and $\beta = 0.55$ for $\Delta G° = 4.57$ kcal/mol. For **7**, $\Delta G_0^\ddagger \approx 14.72$ kcal/mol with $\Delta G°$ ranging from –0.08 to 2.37 kcal/mol. This should lead to $\beta = 0.50$ ($\Delta G° = 0.08$ kcal/mol) to 0.52 ($\Delta G° = 2.37$ kcal/mol).

Solvation effects seem to be the most likely reason why the observed $\beta(\mathrm{RCOO^-})$ values are so much larger than predicted. According to Murray and Jencks,[57] the solvation of a carboxylic acid by hydrogen bonding to the solvent leads to a significant increase in $\beta(\mathrm{RCOO^-})$. This solvation effect may be corrected for by eq 25 in which β_s refers to a Brønsted coefficient for the interaction of RCOOH with the solvent. In water, β_s was

$$\beta_{\mathrm{corr}} = \beta_{\mathrm{obsd}}/(1 - \beta_s) \qquad (25)$$

estimated to be $\sim$–0.2.[57] If the same β_s is applied in 90% $\mathrm{Me_2SO}$–10% water, our $\beta_{\mathrm{corr}}(\mathrm{RCOO^-})$ would become $\sim$0.62. Since $\mathrm{Me_2SO}$ is a much better hydrogen-bond acceptor than water,[58] β_s is likely to be more negative, perhaps $\sim$–0.4. In this case, $\beta_{\mathrm{corr}}(\mathrm{RCOO^-})$ would be $\sim$0.54, close to the values calculated from eq 24.

Another contributing factor to the high $\beta(\mathrm{RCOO^-})$ values may be related to the solvation of the *carboxylate ion*. In water or 10% $\mathrm{Me_2SO}$, $\beta(\mathrm{RCOO^-})$ for **2** and phenylnitromethane is close to 0.5,[32] as predicted by eq 24. If the free energy of transfer of $\mathrm{RCOO^-}$ from water to 90% $\mathrm{Me_2SO}$–10% water increases with increasing $\mathrm{p}K_\mathrm{a}$ of $\mathrm{RCOO^-}$, as appears to be the case,[30] it can be shown that this would lead to a larger $\beta(\mathrm{RCOO^-})$ provided that desolvation of $\mathrm{RCOO^-}$ has made greater progress in the transition state than has proton transfer.[30] There exists substantial evidence that such desolvation is indeed typically ahead of bond changes.[3a,8b,30,34,59,60]

The β(pip/mor) and $\beta(1°\mathrm{RNH_2})$ values are more erratic but, on the whole, deviate much less from 0.5 than $\beta(\mathrm{RCOO^-})$. Again solvation effects, particularly of the protonated amine, are likely to play a role in making these β-values larger than 0.5, as discussed elsewhere.[30]

Conclusions. (1) Intrinsic rate constants (intrinsic barriers) for the reaction of **2**-**7** with $\mathbf{1\text{-}X}^-$ are significantly lower (higher) than those for the reaction of **2**-**7** with the piperidine/morpholine pair (Table III). This result is reasonable in the context of Marcus theory and qualitatively consistent with eqs 9, 12, and 13 and the assumption that $\Delta G_0^\ddagger(\mathrm{CH/C^-}) > \Delta G_0^\ddagger(\mathrm{AH^+/A})$ and $\Delta G_0^\ddagger(\mathrm{BH/B^-}) > \Delta G_0^\ddagger(\mathrm{AH^+/A})$ for the identity reactions 10, 11, and 16, respectively.

(2) Intrinsic barriers for identity reaction 10 for **2**-**7** have been estimated by two different methods. Both sets show an increase in $\Delta G_0^\ddagger(\mathrm{CH/C^-})$ with increasing resonance stabilization of $\mathrm{C^-}$, as expected. However, the reasons for the rather large differences in the identity barriers calculated by the two methods need to be further investigated before the validity and scope of the Marcus equation can be firmly evaluated. Nevertheless, it appears that the 9-cyanofluorene method gives a reasonable set of identity barriers and supports the validity of the Marcus equations; the perhaps unexpectedly high $\Delta G_0^\ddagger(\mathrm{AH^+/A})$ value predicted by this method is consistent with recent results obtained by Ritchie et al.[50] in pure $\mathrm{Me_2SO}$.

