rate, 0.8 mL/min; *S* isomer 37.8, *R* isomer, 39.9. For 1-(*p*-methoxyphenyl)propanol: 0.2% 2-propanol in hexane; flow rate 0.9 mL/min; *S* isomer 67.0, *R* isomer 70.3.

General Procedure for the Enantioselective Alkylation of Aldehydes Using the Lithium Salt of Pyrrolidinylmethanol as Catalyst. To a chiral pyrrolidinylmethanol (0.05 mmol, 2 mol %) in a suitable solvent such as cyclohexane (6.3 mL) was added 0.035 mL of *n*-butyllithium (0.05 mmol, 1.51 M hexane solution). After the mixture was stirred for 15 min, an aldehyde (2.5 mmol) in cyclohexane was added, and stirring was continued for an additional 20 min. Then the mixture was cooled to 0 °C, and 5.6 mL of dialkylzinc (5.6 mmol, 1 M hexane solution) was added. The mixture was stirred for 4–24 h, 1 M HCl (20 mL) was added, and the mixture was extracted with CH_2Cl_2 (4 × 20 mL). The extract was dried over Na_2SO_4 and was evaporated. Purification, identification, and the determination of ee of the products were performed as described above.

Acknowledgment. We thank Tri Chemical Laboratory Inc. for a generous gift of Me_2Zn.

Registry No. **1** (Z = $PhCH_2OC(O)$), 5211-23-4; **3**, 110529-22-1; **8**, 74936-95-1; **9**, 110529-23-2; **10**, 110529-24-3; **12**, 74936-96-2; **12**·HCl, 110529-25-4; **13**, 74936-98-4; **14a**, 110529-26-5; **14b**, 110529-27-6; (*S*)-$PhCH(OH)CH_2CH_3$, 613-87-6; (*R*)-$PhCH(OH)CH_2CH_3$, 1565-74-8; (*S*)-*p*-$ClC_6H_4CH(OH)CH_2CH_3$, 73890-73-0; (*R*)-*p*-$ClC_6H_4CH(OH)CH_2CH_3$, 110611-21-7; (*S*)-*p*-$MeOC_6H_4CH(OH)CH_2CH_3$, 73854-04-3; (*R*)-*p*-$MeOC_6H_4CH(OH)CH_2CH_3$, 105836-14-4; (*S*)-(*E*)-$PhCH{=}CHCH(OH)CH_2CH_3$, 103729-97-1; (*R*)-(*E*)-$PhCH{=}CHCH(OH)CH_2CH_3$, 110611-22-8; (*S*)-$Ph(CH_2)_2CH(OH)CH_2CH_3$, 71747-37-0; (*R*)-$Ph(CH_2)_2CH(OH)CH_2CH_3$, 105836-17-7; (*S*)-$CH_3(CH_2)_5CH(OH)CH_2CH_3$, 61925-49-3; (*R*)-$CH_3(CH_2)_5CH(OH)CH_2CH_3$, 61925-50-6; (*S*)-$CH_3(CH_2)_5CH(OH)CH_3$, 5978-70-1; (*S*)-c-$C_6H_{11}CH(OH)CH_2CH_3$, 110529-28-7; (*R*)-c-$C_6H_{11}CH(OH)CH_2CH_3$, 38636-38-3; (*S*)-$(CH_3)_2CHCH_2CH(OH)CH_2CH_3$, 93031-24-4; (*R*)-$(CH_3)_2CHCH_2CH(OH)CH_2CH_3$, 39003-07-1; (*S*)-$PhCH(OH)CH_3$, 1445-91-6; (*R*)-$PhCH(OH)CH_3$, 1517-69-7; (*S*)-(*E*)-$PhCH{=}CHCH(OH)CH_3$, 81176-43-4; (*R*)-(*E*)-$PhCH{=}CHCH(OH)CH_3$, 62413-47-2; benzaldehyde, 100-52-7; *p*-chlorobenzaldehyde, 104-88-1; *p*-methoxybenzaldehyde, 123-11-5; (*E*)-cinnamaldehyde, 14371-10-9; 3-phenylpropanal, 104-53-0; heptanal, 111-71-7; cyclohexanecarboxaldehyde, 2043-61-0; 3-methylbutanal, 590-86-3.

Ionization of 9-Cyano- and 9-(Carbomethoxy)fluorene in Dimethyl Sulfoxide–Water Mixtures. How Important Is Solvent Reorganization?[1]

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Contribution from the Thimann Laboratories of the University of California, Santa Cruz, California 95064. *Received April 27, 1987*

Abstract: Rate constants (k_1^B, k_{-1}^{BH}) for the reversible deprotonation of 9-cyanofluorene (Fl-CN) and 9-(carbomethoxy)fluorene (Fl-COOMe) by primary aliphatic amines and by piperidine and morpholine have been measured in 10%, 50%, and 90% aqueous Me_2SO at 20 °C. Intrinsic rate constants, defined as $k_0 = k_1^B/q = k_{-1}^{BH}/p$ at $\Delta pK + \log(p/q) = 0$, were calculated by suitable interpolation of Brønsted plots. Increased Me_2SO content of the solvent has virtually no effect on k_0 for Fl-CN and increases k_0 of Fl-COOMe by a very small amount. This contrasts with the large increase in k_0 reported by Ritchie for the ionization of Fl-COOMe by oxyanions when the reaction was conducted in Me_2SO instead of methanol. It also contrasts with the large increases in k_0 for similar solvent changes in the ionization of acetylacetone, 1,3-indandione, nitromethane, and phenylnitromethane by amines. A formalism which breaks down the solvent effect on k_0 into contributions from late solvation of the developing carbanion and late solvation of the developing ammonium ion (amine reaction) or early desolvation of the oxyanion (oxyanion reactions) accounts for these various observations quite well in a qualitative way. A more quantitative analysis indicates that an additional factor contributes significantly to the solvent effect, though. It is suggested that this factor represents solvent reorganization in the sense of a dynamic solvent effect. Rate constants for the reaction of Fl-CN with the anion of Fl-COOMe were also measured in 90% Me_2SO. The intrinsic rate constant for carbon to carbon proton transfer estimated from the results appears to be substantially higher than expected on the basis of the Marcus relation.

It is well-known that proton transfers to and from carbon are usually much slower than proton transfers to and from oxygen, nitrogen, and sulfur.[3] This is particularly true for systems in which the carbanion benefits extensively from resonance stabilization. Three main factors have variously been invoked as contributing to this behavior. (1) The poor hydrogen bonding capability of carbon acids and of the carbanionic carbon.[3a,d,4] (2) The need for structural reorganization which accompanies the delocalization of the negative charge.[3,4b,5] (3) The need for solvent reorganization.[4b,6-8]

The meaning of the term "solvent reorganization" or "solvent reorientation" has evolved over time and different authors use the term to describe different phenomena. One of the most influential early studies which led to the suggestion that solvent reorganization plays an important role in proton transfers was Ritchie's's[7] investigation of the solvent effect on the ionization of aromatic hydrocarbons. Defining k at $\Delta pK = 0$ as the *intrinsic* rate constant, k_0, he found, for example, that k_0 for the deprotonation of 9-(carbomethoxy)fluorene by a series of benzoate ions in Me_2SO was approximately 100-fold higher than k_0 for the ionization of the same carbon acid by methoxide ion in methanol.

