slower this step will be, and thus the more important that it is catalyzed effectively. In a single-base enzyme, this can be done by the general acid generated by the removal of the C–H proton, as long as the leaving group oxygen is syn to it. For an unstable intermediate, spontaneous (water-catalyzed) C–O cleavage would be faster and anti stereochemistry more necessary, as described above. Eventually, as the general level of catalytic efficiency rose, evolutionary pressure would increase for catalysis even of relatively fast C–O cleavage, leading to enzymes with a second active site catalytic group, but naturally retaining anti stereochemistry.

Acknowledgment. We are grateful to the Science and Engineering Research Council for a studentship to T.L.A. and to Dr. J. P. Richard for helpful discussion.

Rate and Equilibrium Constants of Ionization of (α-Cyanodiphenylmethane)bis(tricarbonylchromium(0)) in Me_2SO–Water Mixtures. Unusual Solvent Effect on the Intrinsic Rate Constant

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Contribution from the Thimann Laboratories of the University of California, Santa Cruz, California 95064, and the Laboratoire de Physicochimie des Solutions, UA CNRS 403, ENSCP, 11 Rue Curie, 75231 Paris Cedex 05, France. *Received March 17, 1988*

Abstract: The kinetics of the ionization of (α-cyanodiphenylmethane)bis(tricarbonylchromium(0)) by carboxylate ions, primary amines, and the piperidine/morpholine pair have been measured in 50%, 70%, and 90% aqueous Me_2SO. The Brønsted plots for the carboxylate ion reactions in 70% and 90% Me_2SO show some downward curvature which is reminiscent of recent reports of such curvature in the ionization of acetylacetone and 1,3-indandione, and is attributed to a solvation effect. Intrinsic rate constants, defined as $k_0 = k_1^{B}/q = k_{-1}^{BH}/p$ at $\Delta pK + \log(p/q) = 0$, were determined by suitable interpolation or extrapolation of the Brønsted plots. For the piperidine/morpholine pair in 50% Me_2SO $\log k_0 = 3.30$. Even if one allows for a rate lowering steric effect of up to one log unit, giving a corrected $\log k_0 \approx 4.3$, this value is still close to that for 4-nitrophenylacetonitrile ($\log k_0 = 3.95$). This suggests that the resonance effect of the $Cr(CO)_3$–phenyl groups is substantial and comparable to that of the combination of a 4-nitrophenyl and a cyano group, in agreement with some literature reports but in disagreement with others. The effect of increasing the Me_2SO content of the solvent is to significantly decrease k_0 for both the carboxylate ion and amine reactions. This contrasts with either sharp *increases* in k_0 or solvent independent k_0 values with six other carbon acids for which similar data are available. The decrease in k_0 can be attributed to carbanion solvation being substantially stronger in Me_2SO than in water, as confirmed by measurements of the solvent activity coefficient for the transfer from 50% to 70% and from 50% to 90% Me_2SO. Since it appears that carbanion solvation generally lags behind proton transfer at the transition state, this lag produces a decrease in k_0 in the better solvating medium. Surprisingly, the solvent effect on k_0 is essentially independent of the ionizing agent, again in contrast to findings in other systems where the addition of Me_2SO enhanced k_0 for the carboxylate ion reactions more strongly than for the amine reactions. A possible explanation of our results is that the main factor usually responsible for the larger solvent effects in the carboxylate ion reactions, i.e., the lag of the proton transfer behind the desolvation of the carboxylate ion, becomes insignificant because proton transfer is nearly complete at the transition state, as implied by very high Brønsted β-values.

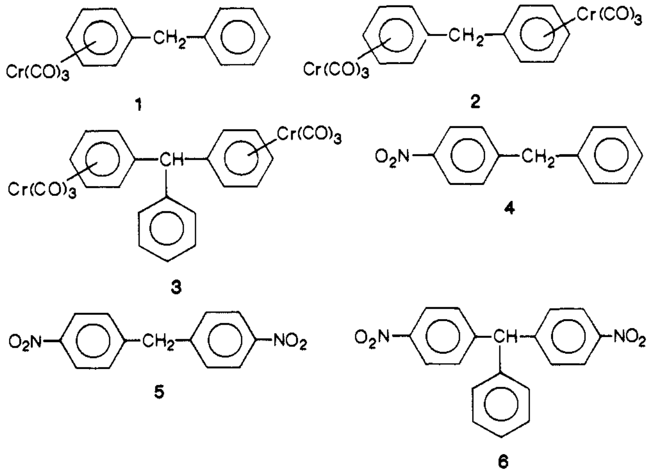
The tricarbonylchromium(0) group ($Cr(CO)_3$) is known to be strongly electron withdrawing as reflected in a pK_a value of $Cr(CO)_3$–phenylacetic acid that is virtually identical with that of 4-nitrophenylacetic acid.[1] Despite its strong electronic effect it has not been widely used as an activating group in the study of proton transfers from carbon acids. In a first quantitative study Terrier et al.[2] recently compared kinetic and thermodynamic acidities of the $Cr(CO)_3$-substituted di- and triphenylmethanes **1**–**3** with the corresponding 4-nitro-substituted analogues **4**–**6** in Me_2SO–methanol mixtures. Their major findings can be summarized as follows.

(1) The nitro group is more effective in stabilizing the diphenyl and triphenylmethane anions as reflected in much higher acidity constants of **4** vs **1**, **5** vs **2**, and **6** vs **3**.

(2) One $Cr(CO)_3$–phenyl group is *kinetically* more acidifying than one 4-nitrophenyl group, as reflected in an approximately 3-fold higher rate constant of deprotonation of **1** vs **4** by methoxide ion.