(3) Brønsted β values for the reaction of **2**-**6** with $\mathbf{1\text{-}X}^-$ are all very close to 0.50, consistent with predictions based on the Marcus treatment (eq 24). This contrasts with β values for the reactions of **3** and **7** with carboxylate ions and for the reactions of **2**-**4** and **7** with amines, which are larger than those predicted by eq 24, probably because of special solvation effects.

Experimental Section

Materials. Benzylmalononitriles (**1-X**) were prepared by $\mathrm{NaBH_4}$ reduction of the corresponding benzylidenemalononitriles, while these latter were synthesized by condensation of the appropriate benzaldehyde with malononitrile. For **1-H**, the procedures of Compaigne et al.[61] (condensation) and of Fuentes et al.[62] (reduction) were used; mp 90 °C (lit.[62] mp 90 °C). For **1-Cl** and **1-OMe**, the condensation reaction was performed as described by Sturz et al.[63] and for **1-NMe₂**, as described by Horner et al.,[64] while the reduction followed Fuentes et al.;[62] **1-Cl**, mp 93.5-94 °C (lit.[62] mp 93 °C); **1-OMe**, mp 88.5-90 °C (lit.[62] mp 89-90 °C); **1-NMe₂**, mp 77-78 °C (lit.[62] mp 74-75 °C).

(3-Nitrophenyl)- and (4-nitrophenyl)nitromethane (**5** and **6**) were prepared by the reaction of $\mathrm{AgNO_2}$ with the corresponding benzyl bromides, following the procedure of Kornblum;[65] **6**, mp 90-91 °C (lit.[66] mp 90-91 °C); **5**, mp 91-92 °C. ^{1}H NMR (60 MHz, $\mathrm{CDCl_3}$): 5.50 (2H, s, $\mathrm{CH_2}$), 7.36-8.26 (4H, s, ArH).

The other carbon acids were either available from previous studies (9-cyanofluorene,[31] 1,3-indandione[30]) or commercial sources (4-nitrophenylacetonitrile, Eastman).

Piperidine, morpholine, n-butylamine, 2-methoxyethylamine, and acetic and methoxyacetic acids were purified or used directly as described previously.[60] $\mathrm{Me_2SO}$ was distilled under $\mathrm{N_2}$ and reduced pressure.

Reaction Solutions; pH and pK_a Measurements. A solution of 90% $\mathrm{Me_2SO}$–10% water was prepared by adding 10 mL of water to a 100-mL volumetric flask and topping off with $\mathrm{Me_2SO}$. pH measurements were made in mock solutions with a Corning no. 476022 glass electrode and a Beckman no. 39400 calomel reference electrode on an Orion 611 pH meter. The meter was calibrated with substituted phenol buffers according to Hallé et al.,[67] who have established a pH scale based on measurements with a hydrogen electrode. All reactions were adjusted to have an ionic strength of 0.06 M by addition of KCl. The pK_a values of the various substituted benzylmalononitriles were determined in piperidine, *n*-butylamine, and 2-methoxyethylamine buffers by classical spectrophotometric procedures at $\lambda = 254$ nm. In a similar way, the pK_a of (3-nitro- and (4-nitrophenyl)nitromethane were determined ($\lambda = 340$ nm, acetic acid buffer for **5** and $\lambda = 471$ nm, methoxyacetic buffer for **6**).

Rate Measurements. Rates were determined spectrophotometrically in a Durrum-Gibson stopped-flow spectrophotometer. With all but 4-nitrophenylacetonitrile, the reactions were conducted by mixing a slightly acidic solution of CH with a basic solution of the buffer and the slopes of the plots of τ^{-1} vs $[\mathrm{B^-}]$ were evaluated according to eq 4. Due to the high pK_a of 4-nitrophenylacetonitrile (**4**), the reaction was conducted by mixing a strongly basic solution of $\mathbf{4}^-$ with a less basic buffer solution and the slopes of the plots of τ^{1} vs [BH] were evaluated according to eq 5. The wavelengths for monitoring the reactions were chosen to minimize interference between the spectrum of $\mathrm{C^-}$ and $\mathbf{1\text{-}X}^-$. The following wavelengths were used for monitoring: 412 nm for 9-cyanofluorene, 406 nm for 1,3-indandione, 536 nm for 4-nitrophenylacetonitrile,[68] 380 nm for (3-nitrophenyl)nitromethane; and 477 nm for (4-nitrophenyl)nitromethane.

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(68) The same λ was used to monitor the reactions with piperidine and morpholine.