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(2) On leave from the Dēpartement de Chimie, Facultē des Sciences de Rouen, 76130 Mont Saint Aignan, France.

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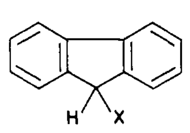
Ritchie viewed these results in terms of a rate-retarding effect of solvent reorientation in methanol. The basic idea was that the amount of energy required to reorganize methanol (or hydroxylic solvents in general) around reactants and products, as they interconvert, is greater than for Me_2SO, because of the presence of strong oriented hydrogen bonds.

Similar notions had already been expressed earlier by Caldin[6b] and by Ogg and Polanyi.[6a] In the intervening years since Ritchie's proposal, a number of workers have drawn attention to the importance of solvent reorganization effects.[8-19] Many of these studies have demonstrated that at least part of the rate-retarding effects of solvent reorganization should be understood as the consequence of early desolvation of reactant ions and/or late solvation of product ions.[8,13-19] Nevertheless, it is quite possible that in addition to the early desolvation/late solvation effects, solvent reorganization in the sense of dynamic solvent effects,[20,21] which is more in keeping with Ritchie's original proposal, also plays a role.

In this paper we examine the role played by solvent reorganization in the ionization of 9-cyanofluorene (Fl-CN) and 9-(carbomethoxy)fluorene (FL-COOMe). To this end we have measured rates of deprotonation of Fl-CN and Fl-COOMe by aliphatic amines in various Me_2SO–water mixtures, with the objective of comparing the solvent effect on the intrinsic rate constants with that found by Ritchie in the ionization of Fl-COOMe by oxyanions. It will be shown that our findings, as well as results from similar studies with a variety of other carbon acids, can be understood in terms of contributions both by late solvation/early desolvation effects and by a dynamic solvent effect.



X = CN(Fl-CN)
X = COOMe(Fl-COOMe)

Our results,[1] which include the rate constant of the proton transfer from Fl-CN to the anion of Fl-COOMe, are also relevant to the application of Marcus[22] theory to proton transfers.

Results

pK_a Determinations. The pK_a^{CH} values of Fl-CN and Fl-COOMe in the various solvents were determined by standard spectrophotometric procedures, exploiting the large difference in the UV spectra of the fluorenes and their respective conjugate bases. Typically pK_a^{CH} was obtained as the intercept of plots of log $(A_{C^-} - A)/(A - A_{CH})$[23] versus pH measured in 10–15 amine buffers, which gave excellent straight lines of unit slope. The pK_a^{BH} values of amines in the various solvents were known from a previous study.[18] They are, along with pK_a^{CH}, listed in Tables I and II.

Table I. Rate Constants and pK_a Values for the Ionization of 9-Cyanofluorene in Me_2SO–Water Mixtures at 20 °C

base	pK_a^{BH}	k_1^B, M^{-1} s^{-1}	k_{-1}^{BH}, M^{-1} s^{-1}
10% Me_2SO–90% H_2O (v/v) (pK_a^{CH} = 10.71)			
piperidine	11.41	3.26×10^4	1.30×10^4
n-$BuNH_2$	10.98	1.07×10^4	6.90×10^3
$HOCH_2CH_2NH_2$	9.83	2.10×10^3	1.59×10^4
$MeOCH_2CH_2NH_2$	9.73	2.75×10^3	2.64×10^4
OH^-	15.93	9.80×10^4	5.91×10^{-1} [a]
50% Me_2SO–50% H_2O (v/v) (pK_a^{CH} = 9.53)			
piperidine	11.02	2.18×10^5	7.05×10^3
morpholine	8.72	2.29×10^4	1.48×10^5
n-$BuNH_2$	10.65	4.46×10^4	3.39×10^3
$HOCH_2CH_2NH_2$	9.73	8.10×10^3	5.10×10^3
$MeOCH_2CH_2NH_2$	9.62	9.60×10^3	7.80×10^3
$H_2NCOCH_2NH_2$	8.27	1.17×10^3	2.15×10^4
$EtOOCCH_2NH_2$	7.87	1.90×10^3	8.61×10^4
OH^-	17.34	$\approx 7.5 \times 10^5$	1.16×10^{-2} [a]
H_2O	−1.44	$\approx 1.60 \times 10^{-2}$ [a]	$\approx 1.5 \times 10^9$
90% Me_2SO–10% H_2O (v/v) (pK_a^{CH} = 8.01)			
n-$BuNH_2$	10.96	4.10×10^5	4.60×10^2
$MeOCH_2CH_2NH_2$	10.16	1.22×10^5	8.66×10^2
$H_2NCOCH_2NH_2$	9.19	2.01×10^4	1.33×10^3
$EtOOCCH_2NH_2$	8.22	1.26×10^4	7.78×10^3
$NCCH_2NH_2$	5.94	4.50×10^2	5.37×10^4
H_2O	−0.74	$\approx 1.75 \times 10^{-1}$ [a]	$\approx 1.0 \times 10^8$

[a] In units of M^{-1} s^{-1} after dividing first-order rate constant by water concentration.

Table II. Rate Constants and pK_a Values for the Ionization of 9-(Carbomethoxy)fluorene in Me_2SO–Water Mixtures at 20 °C

base	pK_a^{BH}	k_1^B, M^{-1} s^{-1}	k_{-1}^{BH}, M^{-1} s^{-1}
50% Me_2SO–50% H_2O (v/v) (pK_a^{CH} = 10.97)			
n-$BuNH_2$	10.65	9.00×10^2	1.88×10^3
$MeOCH_2CH_2NH_2$	9.62	2.20×10^2	4.93×10^3
$EtOOCCH_2NH_2$	7.87	3.70×10^1	5.58×10^4
OH^-	17.34	6.58×10^3	2.92×10^{-3} [a]
H_2O	−1.44	$\approx 4.25 \times 10^{-4}$ [a]	$\approx 1.10 \times 10^9$
90% Me_2SO–10% H_2O (v/v) (pK_a^{CH} = 10.03)			
n-$BuNH_2$	10.96	9.30×10^3	1.10×10^3
$MeOCH_2CH_2NH_2$	10.16	2.68×10^3	1.99×10^3
$EtOOCCH_2NH_2$	8.22	2.00×10^2	1.29×10^4
H_2O	−0.74	2.19×10^{-2} [a]	$\approx 1.30 \times 10^9$

[a] In units of M^{-1} s^{-1} after dividing first-order rate constant with water concentration.