(3) In the comparisons **2** vs **5** and **3** vs **6** the respective nitro compound is deprotonated slightly more rapidly than the $Cr(CO)_3$ compound, but if the results are adjusted to compensate for the different thermodynamic acidities, **2** is faster than **5** while **3** and **6** show comparable kinetic reactivities.

Chart I



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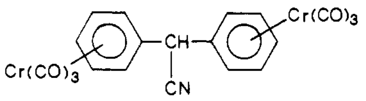
These results show that the *intrinsic* rate constants (k for $K = 1$) for the $Cr(CO)_3$-phenyl activated carbon acids are higher than for the 4-nitrophenyl ones. The reduced kinetic advantage of the $Cr(CO)_3$ compounds in the series **1** → **2** → **3** was attributed to a steric effect that progressively lowers the rate of proton transfer.

Since low intrinsic rate constants of proton transfers are generally associated with the formation of resonance stabilized carbanions,[3,4] it was suggested that, in contrast to the nitro group, the mode of action of the $Cr(CO)_3$ group is more by an inductive effect than by a resonance effect.[2] This conclusion is in agreement with findings based on rate effects in E2-elimination reactions,[5] but it is difficult to reconcile with the effect of the $Cr(CO)_3$ group on the pK_a of phenol,[6] or the rate of S_NAr reactions[6] and other phenomena.[7]

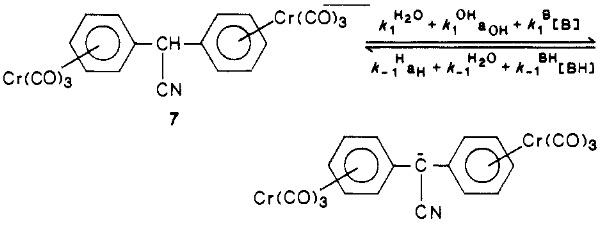
In an attempt to shed more light on the mode of action of the $Cr(CO)_3$ group in proton transfers we have studied the ionization of **7** in Me_2SO–water mixtures. A major virtue of **7** is that it is more acidic than **1–3**, which allows kinetic measurements with the same amine and carboxylate buffers used to measure intrinsic rate constants of ionization of several other carbon acids studied recently. Our work includes an investigation of the effect of changing the solvent from 50% Me_2SO–50% water to 70% Me_2SO–30% water and 90% Me_2SO–10% water on rate and equilibrium constants, and thus on the intrinsic rate constant, of the ionization of **7**. Coupled with a determination of solvent activity coefficients for the transfer of **7** and its anion from 50% Me_2SO–50% water to the other solvents, this solvent effect study is aimed at testing a recently proposed theoretical framework[4,8] for understanding solvent effects on intrinsic rate constants of proton transfers.



7

Results

Kinetic Measurements. Rates were measured in the stopped-flow apparatus. The reaction can be described by eq 1.



(1)

7⁻

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

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

When the pK_a of the buffer (pK_a^{BH}) was higher than the pK_a of the carbon acid (pK_a^{CH}) the equilibrium was approached from left to right. When pK_a^{BH} < pK_a^{CH} the equilibrium was approached from right to left by first generating **7⁻** in a 2×10^{-3} M or 10^{-2} M KOH solution and then reacting it with the appropriate buffer.

Table I. Rate Constants and pK_a Values for Equation 1 in 50% Me_2SO–50% Water (v/v) at 20 °C, $\mu = 0.5$ M

B	pK_a^{BH} [a]	k_1^{B},[b] M^{-1} s^{-1}	k_{-1}^{BH},[b] M^{-1} s^{-1}	ΔpK[c] + log (p/q)
piperidine	11.05	1.20×10^4	1.94×10^3	1.09
morpholine	8.70	2.66×10^2	8.61×10^3	−1.26
n-$BuNH_2$	10.68	4.25×10^3	1.60×10^3	0.90
$CH_3OCH_2CH_2NH_2$	9.63	5.89×10^2	2.40×10^3	−0.15
$H_2NCOCH_2NH_2$	8.28	7.75×10^1	7.07×10^3	−1.50
$EtOOCCH_2NH_2$	7.83	3.71×10^1	8.50×10^3	−1.95
$NCCH_2NH_2$	5.39	4.40×10^{-1}	3.00×10^4	−4.39

[a] From ref 11b. [b] Estimated error limits ≤7%. [c] ΔpK = pK_a^{BH} − pK_a^{CH} with pK_a^{CH} = 10.26.

Table II. Rate Constants and pK_a Values for Equation 1 in 70% Me_2SO–30% Water (v/v) at 20 °C, $\mu = 0.25$ M

B	pK_a^{BH} [a]	k_1^{B},[b] M^{-1} s^{-1}	k_{-1}^{BH},[b] M^{-1} s^{-1}	ΔpK[c] + log (p/q)
piperidine	10.66	1.77×10^4	7.72×10^2	1.72
morpholine	8.66	7.04×10^2	3.96×10^3	−0.28
n-$BuNH_2$	10.49	6.94×10^3	3.99×10^2	1.73
$CH_3OCH_2CH_2NH_2$	9.57	1.50×10^3	7.04×10^2	0.81
$H_2NCOCH_2NH_2$	8.34	2.62×10^2	2.13×10^3	−0.42
$EtOOCCH_2NH_2$	7.75	1.03×10^2	5.05×10^3	−1.01
$NCCH_2NH_2$	5.42	1.70×10^0	1.51×10^4	−3.34
AcO^-	6.90	1.76×10^2	2.66×10^4	−2.64
$CH_3OCH_2COO^-$	5.67	2.09×10^1	5.50×10^4	−3.87
$ClCH_2COO^-$	4.65	2.37×10^0	7.85×10^4	−4.89
$NCCH_2COO^-$	4.13	7.43×10^{-1}	7.29×10^4	−5.41

[a] From ref 11b. [b] Estimated error limits ≤10%. [c] ΔpK = pK_a^{BH} − pK_a^{CH} with pK_a^{CH} = 9.24.