Kinetics of Proton Transfer in Amine Buffers. Rates were measured in the stopped-flow apparatus. The reaction can be described by

$$\text{Fl-X} \underset{k_{-1}^{H}a_{H^+} + k_{-1}^{BH}[BH] + k_{-1}^{H_2O}}{\overset{k_1^{H_2O} + k_1^{B}[B] + k_1^{OH}a_{OH^-}}{\rightleftharpoons}} \text{Fl-X}^- \qquad (1)$$

Under pseudo-first-order conditions, which were used throughout, the first-order rate constant for equilibrium approach is given by

$$k_{obsd} = k_1^{H_2O} + k_1^{B}[B] + k_1^{OH}a_{OH^-} + k_{-1}^{H}a_{H^+} + k_{-1}^{BH}[BH] + k_{-1}^{H_2O} \qquad (2)$$

Because of generally high rates only amines whose pK_a^{BH} values are relatively close to pK_a^{CH} were amenable to study; for $pK_a^{BH} \gg pK_a^{CH}$ the $k_1^B[B]$ term would become too large to measure and for $pK_a^{BH} \ll pK_a^{CH}$ the $k_{-1}^{BH}[BH]$ term would become too large to measure. These restrictions were the most severe in water-rich solvents and precluded rate measurements in 10% Me_2SO–90% water for Fl-COOMe altogether. In most cases the rates with secondary cyclic amines such as piperidine and morpholine were also too fast for the stopped-flow technique because for a given

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(23) A_{C^-} and A_{CH} are the absorbance of the carbanion and the carbon acid, respectively; A is the absorbance of the mixture.

Table III. Intrinsic Rate Constants ($\log k_0$), Brønsted β-Values, and Transfer Coefficients ($\log \gamma_{C^-}$) for 9-Cyano– and 9-(Carbomethoxy)fluorene Anions

% Me_2SO	pK_a^{CH}	$\log k_0(RNH_2)$	$\beta(RNH_2)$	$\log k_0$(pip/mor)	β(pip/mor)	$\log {}^{10}\gamma_{C^-}^{D}$	$\log {}^{50}\gamma_{C^-}^{90}$
			9-Cyanofluorene				
10	10.71 ± 0.02	3.62 ± 0.07	0.53 ± 0.12				
50	9.53 ± 0.02	3.76 ± 0.09	0.47 ± 0.08	4.58	0.43	-1.37	
90	8.01 ± 0.07	3.57 ± 0.09	0.58 ± 0.04			-4.02	-2.65
			9-(Carbomethoxy)fluorene				
50	10.97 ± 0.01	2.84 ± 0.06	0.49 ± 0.04				
90	10.03 ± 0.02	3.09 ± 0.03	0.60 ± 0.02				-2.12

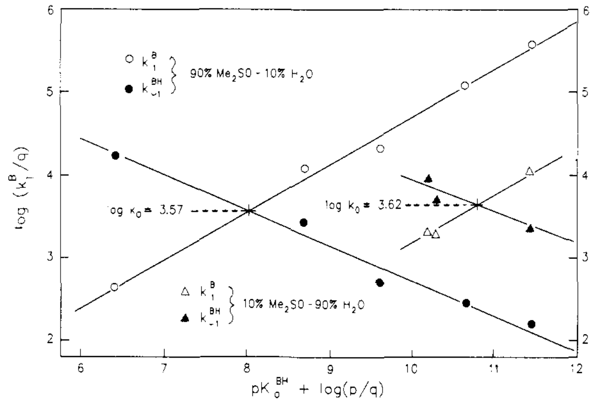

Figure 1. Brønsted plots for the ionization of 9-cyanofluorene by primary amines in 10% Me_2SO–90% water (triangles) and 90% Me_2SO–10% water (circles); $\log k_0$ obtained where $\log (k_1^B/q) = \log (k_{-1}^{BH}/p)$, indicated by crosses.

pK_a^{BH} these amines react considerably faster than primary amines, a well-known phenomenon.[3b,18,19,24]

For each amine buffer of a given buffer ratio k_{obsd} was measured at 6–8 concentrations. In most cases a second or even third series of similar experiments was performed at a different buffer ratio, with excellent consistency among the different series. The procedures used in evaluating the various rate constants were essentially the same as those described previously.[25] The results are summarized in Tables I and II. In general we estimate the experimental error in the rate constants to be less than ±10%; in those cases where the rates approached the time resolution of the stopped-flow apparatus the error limits may reach ±20%.

Kinetics of Proton Transfer from Carbon to Carbon. A few experiments were performed in which the proton transfer of eq 3 was measured in 90% Me_2SO. Fl-COOMe/Fl-COOMe⁻ was

$$\text{Fl-CN} + \text{Fl-COOMe}^- \underset{k_{-1}^{C}}{\overset{k_1^{C}}{\rightleftharpoons}} \text{Fl-CN}^- + \text{Fl-COOMe} \qquad (3)$$

used as the "buffer" (excess component), and Fl-CN/Fl-CN⁻ was used as the "substrate". k_{obsd}, given by eq 4,[26] was measured at

$$k_{obsd} = k_1^C[\text{Fl-COOMe}^-] + k_{-1}^C[\text{Fl-COOMe}] \qquad (4)$$

six different concentrations of a 1:1 Fl-COOMe/Fl-COOOMe⁻ buffer. An excellent straight line with zero intercept was obtained. It yields $k_1^C = 3400\ M^{-1}\ s^{-1}$ and $k_{-1}^C = 32\ M^{-1}\ s^{-1}$.

Discussion

Brønsted Plots. The various Brønsted plots obtained in this investigation are shown in Figures 1–3. As pointed out in the Results, the number and type of catalysts amenable to study were restricted by the time resolution of the stopped-flow apparatus. The situation was worst in 10% Me_2SO, where none of the rates could be measured with Fl-COOMe, and only *n*-butylamine, 2-ethanolamine, and 2-methoxyethylamine could be used with Fl-CN.

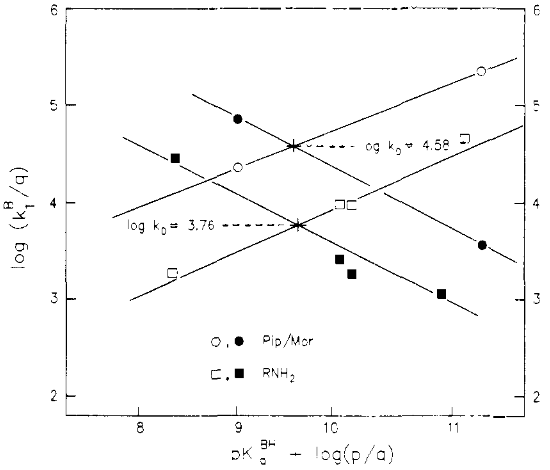

Figure 2. Brønsted plots for the ionization of 9-cyanofluorene by primary amines (squares) and by piperidine/morpholine (circles) in 50% Me_2SO–50% Me_2SO; $\log k_0$ obtained as in Figure 1.

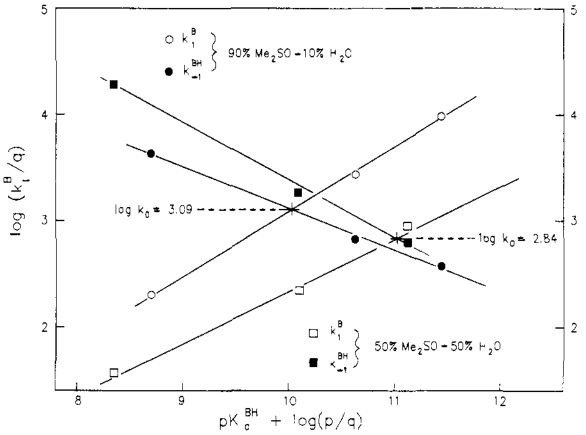

Figure 3. Brønsted plots for the ionization of 9-(carbomethoxy)fluorene by primary amines in 50% Me_2SO–50% water (squares) and 90% Me_2SO–10% water (circles); $\log k_0$ obtained as in Figure 1.

Brønsted β-values are summarized in Table III. They are, within experimental error, independent of the fluorene substituent. On the other hand, when comparing 50% with 90% Me_2SO there appears to be an increase in β which, at least for Fl-COOMe, is outside the estimated uncertainty based on standard deviations. This is consistent with a similar increase in β for the ionization of acetylacetone[18] and 1,3-indandione[19] by the same amines and can be understood as a solvation effect of the developing ammonium ion in the transition state.[19]

The high β-value for Fl-CN in 10% Me_2SO, if real (considering the large standard deviation), is puzzling. We believe that it is an artifact caused by the Brønsted line being defined only by *n*-butylamine, 2-ethanolamine, and 2-methoxyethylamine. Inspection of Figures 1–3 reveals that the point for 2-methoxy-

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[26] The $k_1^{H_2O}$, $k_1^{OH}a_{OH^-}$, $k_{-1}^{H}a_{H^+}$, and $k_{-1}^{H_2O}$ terms were all negligible under the reaction conditions.

Table IV. Solvent Effect on k_0 in the Ionization of Various Carbon Acids

CH acid	solvent change	δ log ${}^{\mathrm{H}}k_0^{\mathrm{D}}(\mathrm{CH/B^-})$ $\mathrm{B^-} = \mathrm{RCOO^-}$	δ log ${}^{\mathrm{H}}k_0^{\mathrm{D}}(\mathrm{CH/N})$ $\mathrm{N} = \mathrm{RNH_2}$	δ log ${}^{\mathrm{H}}k_0^{\mathrm{D}}(\mathrm{CH/N})$ N = pip/mor
CH_3NO_2[a]	H_2O → 90% Me_2SO			3.65
	50% Me_2SO → 90% MeSO			2.33
$PhCH_2NO_2$[a]	H_2O → 90% Me_2SO	~3.94		2.97
	50% Me_2SO → 90% Me_2SO			2.00
AcAc[b,c]	H_2O → 90% Me_2SO	~2.13	1.01	1.04
	50% Me_2SO → 90% Me_2SO	~1.47	0.85	0.89
ID[d,e]	10% Me_2SO → 90% Me_2SO	1.89	0.70	0.88
	50% Me_2SO → 90% Me_2SO	1.35	0.53	0.72
Fl-COOMe[f,g]	MeOH → Me_2SO	~2.0		
	50% Me_2SO → 90% Me_2SO		0.25	
Fl-CN[h]	10% Me_2SO → 90% Me_2SO		−0.05	
	50% Me_2SO → 90% Me_2SO		−0.19	

[a] Reference 28. [b] AcAc = acetylacetone. [c] Reference 18. [d] ID = 1,3-indandione. [e] Reference 19. [f] MeOH → Me_2SO, ref 7b. [g] 50% Me_2SO → 90% Me_2SO, this work. [h] This work.

ethylamine is invariably low, a phenomenon observed before,[18,19] particularly in the more aqueous solvents. This has the effect of increasing β if β is based mainly on *n*-butylamine and 2-methoxyethylamine. For example, if β for Fl-CN in 50% Me_2SO had been calculated on the basis of these two amines only, a value of 0.65 rather than 0.47 (Table III) would have been obtained. Hence we believe that the "true" β in 10% Me_2SO is approximately the same as in 50% Me_2SO or possibly even somewhat lower.[18]

With Fl-CN we were able to obtain data for the piperidine/morpholine pair in 50% Me_2SO, but only for piperidine in 10% Me_2SO. The two-point Brønsted plot in 50% Me_2SO (Figure 2) shows the common[3b,18,19,24,25b] upward displacement ($\Delta \log k_0 = 0.76$) from the line defined by the primary amines. The β-value of 0.43 is slightly lower than that for primary amines ($\beta = 0.47$). Even though the difference is hardly statistically significant we note that in the ionization of acetylacetone[18] and 1,3-indandione[19] β for the piperidine/morpholine pair was also found to be slightly lower in all solvents.

A few approximate rate constants for proton transfer involving OH^-/H_2O and H_2O/H_3O^+ could also be determined (Tables I and II). They are not included in the Brønsted plots but the following deviations, in log units, from the Brønsted lines were calculated. k_1^{OH}: −1.64 for Fl-CN in 10% Me_2SO, −1.86 for Fl-CN in 50% Me_2SO, and −2.36 for Fl-COOMe in 50% Me_2SO; $k_1^{\mathrm{H_2O}}$: −0.24 for Fl-CN in 50% Me_2SO, +0.79 for Fl-CN in 90% Me_2SO, −0.03 for Fl-COOMe in 50% Me_2SO, +1.78 for Fl-COOMe in 50% Me_2SO.

Because of the approximate nature of the k_1^{OH} and $k_1^{\mathrm{H_2O}}$ values and, more seriously, because of the inherent uncertainties in β and the long extrapolations involved, the reported deviations can only serve to illustrate qualitative trends. They show the commonly observed negative deviation for the hydroxide ion reaction and the increase in this negative deviation in Me_2SO-rich solvents.[18,19] They also show the previously noted trend toward less negative and eventually positive deviations for $k_1^{\mathrm{H_2O}}$ in solvents with increasing Me_2SO content.[19] The likely reasons for these trends have been discussed previously.[19]

Solvent Effects on k_0. Qualitative Considerations. We have determined k_0 as $k_1^{\mathrm{B}}/q = k_{-1}^{\mathrm{BH}}/p$ at $\mathrm{p}K_\mathrm{a}^{\mathrm{BH}} - \mathrm{p}K_\mathrm{a}^{\mathrm{CH}} + \log (p/q) = 0$ from the Brønsted plots in Figures 1–3. The results are summarized in Table III. Broadly speaking, k_0 appears to be virtually solvent independent. If the small trends are significant at all, they suggest that an increase in the Me_2SO content of the solvent increases k_0 slightly for Fl-COOMe but decreases k_0 for Fl-CN by a very small amount. These results are in marked contrast to Ritchie's[7] report of an approximately 100-fold increase in k_0 for the ionization of Fl-COOMe by oxyanions brought about by a change in solvent from methanol to Me_2SO.

The large discrepancy between Ritchie's findings and ours can, to a large extent, be traced to the use of different ionizing agents, i.e., oxyanions in Ritchie's study and amines in ours. That the solvent effect on k_0 for ionization of carbon acids greatly depends on the type of bases used has recently been shown in the deprotonation of acetylacetone,[18,28] 1,3-indandione,[19,28] and phenylnitromethane.[28] Table IV summarizes some relevant data. All the data in the table indicate that the solvent effect, $\delta \log k_0$, is substantially larger for $\mathrm{B} = \mathrm{RCOO^-}$ than when B is an amine.