Me_2SO solutions (50%) of **7⁻** were quite unstable and completely decomposed within 2 to 3 min. This problem was circumvented by generating **7⁻** in a multimixing stopped-flow apparatus that allowed reaction of **7⁻** with the buffer to be carried out a few seconds after **7⁻** was generated. In 70% and 90% Me_2SO the decomposition of **7⁻** was significantly slower and did not require the use of the multimixing stopped-flow apparatus.

In 50% Me_2SO rates could only be measured with amine buffers but not with carboxylic acids because these latter were outside the time resolution of the stopped-flow method. In the other solvents these rates were much slower, mainly because of lower pK_a^{CH} and higher pK_a^{BH} values, and thus these rates were measurable.

A typical set of experiments with a given buffer consisted of measuring k_{obsd} for five different buffer concentrations at a constant buffer ratio. Plots of k_{obsd} vs buffer concentration were all linear; in most cases, particularly in the Me_2SO-rich solvents, intercepts were quite small or negligible, indicating that $k_1^{B}[B] + k_{-1}^{BH}[BH] \gg k_1^{H_2O} + k_1^{OH}a_{OH^-} + k_{-1}^{H}a_{H^+} + k_{-1}^{H_2O}$, and no attempts were made to measure $k_1^{H_2O}$, k_1^{OH}, k_{-1}^{H}, or $k_{-1}^{H_2O}$. The buffer ratio was usually 1:1 and hence a plot of k_{obsd} vs [B] (or [BH⁺]) would provide a slope given by eq 3

$$\text{slope} = k_1^{B} + k_{-1}^{BH} \tag{3}$$

In conjunction with eq 4

$$k_1^{B}/k_{-1}^{BH} = K_a^{CH}/K_a^{BH} \tag{4}$$

k_1^{B} and k_{-1}^{BH} could be determined from the known pK_a^{BH} and pK_a^{CH}, the latter being obtained as follows.

Since the instability of **7⁻** precluded a precise spectrophotometric determination of pK_a^{CH}, this quantity was measured kinetically in buffers whose pK_a^{BH} was close to pK_a^{CH}. For these experiments k_{obsd} was determined as a function of buffer concentration at several different buffer ratios. The slope of a plot of k_{obsd} vs [B] is then given by

$$\text{slope} = k_1^{B} + k_{-1}^{BH}a_{H^+}/K_a^{BH} \tag{5}$$

From the pH dependence of this slope k_1^{B} and k_{-1}^{BH} could be obtained and thus pK_a^{CH} could be determined by solving eq 4 for K_a^{CH}.

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Table III. Rate Constants and pK_a Values for Equation 1 in 90% Me_2SO–10% Water (v/v) at 20 °C, μ = 0.06 M

B	p$K_a^{BH\,a}$	k_1^{B},[b] M^{-1} s^{-1}	k_{-1}^{BH},[b] M^{-1} s^{-1}	ΔpK^c + log (p/q)
piperidine	10.74	1.87×10^4	5.28×10^3	1.92
morpholine	8.91	1.15×10^3	2.06×10^3	0.09
n-$BuNH_2$	10.96	1.11×10^4	2.21×10^2	2.32
$CH_3OCH_2CH_2NH_2$	10.16	3.36×10^3	3.52×10^2	1.52
$H_2NCOCH_2NH_2$	9.19	5.82×10^2	4.52×10^2	0.55
$EtOOCCH_2NH_2$	8.22	1.68×10^2	1.40×10^3	−0.42
$NCCH_2NH_2$	5.94	2.89×10^0	3.72×10^3	−2.70
AcO^-	9.53	1.77×10^4	5.00×10^3	0.11
$CH_3OCH_2COO^-$	8.17	2.24×10^3	1.29×10^4	−1.25
$ClCH_2COO^-$	6.84	1.21×10^2	1.71×10^4	−2.58
$NCCH_2COO^-$	6.25	2.71×10^1	1.56×10^4	−3.17
Cl_2CHCOO^-	4.68	7.87×10^{-1}	1.85×10^4	−4.74

[a] From ref 11b. [b] Estimated error limits ≤10%. [c] ΔpK = pK_a^{BH} − pK_a^{CH} with pK_a^{CH} = 9.12.

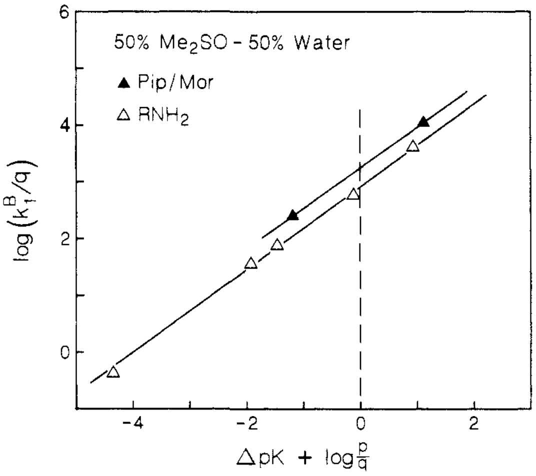


Figure 1. Brønsted plots in 50% Me_2SO–50% water.

Our results are summarized in Tables I (50% Me_2SO), II (70% Me_2SO), and III (90% Me_2SO).