These differences in the solvent effects for oxyanion- versus amine-promoted proton transfer as well as the magnitude of the solvent effects as a function of the type of carbon acid can, to a large degree, be attributed to solvation of product ions and/or desolvation of reactant ions not being synchronous with bond changes. There is growing evidence which indicates that solvation of developing ions typically lags behind, or desolvation of reacting ions is typically ahead of these bond changes at the transition state.[3b,13-16,18,19] The evidence is particularly strong for ions, including carbanions, that are solvated by hydrogen bonding. However, a recent study by Murdoch et al.[12] indicates that solvation of developing fluorenyl anions by a nonhydroxylic solvent (ether) also lags behind bond changes.

According to the principle of nonperfect synchronization (PNS),[15,29] the late solvation of product ions or early desolvation of reactant ions leads to a decrease in k_0 upon transfer to a better solvating solvent and to an increase in k_0 upon transfer to poorer solvent. Using a recently introduced formalism[15,29] one can understand the solvent effect on $\log k_0$ as the sum of three major contributors. For the reaction with a carboxylate ion ($\mathrm{B^-}$) we express the change in $\log k_0$ upon transfer from a hydroxylic solvent (H) to Me_2SO or a Me_2SO–water mixture (D) by

$$\delta \log {}^{\mathrm{H}}k_0^{\mathrm{D}}(\mathrm{CH/B^-}) \approx \delta_{\mathrm{B^-}} + \delta_{\mathrm{C^-}} + \delta_{\mathrm{SR}} \qquad (5)$$

$\delta_{\mathrm{B^-}}$ is the contribution from early desolvation of $\mathrm{B^-}$, $\delta_{\mathrm{C^-}}$ is the contribution from the late solvation of the carbanion, and δ_{SR} is that part of $\delta \log {}^{\mathrm{H}}k_0^{\mathrm{D}}(\mathrm{CH/B^-})$ which cannot be accounted for by $\delta_{\mathrm{B^-}}$ and $\delta_{\mathrm{C^-}}$. δ_{SR} may contain a contribution by a dynamic solvent effect and possibly other factors which cannot be treated in the context of the PNS, as discussed in detail below.

As shown elsewhere,[29] $\delta_{\mathrm{B^-}}$ and $\delta_{\mathrm{C^-}}$ can be approximated by

$$\delta_{\mathrm{B^-}} \approx (\alpha_{\mathrm{des}}^{\mathrm{B^-}} - \beta) \log {}^{\mathrm{H}}\gamma_{\mathrm{B^-}}^{\mathrm{D}} \qquad (6)$$

$$\delta_{\mathrm{C^-}} \approx (\alpha_{\mathrm{sol}}^{\mathrm{C^-}} - \beta)(-\log {}^{\mathrm{H}}\gamma_{\mathrm{C^-}}^{\mathrm{D}}) \qquad (7)$$

${}^{\mathrm{H}}\gamma_{\mathrm{B^-}}^{\mathrm{D}}$ and ${}^{\mathrm{H}}\gamma_{\mathrm{C^-}}^{\mathrm{D}}$ are the solvent activity coefficients[30] for transfer from "H" to "D", $\alpha_{\mathrm{des}}^{\mathrm{B^-}}$ measures the degree of desolvation of $\mathrm{B^-}$, $\alpha_{\mathrm{sol}}^{\mathrm{C^-}}$ measures the degree of solvation of $\mathrm{C^-}$ at the transition state, and β is the Brønsted coefficient ($\beta = \mathrm{d} \log k_1^{\mathrm{B}}/\mathrm{dp}K_\mathrm{a}^{\mathrm{BH}}$). Early desolvation of $\mathrm{B^-}$ implies $\alpha_{\mathrm{des}}^{\mathrm{B^-}} > \beta$, and late solvation of $\mathrm{C^-}$ implies $\alpha_{\mathrm{sol}}^{\mathrm{C^-}} < \beta$.

For deprotonation of a carbon acid by an *amine* (N) we have

$$\delta \log {}^{\mathrm{H}}k_0^{\mathrm{D}}(\mathrm{CH/N}) \approx \delta_{\mathrm{NH^+}} + \delta_{\mathrm{C^-}} + \delta_{\mathrm{SR}} \qquad (8)$$

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(27) Kresge, A. J. *Chem. Soc. Rev.* **1973**, *2*, 475.

(28) Bernasconi, C. F.; Bunnell, R. D.; Kliner, D. A.; Mullin, A.; Paschalis, P.; Terrier, F. *Physical Organic Chemistry 1986*; Kobayashi, M., Ed.; Elsevier: New York, 1987; p 583.

(29) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, 20, 301.

(30) Parker, A. J. *Chem. Rev.* **1969**, *69*, 1.

Table V. Solvent Activity Coefficients for the Transfer of Ions from Water to Me_2SO–Water Mixtures ($\log {}^{H}\gamma^{D}$), from 10% Me_2SO to Other Me_2SO–Water Mixtures ($\log {}^{10}\gamma^{D}$), and from 50% Me_2SO to 90% Me_2SO ($\log {}^{50}\gamma^{90}$) at 20 °C

ion	% Me_2SO	$\log {}^{H}\gamma^{D}$	$\log {}^{10}\gamma^{D}$	$\log {}^{50}\gamma^{90}$
AcO^- [a]	10	1.12	0	
	50	3.08	1.96	
	90	~6.50	~5.38	~3.42
$CH_3CH_2CH_2NH_3^+$ [a]	10	−0.40	0	
	50	−1.81	−1.41	
	90	~−2.8	~−2.4	~−0.99
$CH_2{=}NO_2^-$ [b]	50	2.87		
	90	6.70		3.83
$PhCH{=}NO_2^-$ [b]	50	1.99		
	90	4.09		2.10
$AcAc^-$ [b,c]	50	2.07		
	90	4.50		2.43
ID^- [b,d]	50		0.38	
	90		1.79	1.41
Fl-COOMe$^-$ [b]	50			
	90			−2.12
Fl-CN$^-$ [b]	50		−1.37	
	90		−4.02	−2.65

[a] Wells, C. F. In *Thermodynamic Behavior of Electrolytes in Mixed Solvents–II*; Furter, W. F., Ed.; Advances in Chemistry 177; American Chemical Society, Washington, DC, 1979. [b] Bernasconi, C. F.; Bunnell, R. D., unpublished results. [c] Acetylacetone anion. [d] 1,3-Indandione anion.

with δ_{NH^+} being the contribution from the late solvation of the incipient ammonium ion, approximated by

$$\delta_{NH^+} \approx (\alpha_{sol}^{NH^+} - \beta)(-\log {}^{H}\gamma_{NH^+}^{D}) \tag{9}$$

Here the late solvation of the ammonium ion is equivalent to $\alpha_{sol}^{NH^+} < \beta$.

It should be noted that eq 5 and 8 are only approximations because they do not take into account possible effects arising from nonsynchronous solvation/desolvation of neutral products/reactants. This point will be addressed further below.

Relevant $\log {}^{H}\gamma^{D}$ values are summarized in Table V. We can use these values to estimate relative magnitudes of δ_{B^-}, δ_{C^-}, and δ_{NH^+} if some assumptions about $\alpha_{des}^{B^-}$, $\alpha_{sol}^{C^-}$, and $\alpha_{sol}^{NH^+}$ are made. One assumption that seems reasonable is that in the ionizations induced by carboxylate ions the degree by which the desolvation of the carboxylate ion is ahead of the proton transfer is essentially independent of the carbon acid; i.e., $\alpha_{des}^{B^-} - \beta$ is constant. By the same token it is reasonable to assume that in the deprotonation by amines $\alpha_{sol}^{NH^+} - \beta$ is essentially independent of the carbon acid. We shall further assume that $|\alpha_{des}^{B^-} - \beta| \approx |\alpha_{sol}^{NH^+} - \beta|$.