Solvent Activity Coefficients. The solvent activity coefficients for the transfer of **7** from 50% Me_2SO–50% water to 70% Me_2SO–30% water (${}^{50}\gamma_{CH}^{70}$) and from 50% Me_2SO–50% water to 90% Me_2SO–10% water (${}^{50}\gamma_{CH}^{90}$) were determined from partition experiments between n-heptane and the above Me_2SO–water mixtures. The solvent activity coefficients[9] are given by

$$ {}^{50}\gamma_{CH}^{70} = {}^{70}P^{H}/{}^{50}P^{H} \tag{6}$$

$$ {}^{50}\gamma_{CH}^{90} = {}^{90}P^{H}/{}^{50}P^{H} \tag{7}$$

with ${}^{50}P^{H}$, ${}^{70}P^{H}$, and ${}^{90}P^{H}$ respectively being the partition coefficients between n-heptane and 50%, 70%, and 90% Me_2SO. ${}^{50}P^{H} = 1.02 \times 10^{-1}$, ${}^{70}P^{H} = 2.00 \times 10^{-3}$, and ${}^{90}P^{H} < 3 \times 10^{-4}$ were determined as described in the Experimental Section, from which we obtain ${}^{50}\gamma_{CH}^{70} = 1.96 \times 10^{-2}$ ($\log {}^{50}\gamma_{CH}^{70} = -1.71$) and ${}^{50}\gamma_{CH}^{90} < 2.94 \times 10^{-3}$ ($\log {}^{50}\gamma_{CH}^{90} < -2.53$).

From the relationship between the solvent effect on pK_a^{CH} and the solvent activity coefficients of the carbon acid, the carbanion, and the hydronium ion,[10] eq 8 and 9, we obtained $\log {}^{50}\gamma_{C^-}^{70} = -1.83$ and $\log {}^{50}\gamma_{C^-}^{90} < -2.56$ for **7**⁻.

$$ {}^{50}\Delta^{70}\mathrm{p}K_a^{CH} = \log {}^{50}\gamma_{C^-}^{70} + \log {}^{50}\gamma_{H^+}^{70} - \log {}^{50}\gamma_{CH}^{70} \tag{8}$$

$$ {}^{50}\Delta^{90}\mathrm{p}K_a^{CH} = \log {}^{50}\gamma_{C^-}^{90} + \log {}^{50}\gamma_{H^+}^{90} - \log {}^{50}\gamma_{CH}^{90} \tag{9}$$

Discussion

Tables I–III summarize the rate constants k_1^{B} and k_{-1}^{BH} defined in eq 1, obtained in the three solvents 50%, 70%, and 90% Me_2SO, while Figures 1–3 show the Brønsted plots for k_1^{B}. As has been observed in numerous cases,[11-13] the three families of bases form separate Brønsted plots, with the statistically corrected rate constants for a given ΔpK + log (p/q) being in the order $RCOO^-$ > secondary amines > primary amines. Another similarity with recently reported results on the ionization of acetylacetone[11a] and 1,3-indandione[11b] is the downward curvature of the Brønsted plots for the carboxylate ions in 70% and 90% Me_2SO. This downward

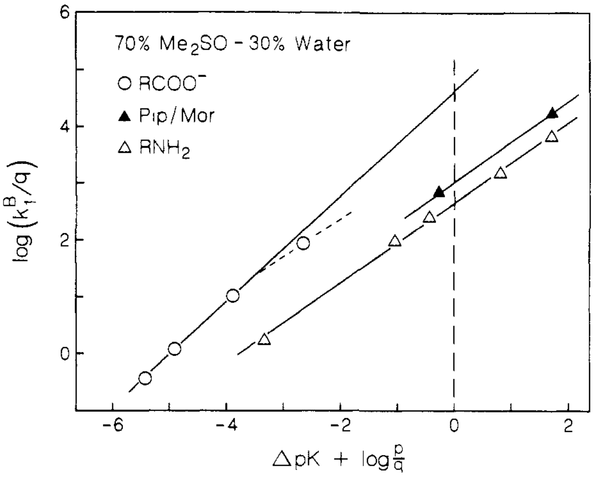


Figure 2. Brønsted plots in 70% Me_2SO–30% water.

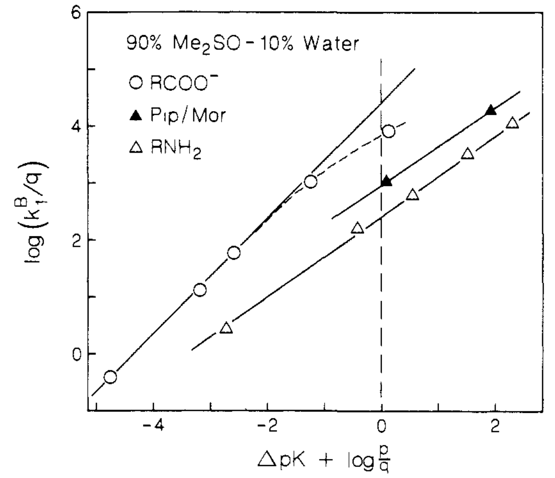
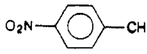
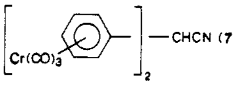
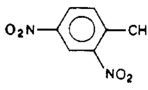


Figure 3. Brønsted plots in 90% Me_2SO–10% water.