It also seems likely that $\alpha_{sol}^{C^-} - \beta$ should be essentially independent of the base. A more questionable assumption is that $\alpha_{sol}^{C^-} - \beta$ is also independent of the *carbon acid.* We shall make it here for the sake of simplicity, though, and further assume that $|\alpha_{sol}^{C^-} - \beta| \approx |\alpha_{des}^{B^-} - \beta|$, but in a later section this latter assumption will be modified.

On the basis of the above assumptions one can anticipate that the relative magnitudes of δ_{B^-}, δ_{NH^+}, and δ_{C^-} are roughly proportional to the relative magnitudes of $\log {}^{H}\gamma_{B^-}^{D}$, $(-\log {}^{H}\gamma_{NH^+}^{D})$, and $(-\log {}^{H}\gamma_{C^-}^{D})$, respectively. Hence one expects $\delta_{B^-} \gg 0$, $\delta_{C^-} \gg 0$ for $PhCH_2NO_2$, $\delta_{C^-} > 0$ for 1,3-indandione and acetylacetone, $\delta_{C^-} \approx 0$ for Fl-COOMe, $\delta_{C^-} < 0$ for Fl-CN, and $\delta_{NH^+} < 0$.

These relationships offer a simple explanation for the smaller solvent effect on k_0 when the base is an amine instead of an oxyanion: it reflects the fact that $\delta_{NH^+} < 0$ but $\delta_{B^-} \gg 0$. And we note that for a given base the solvent effect on k_0 essentially follows the relative magnitude of δ_{C^-}.

The results for the fluorenes, even though consistent with the above general trends, suggest that the δ_{SR} terms in eqs 5 and 8 are not negligible: the δ_{C^-} and δ_{NH^+} terms alone should add up to a *significant decrease* in k_0 while k_0 is in fact virtually solvent independent, suggesting $\delta_{SR} > 0$. As shown elsewhere[19] the presence of a positive δ_{SR} term cannot be attributed to the neglect of possible PNS effect which may arise from early desolvation of *uncharged* reactants (CH, N) or late solvation of neutral products (BH). To the contrary, these effects would tend to depress k_0,[19] suggesting that δ_{SR} may actually be larger than our simple analysis indicates.

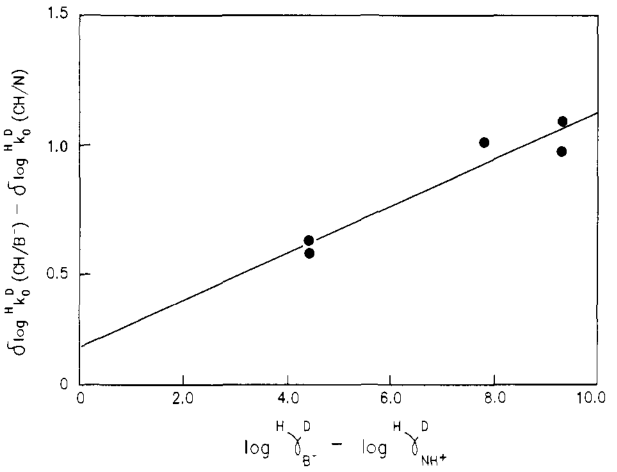


Figure 4. Plot according to eq 10; see text.

Table VI. Estimates for δ_{B^-} and δ_{NH^+}

solvent change	δ_{B^-}	δ_{NH^+}
0% → 90% Me_2SO	0.59	−0.25
10% → 90% Me_2SO	0.48	−0.22
50% → 90% Me_2SO	0.31	−0.09

We conclude then that the solvent effect on k_0 cannot be entirely attributed to nonsynchronous solvation/desolvation effects but that there must be another factor which either enhances k_0 in the presence of Me_2SO or retards the rate in the more hydroxylic solvents. It appears plausible that this factor is the solvent reorganization effect envisioned by Ritchie, or, in modern parlance, a dynamic solvent effect, although our results cannot prove it. An alternative interpretation of δ_{SR} could be that it represents a special transition state stabilization by Me_2SO which has no counterpart in either the reactants or products and hence is not a PNS effect. However, the semiquantitative analysis presented in the next section renders this hypothesis unattractive.

Semiquantitative Analysis. In this section we show how crude estimates for δ_{B^-}, δ_{NH^+}, δ_{C^-}, and δ_{SR} in eqs 5 and 8 may be obtained. We retain the assumptions that $\alpha_{des}^{B^-} - \beta$ and $\alpha_{sol}^{NH^+} - \beta$ are independent of the carbon acid, that their absolute values are comparable, and that $\alpha_{sol}^{C^-} - \beta$ is independent of the carbon acid. On the other hand, the previous assumption that $|\alpha_{sol}^{C^-} - \beta| \approx |\alpha_{des}^{B^-} - \beta|$ is not necessary (more on this below), and we shall also allow for the possibility that the δ_{SR}-terms in eqs 5 and 8 are dependent on the *base* by labeling them $\delta_{SR}(CH/B^-)$ and $\delta_{SR}(CH/N)$, respectively.

Subtracting eq 8 from eq 5 then affords

$$\delta \log {}^{H}k_0^{D}(CH/B^-) - \delta \log {}^{H}k_0^{D}(CH/N) \approx \delta_{B^-} - \delta_{NH^+} + \delta_{SR}(CH/B^-) - \delta_{SR}(CH/N) \approx (\alpha_{des}^{B^-} - \beta)(\log {}^{H}\gamma_{B^-}^{D} - \log {}^{H}\gamma_{NH^+}^{D}) + \delta_{SR}(CH/B^-) - \delta_{SR}(CH/N) \tag{10}$$

There are five entries in Table IV for which $\delta \log {}^{H}k_0^{D}(CH/B^-) - \delta \log {}^{H}k_0^{D}(CH/N)$ can be calculated. A plot according to eq 10 is shown in Figure 4. It forms an approximate straight line, an encouraging fact that suggests that our assumptions may not be far off the mark. From slope and intercept we obtain $\alpha_{des}^{B^-} - \beta = 0.090 \pm 0.016$ and $\delta_{SR}(CH/B^-) - \delta_{SR}(CH/N) = 0.22 \pm 0.12$, respectively. In conjunction with eqs 6 and 9, δ_{B^-} and δ_{NH^+} can now be calculated as $\approx 0.09 \log {}^{H}\gamma_{B^-}^{D}$ and $0.09 \log {}^{H}\gamma_{NH^+}^{D}$, respectively. The results are given in Table VI.