Table IV. Intrinsic Rate Constants (log k_0) and pK_a Values for the Ionization of Cyano Carbon Acids by Amines in Water or 50% Me_2SO–50% Water

acid	solvent	temp, °C	pK_a	log k_0
HCN[c]	H_2O	25	9.0	≈7.5[a]
$CH_2(CN)_2$[d]	H_2O	25	11.1	≈7.0[b]
 (8)[e]	50% Me_2SO	20	12.62	3.95[b]
 (7)	50% Me_2SO	20	10.23	3.30[b]
 (9)[e]	50% Me_2SO	20	8.06	2.90[b]

[a] Primary and tertiary amines. [b] Piperidine/morpholine. [c] Reference 17. [d] Reference 3d. [e] Reference 16. [f] This work.

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Table V. Intrinsic Rate Constants, log k_0,[a] and Solvent Effects ($\delta \log {}^{W}k_0{}^{D}$)[b]

% Me_2SO (χ_{Me_2SO})	$RCOO^-$ [c]	RNH_2	pip/mor
		7	
50 (0.203)		2.94 ± 0.04	3.30 ± 0.06
70 (0.372)	4.59 ± 0.08	2.65 ± 0.03 (−0.29 ± 0.07)	3.04 ± 0.06 (−0.26 ± 0.12)
90 (0.696)	4.35 ± 0.10 (−0.24 ± 0.18)	2.42 ± 0.03 (−0.52 ± 0.07)	2.98 ± 0.10 (−0.32 ± 0.16)
		9-Cyanofluorene[d] (**10**)	
10 (0.028)		3.62 ± 0.07	≈4.44
50 (0.203)		3.76 ± 0.09 (0.14 ± 0.16)	4.58 ± 0.05 (≈0.14)
90 (0.696)		3.57 ± 0.09 (−0.05 ± 0.16)	≈ 4.39 (≈−0.05)
		9-Carbomethoxyfluorene[d] (**11**)	
50 (0.203)		2.84 ± 0.06	
90 (0.696)		3.09 ± 0.03 (0.25 ± 0.09)	
		1,3-Indandione[e] (**12**)	
10 (0.028)	2.64 ± 0.26	2.27 ± 0.13	2.97 ± 0.10
50 (0.203)	3.18 ± 0.10 (0.54 ± 0.36)	2.44 ± 0.17 (0.17 ± 0.30)	3.13 ± 0.10 (0.16 ± 0.20)
70 (0.372)	3.77 ± 0.10 (1.13 ± 0.36)	2.59 ± 0.18 (0.32 ± 0.31)	3.33 ± 0.10 (0.36 ± 0.20)
90 (0.696)	4.53 ± 0.05 (1.89 ± 0.31)	2.97 ± 0.05 (0.70 ± 0.18)	3.85 ± 0.10 (0.88 ± 0.20)
		Acetylacetone[f] (**13**)	
0 (0)	≈3.14	1.90 ± 0.03	2.60 ± 0.06
50 (0.203)	≈3.80 (≈0.66)	2.06 ± 0.02 (0.16 ± 0.05)	2.75 ± 0.06 (0.15 ± 0.12)
90 (0.696)	≈5.27 (≈2.13)	2.91 ± 0.05 (1.01 ± 0.08)	3.64 ± 0.06 (1.04 ± 0.12)
		Phenylnitromethane[g] (**14**)	
0 (0)	−2.10 ± 0.05		−1.22 ± 0.10
50 (0.203)	≈0.57 (≈2.67)		−0.25 ± 0.10 (0.97 ± 0.20)
90 (0.696)	1.88 ± 0.05 (3.98 ± 0.10)	0.97 ± 0.07	1.75 ± 0.10 (2.97 ± 0.20)
		Nitromethane[g] (**15**)	
0 (0)			−0.59 ± 0.10
50 (0.203)			0.73 ± 0.10 (1.32 ± 0.20)
70 (0.372)			1.76 ± 0.10 (2.35 ± 0.20)
90 (0.696)		2.77 ± 0.05	3.06 ± 0.10 (3.65 ± 0.20)

[a] Error limits are standard deviations except for pip/mor where the limits are estimated. [b] $\delta \log {}^{W}k_0{}^{D} = \log k_0$ (high Me_2SO content) − $\log k_0$ (lowest Me_2SO content), values in parentheses. [c] Based on the linear portion of the Brønsted plots. [d] Reference 8. [e] Reference 11b. [f] Reference 11a. [g] Reference 12.

curvature was shown[11] not to constitute a Hammond effect[14] or "Marcus curvature"[14,15] but to be a solvation effect. The same interpretation of the curvature seems to be called for in the present case.

Resonance or Inductive Effect by the $Cr(CO)_3$ Group? From the Brønsted plot with piperidine and morpholine one finds log k_0 = 3.30 for the statistically corrected intrinsic rate constant (log $k_0 = \log (k_1^B/q)$ at $\Delta pK + \log (p/q) = 0$) for the ionization of **7** with secondary cyclic amines. It is instructive to compare this parameter with log k_0 for the ionization of other cyano carbon acids under similar reaction conditions. Table IV summarizes such data along with pK_a^{CH} values. We note that log k_0 for **7** is of the same order of magnitude as for 4-nitrophenylacetonitrile (**8**) and 2,4-dinitrophenylacetonitrile (**9**),[16] but much lower than log k_0 for malononitrile[3d] or HCN.[17] Low intrinsic rate constants are generally attributed to substantial resonance stabilization of the carbanion while high intrinsic rate constants are found in systems in which resonance plays no role (CN^-) or only a modest one ($CH(CN)_2^-$).[3,4,17] According to this criterion the resonance effect of the $Cr(CO)_3$–phenyl groups in 7^- is quite substantial and lies approximately halfway between that of the 4-nitrophenyl and that of the 2,4-dinitrophenyl group.

The above analysis fails to consider steric effects, though. Comparisons between **1** and **2**, and particularly between **2** and **3**, have shown that steric hindrance reduces the intrinsic rate constant for deprotonation of bis($Cr(CO)_3$–phenyl) activated CH acids substantially, but not for the deprotonation of bis(4-nitrophenyl) activated CH acids.[2] The reduction in k_0 for **3** relative to **2** can be estimated to be 10- to 20-fold.

It is more difficult to estimate the steric effect on k_0 in the deprotonation of **7** compared to **8** or **9**. Since the cyano group is much less bulky than a phenyl group the steric crowding in **7** is expected to be significantly less than in **3**, with a correspondingly less dramatic reduction in k_0. However, having two $Cr(CO)_3$–phenyl groups in **7** compared to one 4-nitrophenyl or 2,4-dinitrophenyl group in **8** or **9**, respectively, may put **7** at a further kinetic disadvantage compared to **8** or **9**. We shall assume that the combined steric factors reduce k_0 for **7** by not more than 10-fold compared to k_0 for **8** and **9**. The assumption of a much larger steric effect would be difficult to reconcile with the fact that log k_0 for the piperidine/morpholine reactions is higher than log k_0 for the reactions with the less bulky primary amines, as is commonly observed for proton transfers (see Table V, below). The difference log k_0 (pip/mor) − log $k_0(RNH_2)$ of about 0.4 for **7** is only slightly smaller than that observed for the other carbon acids in Table V (≈0.7 to 0.8), suggesting that the steric effect, even though real, is not dramatic.

A log k_0 value which after correction for the steric effect would be about 4.3 is still fairly close to that for **8** (log k_0 = 3.95) and still indicates a substantial resonance effect in the anion of **7**. This contrasts with an estimated 1.0 to 1.5 log units difference in k_0 between **1** and **4** or **2** and **5**.[2] A possible reason why the difference in the resonance effect between the $Cr(CO)_3$–phenyl and 4-nitrophenyl groups appears so much smaller in the comparison of **7** with **8** than in the comparisons of **1** with **4**, and of **2** with **5** is the presence of the α-cyano group in **7** and **8**. By virtue of its strong electron-withdrawing effect the cyano group diminishes the charge stabilizing role played by the $Cr(CO)_3$–phenyl and 4-nitrophenyl groups. The reduced demand placed on these groups would decrease the resonance effect of both of them, thereby attenuating the superiority of the 4-nitrophenyl over the $Cr(CO)_3$–phenyl group.

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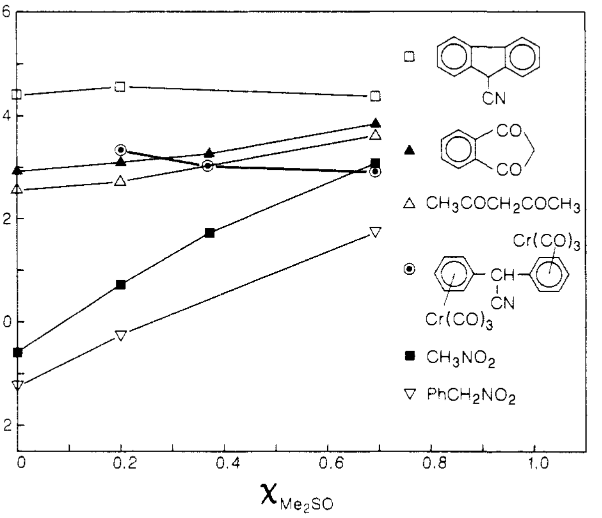


Figure 4. Solvent effects on log k_0 for the piperidine/morpholine reactions.

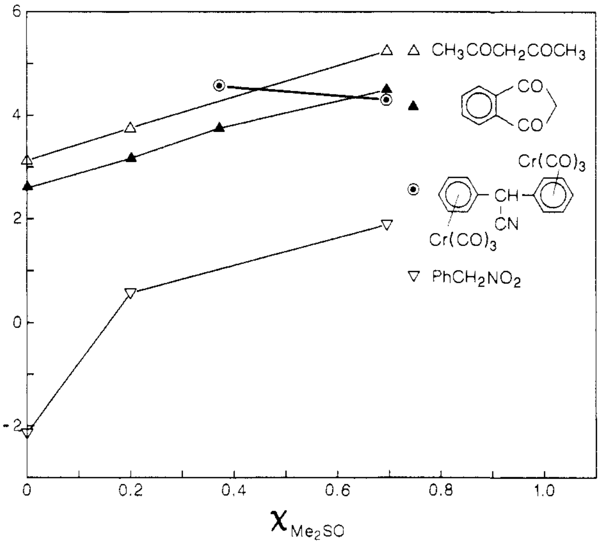


Figure 5. Solvent effects on log k_0 for the carboxylate ion reactions.

Another difference between the two studies is that the data for **1**, **2**, **4**, and **5** were obtained in 98% Me_2SO–2% MeOH; in the absence of a solvent effect study on k_0 for **8** it is difficult to assess how much of the difference in behavior between the two systems is a consequence of using different solvents.

Solvent Effects on Intrinsic Rate Constants. The log k_0 and Brønsted β values for the ionization of **7** by carboxylate ions, primary amines, and piperidine/morpholine in the various solvents are summarized in Tables V and VI, respectively, along with the corresponding parameters for 9-cyanofluorene (**10**), 9-carbomethoxyfluorene (**11**), 1,3-indandione (**12**), acetylacetone (**13**), phenylnitromethane (**14**), and nitromethane (**15**). The dependence of log k_0 on the solvent for the piperidine/morpholine reactions is shown graphically in Figure 4 and for the carboxylate ion reactions in Figure 5. The most striking observation is that among all the systems studied so far, **7** is the only one for which log k_0 clearly decreases with increasing Me_2SO content of the solvent. Another feature which sets **7** apart from the other systems is the very high Brønsted β values, in particular for the carboxylate ion reactions, but also for the amine reactions in water-rich solvents.