If the earlier assumption $|\alpha_{sol}^{C^-} - \beta| \approx |\alpha_{des}^{B^-} - \beta|$ were retained, δ_{C^-} would, analogously, be given as $0.09 \log {}^{H}\gamma_{C^-}^{D}$ (eq 7). It is more likely, though, that $|\alpha_{sol}^{C^-} - \beta| > |\alpha_{des}^{B^-} - \beta|$. Since solvation of the carbanions is coupled to the delocalization of the negative charge, the lag in the solvation of these ions is probably more pronounced than the lag in the solvation of oxyanion (or the degree by which

Table VII. Estimates for δ_{C^-} and δ_{SR}(CH/N)

	δ_{C^-}		δ_{SR}(CH/N)	
CH acid	0% (10%) → 90% Me_2SO	50% → 90% Me_2SO	0% (10%) → 90% Me_2SO	50% → 90% Me_2SO
CH_3NO_2	1.01	0.57	2.81	1.85
$PhCH_2NO_2$	0.61	0.32	2.61	1.77
AcAc	0.68	0.36	0.61	0.62
ID	0.27	0.21	0.83	0.60
Fl-COOMe		−0.32		0.66
Fl-CN	−0.60	−0.40	0.77	0.30

the desolvation of the oxyanion is ahead of proton transfer in the opposite direction). This is because delocalization itself lags behind proton transfer, which compounds the lag in the solvation.[15] A value of 0.15 for $|\alpha_{sol}^{C^-} - \beta|$ or even higher is not unreasonable. The δ_{C^-} values summarized in Table VII were calculated with $|\alpha_{sol}^{C^-} - \beta| = 0.15$.

We are now able to estimate δ_{SR}(CH/N) by rearranging eq 8 to

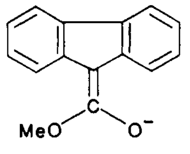
$$\delta_{SR}(CH/N) \approx \delta \log {}^{H}k_0^{P}(CH/N) - \delta_{C^-} - \delta_{NH^+} \qquad (11)$$

δ_{SR}(CH/N) values are summarized in Table VII. Perhaps the most interesting result of this analysis is the large size of the δ_{SR}-terms for the nitroalkanes. In fact for these latter compounds δ_{SR} dominates the solvent effect on k_0.

This state of affairs is more consistent with the notion that δ_{SR} is a dynamic solvent effect than that it represents a special transition state stabilization by Me_2SO. Dynamic solvent effects increase in importance with increasing charge density;[20,21a] the high formal negative charge on the nitro oxygens may very well be viewed as enhanced charge density. On the other hand, if δ_{SR} were mainly due to a transition state stabilization by Me_2SO, it should be most pronounced with the highly polarizable fluorenes, which is contrary to our results.[30,32]

Comparison between Fl-CN and Fl-COOMe. The intrinsic rate constant for ionization of Fl-CN by primary amines is 8.3-fold higher than with Fl-COOMe in 50% Me_2SO while in 90% Me_2SO the difference between the two amounts to a factor of 3.0. In principle, these differences could, at least in part, be attributed to a steric effect by the bulkier COOMe group compared to the CN group. However, much bulkier groups in the 9-position of fluorenes have been shown to have little effect on proton-transfer rates.[12] Hence a nonsteric explanation is called for.

There are two major factors that seem to contribute to the differences in k_0. The first is the difference in the π-acceptor abilities of the COOMe and the CN groups. The anion of Fl-COOMe apparently derives a significant portion of its stabilization from the resonance form **1**.



1

In contrast, the contribution of the CN groups to the stability of the Fl-CN anion must be mainly through its polar effect. The less negative log $^{H}\gamma_{C^-}^{P}$ value of Fl-COOMe⁻ compared to that of Fl-CN⁻ (Table V) constitutes direct evidence for the importance of **1** and for the role of hydrogen-bonding solvation at the oxyanion site. Hence the lower k_0 for Fl-COOMe reflects, in part, the well-known PNS effect of late development of resonance/hydrogen-bonding solvation of carbanions that delocalize part of their negative charge onto oxygen.[15,29] Inasmuch as hydrogen-bonding solvation decreases in Me_2SO-rich solvents, this factor becomes less important and the difference in k_0 for the two fluorenes is reduced. Or, in the context of eq 8, δ_{C^-} is less negative for Fl-COOMe than for Fl-CN, and hence log k_0 for Fl-COOMe increases upon addition of Me_2SO while k_0 for Fl-CN remains about the same.

The second factor is the stronger polar effect of the CN group compared to the COOMe group. The influence of this factor is most easily understood if one considers the situation of two substituents, neither of which is a π-acceptor. In such a scenario one may, to a first approximation, treat the substituents as if they were "remote" substituents. If delocalization of the negative charge into the fluorene moiety lags behind proton transfer, as is indicated by Murdoch et al.'s study of 9-alkylfluorenes,[12] a more electron-withdrawing substituent in the 9-position will produce an increase in k_0.[15,29] This is because in the transition state the negative charge is closer to the 9-substituent than it is in the delocalized product ion, which leads to a disproportionately large substituent effect on the rate compared to the equilibrium constant. Note that this is the same phenomenon that leads to the exalted Brønsted α-values in the deprotonation of substituent phenylnitroalkanes.[16]

Proton Transfer from Carbon to Carbon. For eq 3 we have obtained $k_1^C = 3400\ M^{-1}\ s^{-1}$ and $k_{-1}^{CH} = 32\ M^{-1}\ s^{-1}$ ($K_1^C = 102$) in 90% Me_2SO. These values are very close to those determined in pure Me_2SO by Ritchie[7b] ($k_1^C = 3300\ M^{-1}\ s^{-1}$, $k_{-1}^C = 41.5\ M^{-1}\ s^{-1}$, $K_1^C = 79.4$ at 25 °C).

If one assumes a Brønsted coefficient d log k_1^C/d log K_1^C = −d log k_{-1}^C/d log K_1^C = 0.5, one can calculate an intrinsic rate constant of 337 $M^{-1}\ s^{-1}$ or log $k_0^C = 2.53$. That the assumption of a Brønsted coefficient of 0.5 is probably a fairly good one may be deduced from the effect on k_1^C and K_1^C in the reactions of Fl-COOMe and Fl-CN with fluoradenyl ion in Me_2SO, where a change in log K_1^C of 1.9 leads to a change of 0.91 in log k_1^C.[7b] Even if the Brønsted coefficient were substantially different from 0.5, as seems to be the case in the reaction between 9-alkylfluorenes with (9-alkylfluorenyl)lithium in ether,[12] which would imply a slightly different log k_0 value, the qualitative conclusions to be drawn would not change.

What is striking about the k_0^C value is that it is so high, i.e., only 0.8 log unit lower than the average (3.33) of log k_0 for the reactions of Fl-CN and Fl-COOMe with primary amines (Table III). This result has a bearing on the Marcus[22] relation, according to which the intrinsic barrier of a "cross reaction" such as

$$CH + RNH_2 \underset{0}{\overset{k^{NC}}{\rightleftharpoons}} C^- + RNH_3^+ \qquad (12)$$

(CH = carbon acid) should be the average of the intrinsic barrier of the corresponding "identity reactions", eqs 13 and 14

$$CH + C^- \overset{k_0^{CC}}{\rightleftharpoons} C^- + CH \qquad (13)$$

$$RNH_3^+ + RNH_2 \overset{k_0^{NN}}{\rightleftharpoons} RNH_2 + RNH_3^+ \qquad (14)$$

and thus be given by

$$\Delta G_0^{\ddagger}(NC) = \tfrac{1}{2}[\Delta G_0^{\ddagger}(CC) + \Delta G_0^{\ddagger}(NN)] \qquad (15)$$

If eq 15 is expressed in terms of intrinsic rate constants instead of intrinsic barriers one obtains

$$\log k_0^{NC} = \tfrac{1}{2}(\log k_0^{CC} + \log k_0^{NN}) \qquad (16)$$

Assuming log $k_0^{NN} \approx 8.0$[33] and approximating log k_0^{CC} with log $k_0^C = 2.53$ of eq 3, one calculates log $k_0^{NC} \approx 5.25$ from eq 16. This

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(31) Bernasconi, C. F.; Kliner, D. A.; Mullin, A.; Ni, J., unpublished results.