The question we wish to address now is whether the reactivity pattern of **7**, even though quite different in several respects from that of the other carbon acids, may still be understood within the conceptual framework developed for these other systems. The main points of this framework[4,8] can be summarized as follows.

Table VI. Brønsted β Values[a]

% Me_2SO	$RCOO^-$ [b]	RNH_2	pip/mor
	7		
50		0.75 ± 0.02	0.71 ± 0.03
70	0.94 ± 0.02	0.71 ± 0.02	0.70 ± 0.03
90	1.00 ± 0.03	0.71 ± 0.02	0.66 ± 0.03
	9-Cyanofluorene[c] (**10**)		
10		0.53 ± 0.12	
50		0.47 ± 0.08	0.43 ± 0.03
90		0.58 ± 0.04	
	9-Carbomethoxyfluorene[c] (**11**)		
50		0.49 ± 0.04	
90		0.60 ± 0.02	
	1,3-Indandione[d] (**12**)		
10	0.50 ± 0.05	0.43 ± 0.03	0.41 ± 0.03
50	0.53 ± 0.03	0.42 ± 0.03	0.40 ± 0.03
70	0.63 ± 0.02	0.49 ± 0.04	0.45 ± 0.03
90	0.74 ± 0.01	0.53 ± 0.02	0.47 ± 0.03
	Acetylacetone[e] (**13**)		
0	0.61 ± 0.03	0.40 ± 0.02	0.37 ± 0.03
50	0.69 ± 0.04	0.45 ± 0.01	0.42 ± 0.03
90	0.83 ± 0.01	0.53 ± 0.02	0.51 ± 0.03
	Phenylnitromethane[f] (**14**)		
0	0.54 ± 0.03		0.48 ± 0.03
50	≈0.60		0.52 ± 0.03
90	0.75 ± 0.02	0.65 ± 0.02	0.69 ± 0.03
	Nitromethane[f] (**15**)		
0			0.59 ± 0.03
50			0.62 ± 0.03
70			0.63 ± 0.03
90		0.69 ± 0.02	0.69 ± 0.03

[a] Error limits are standard deviations except for pip/mor where the limits are estimated. [b] Based on the linear portion of the Brønsted plots (low pK_a^{BH} values). [c] Reference 8. [d] Reference 11b. [e] Reference 11a. [f] Reference 12.

The reason why carbon acids that form resonance stabilized carbanions have lower intrinsic rate constants for proton transfer than carbon acids that form purely inductively stabilized carbanions is that development of resonance lags behind proton transfer at the transition state. In contrast, no such lag seems to occur in the development of the inductive effect. The reduction of the intrinsic rate constant by the lag in the resonance development can be understood as a manifestation of the Principle of Nonperfect Synchronization[4] (PNS). As shown elsewhere,[4] this reduction in k_0 may be expressed by eq 10

$$\delta \log k_0^{res}(C^-) = (\alpha_{res}^{C^-} - \beta)\delta \log K_{res}(C^-) \qquad (10)$$

where $\delta \log k_0^{res}(C^-)$ represents the change in log k_0 compared to a system in which the carbanion is only inductively stabilized, $\delta \log K_{res}(C^-)$ is the enhancement of the equilibrium constant that can be attributed to the resonance stabilization of the carbanion, β is the Brønsted β value which is taken as an approximate measure of the progress of proton transfer at the transition state, while $\alpha_{res}^{C^-}$, not to be confused with the Brønsted α, measures the progress in the resonance development at the transition state. Since $\delta \log K_{res}(C^-) > 0$, and the lag in resonance development means $\alpha_{res}^{C^-} < \beta$, we see that $\delta \log k_0^{res}(C^-) < 0$, i.e., k_0 is lower for the resonance stabilized system.

The log k_0 values listed in Table V range from −2.10 ($PhCH_2NO_2$ with $RCOO^-$ in water) to 4.58 (9-cyanofluorene with pip/mor in 50% Me_2SO–50% water), i.e., they span more than six powers of ten, suggesting large differences in the degree of resonance stabilization of the various carbanions.

The solvation of the carbanion is another factor that affects k_0 strongly. The most easily identified effect is hydrogen bonding solvation of carbanions that delocalize their charge onto oxygen atoms, as is the case with enolate ions and even more so with nitronate ions. One way of understanding this factor is to consider it part of what makes resonance forms such as $RCH{=}NO_2^-$ so unusually stable in protic solvents, and thus to include it into the resonance effect. This point of view is implied in the above discussion which equated the differences between the log k_0 values listed in Table V and log $k_0 \approx 7.5$ (amines) to 8.0 (oxyanions) for HCN[17] with different degrees of resonance stabilization of the carbanions. If this point of view is adopted it should be reflected in eq 10 by including the subscript and superscript "sol", e.g.,

$$\delta \log k_0^{\mathrm{res,sol}}(\mathrm{C}^-) = \left(\alpha_{\mathrm{res,sol}}^{\mathrm{C}^-} - \beta\right)\delta \log K_{\mathrm{res,sol}}(\mathrm{C}^-) \qquad (11)$$

The increase in k_0 for the nitroalkanes and diketones upon addition of Me_2SO to the solvent can thus be understood to be essentially the result of a reduction in $\delta \log K_{\mathrm{res,sol}}(\mathrm{C}^-)$. The absence of a similar solvent effect on k_0 for the other carbon acids may then be traced to a $\delta \log K_{\mathrm{res,sol}}(\mathrm{C}^-)$ that depends little on the solvent, which is plausible since hydrogen bonding solvation cannot play an important role in these cases.