(32) Buncel, E.; Wilson, H. *Adv. Phys. Org. Chem.* **1977**, *14*, 133.

(33) In water log $k_0^{NN} \gtrsim 8.6$.[34] In 90% Me_2SO–10% water the rates are probably somewhat lower. If they were the same as in water, the disagreement with the Marcus equation (eq 16) would be even more pronounced.

is ≈ 1.9 log units higher than the above-mentioned average (3.33) of log k_0 for the deprotonation of Fl-CN and Fl-COOMe by amines and indicates a rather large disagreement with the Marcus prediction. Interestingly, if eq 16 is applied to the deprotonation of HCN by primary amines, the *calculated* logk_0^{NC} amounts to ≤6.8 (log $k_0^{\mathrm{CC}} \leq 5.0$,[35] log $k_0^{\mathrm{NN}} \approx 8.6$[34]) while the *observed* log k_0^{NC} is ≈ 7.6;[35] i.e., here the observed log k_0^{NC} value is significantly higher (rather than lower) than the calculated one. It would of course be premature to draw sweeping conclusions from these two cases but they suggest that eq 16 may not have a strong predictive value.

Conclusions. The solvent effect on the intrinsic rate constant of the ionization of a carbon acid can be understood as the result of an interplay of three major factors. If the ionizing agent is an oxyanion, the three factors are early desolvation of the base (δ_{B^-}), late solvation of the developing carbanion (δ_{C^-}), and solvent reorganization δ_{SR}, which probably primarily represents a dynamic solvent effect (see eq 5); if the base is an amine, early desolvation of the oxyanion is replaced by late solvation of the developing ammonium ion (δ_{NH^+}) while the other two factors (δ_{C^-}, δ_{SR}) remain the same (see eq 8).

On the basis of solvent activity coefficients for the transfer of ions from aqueous to Me_2SO rich solvents one predicts $\delta_{\mathrm{B}^-} \gg 0$ and $\delta_{\mathrm{NH}^+} < 0$; δ_{C^-} depends on the carbanion, with $\delta_{\mathrm{C}^-} \gg$ for nitronate ions, > for enolate ions, ≤ for Fl-COOMe⁻, and < 0 for Fl-CN⁻. The large solvent effect on k_0 in the ionization of Fl-COOMe by oxyanions reported by Ritchie, which contrasts with the very small solvent effects in the ionization of Fl-COOMe and Fl-CN by amines reported in the present study, is thus easily understood as the consequence of $\delta_{\mathrm{B}^-} \gg 0$ and $\delta_{\mathrm{NH}^+} < 0$.

A positive δ_{SR}-term seems necessary to explain the solvent dependence of k_0 in all cases for which suitable data are available (CH_3NO_2, $PhCH_2NO_2$, acetylacetone, 1,3-indandione, Fl-COOMe, Fl-CN), but its importance is most compellingly demonstrated in the reaction of Fl-COOMe and Fl-CN with amines. This is because in these reactions k_0 is virtually solvent independent (slight increase in the case of Fl-COOMe) while the sum of $\delta_{\mathrm{NH}^+} + \delta_{\mathrm{C}^-}$ is unequivocally negative, hence requiring a positive δ_{SR} in eq 8.

An, admittedly crude, estimate of the magnitude of δ_{SR} suggests that δ_{SR} is particularly large for the nitroalkanes, consistent with expectations for a dynamic solvent effect but inconsistent with an alternative interpretation of δ_{SR} as a transition state stabilization by Me_2SO.

The larger intrinsic rate constant for the ionization of Fl-CN compared to Fl-COOMe can be attributed to a combination of two factors: (1) the late development of the resonance form **1**, which lowers k_0 for Fl-COOMe; (2) the polar effect of the CN group being stronger than that of the COOMe group, which increases k_0 for Fl-CN because of the late charge delocalization into the fluorenyl moiety.

The intrinsic rate constant for the carbon to carbon proton transfer in eq 3 appears rather high, substantially higher than expected on the basis of the Marcus relation (eq 16).

Experimental Section

Materials. 9-Cyanofluorene (Fl-CN) was prepared from 9-formylfluorene by the method of Wislicenus and Russ.[36] Repeated recrystallizations from ethanol gave white needles: mp 150–151 °C (lit.[36-38] mp 151–152 °C). 9-(Carbomethoxy)fluorene (Fl-COOMe) was obtained from the reaction of fluorenyl anion with dimethyl carbonate in Me_2SO, as described by Bordwell.[38] The product was purified by chromatography on silica gel with benzene as eluent, followed by two crystallizations from methanol: mp 65–66 °C (lit.[37-39] mp 64–65 °C). The carbanions of Fl-CN and Fl-COOMe have $\lambda_{max} = 408$ nm ($\epsilon = 2600$) and $\lambda_{max} = 400$ nm ($\epsilon = 4600$), respectively, in 50% Me_2SO–50% H_2O. The purification of the amines has been described in a previous paper.[18]

Kinetic Experiments and pK_a Determinations. The method used to follow the kinetics of proton transfer from Fl-CN/Fl-CN⁻ and Fl-COOMe/Fl-COOMe⁻ to amine buffers was basically the same as described in previous studies.[18,19] Proton transfers from Fl-CN to Fl-COOMe⁻ were studied at 450 nm using Fl-CN as the indicator (1.05×10^{-4} M) and Fl-COOMe⁻ as the base in excess (0.001–0.002 M). The absorbance of the Fl-COOMe buffer solutions was high at this wavelength, but the formation of Fl-CN⁻ was in all cases accompanied by a change of about 0.1 absorbance unit. With appropriate offsets in the absorbance scale, this change was sufficient to get good kinetics in the stopped-flow apparatus. The observed rate constants k_{obsd} used to derive the kinetic parameters listed in Tables I and II represent average values of two or three single determinations.

The pK_a measurements were carried out as previously described.[18]

Acknowledgment. This research has been supported by Grant No. CHE-8315374 from the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. *n*-$BuNH_2$, 109-73-9; $MeO(CH_2)_2NH_2$, 109-85-3; $EtOC(O)CH_2NH_2$, 459-73-4; $HO(CH_2)_2NH_2$, 141-43-5; $NH_2C(O)CH_2NH_2$, 598-41-4; 9-cyanofluorene, 1529-40-4; 9-(carbomethoxy)fluorene, 3002-30-0; piperidine, 110-89-4; morpholine, 110-91-8.

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