The above point of view, even though qualitatively reasonable, assumes that the lag in solvation of the carbanion is equal to the lag in the resonance development, i.e., if we introduce an $\alpha_{\mathrm{sol}}^{\mathrm{C}^-}$ as measure of solvation at the transition state we would have $\alpha_{\mathrm{sol}}^{\mathrm{C}^-} = \alpha_{\mathrm{res}}^{\mathrm{C}^-} = \alpha_{\mathrm{res,sol}}^{\mathrm{C}^-}$. Since solvation is known to lag behind bond formation even in cases where resonance or charge delocalization does not occur[24-26] (more on this below), it is likely that the lag in the solvation of the carbanion is actually greater than the lag in the charge delocalization. Hence, when dealing with solvent effects on k_0, a more satisfactory approach is to separate the two factors. Thus, we shall understand eq 10 as referring to a nonsolvating medium while the effect of solvation on k_0, relative to the nonsolvating medium, is represented by a separate equation, eq 12.

$$\delta \log k_0^{\mathrm{sol}}(\mathrm{C}^-) = (\alpha_{\mathrm{sol}}^{\mathrm{C}^-} - \beta)\delta \log K_{\mathrm{sol}}(\mathrm{C}^-) \qquad (12)$$

The separation of the two effects allows for the expectation that solvation lags more than charge delocalization, i.e., $\alpha_{\mathrm{sol}}^{\mathrm{C}^-} < \alpha_{\mathrm{res}}^{\mathrm{C}^-}$. Of equal importance, eq 12 provides a convenient formalism to deal with solvent effects on k_0, including solvation effects that are unrelated to hydrogen bonding. Assume eq 13 refers to a Me_2SO-rich solvent (D) and eq 14 to a water rich solvent (W).

$$\delta \log k_0^{\mathrm{sol}}(\mathrm{C}^-)_{\mathrm{D}} = (\alpha_{\mathrm{sol}}^{\mathrm{C}^-} - \beta)_{\mathrm{D}}\delta \log K_{\mathrm{sol}}(\mathrm{C}^-)_{\mathrm{D}} \qquad (13)$$

$$\delta \log k_0^{\mathrm{sol}}(\mathrm{C}^-)_{\mathrm{W}} = (\alpha_{\mathrm{sol}}^{\mathrm{C}^-} - \beta)_{\mathrm{W}}\delta \log K_{\mathrm{sol}}(\mathrm{C}^-)_{\mathrm{W}} \qquad (14)$$

The effect of k_0 of adding Me_2SO is then given by

$$\delta_{\mathrm{C}^-} = \delta \log k_0^{\mathrm{sol}}(\mathrm{C}^-)_{\mathrm{D}} - \delta \log k_0^{\mathrm{sol}}(\mathrm{C}^-)_{\mathrm{W}} = (\alpha_{\mathrm{sol}}^{\mathrm{C}^-} - \beta)_{\mathrm{D}}\delta \log K_{\mathrm{sol}}(\mathrm{C}^-)_{\mathrm{D}} - (\alpha_{\mathrm{sol}}^{\mathrm{C}^-} - \beta)_{\mathrm{W}}\delta \log K_{\mathrm{sol}}(\mathrm{C}^-)_{\mathrm{W}} \qquad (15)$$

If we approximate $(\alpha_{\mathrm{sol}}^{\mathrm{C}^-} - \beta)_{\mathrm{D}} \approx (\alpha_{\mathrm{sol}}^{\mathrm{C}^-} - \beta)_{\mathrm{W}} \approx \alpha_{\mathrm{sol}}^{\mathrm{C}^-} - \beta$,[27] eq 15 simplifies to

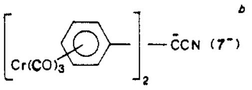
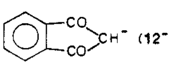
$$\delta_{\mathrm{C}^-} \approx (\alpha_{\mathrm{sol}}^{\mathrm{C}^-} - \beta)(-\log {}^{\mathrm{W}}\gamma_{\mathrm{C}^-}^{\mathrm{D}}) \qquad (16)$$

with ${}^{\mathrm{W}}\gamma_{\mathrm{C}^-}^{\mathrm{D}}$ being the solvent activity coeffcient[9] for the transfer of the carbanion from W to D. log ${}^{\mathrm{W}}\gamma_{\mathrm{C}^-}^{\mathrm{D}}$ for the carbanions derived from **7** and **10**–**15**[28] are summarized in Table VII. For a carbanion that is less solvated in D than in W (e.g., nitronate ions) $\log {}^{\mathrm{W}}\gamma_{\mathrm{C}^-}^{\mathrm{D}} > 0$, hence with $\alpha_{\mathrm{sol}}^{\mathrm{C}^-} < \beta$ one obtains $\delta_{\mathrm{C}^-} > 0$, i.e., the retarded solvation of the carbanion contributes to an increase in k_0, as observed.

Even though δ_{C^-} is a major contributor to the observed solvent effect on k_0 there are other factors as well. For reactions that involve oxyanions (B^-) as the ionizing agent the desolvation of the oxyanion appears to be ahead of proton transfer at the transition state.[11,24,25a,26] This effect can be described by eq 17.

$$\delta_{\mathrm{B}^-} \approx (\alpha_{\mathrm{des}}^{\mathrm{B}^-} - \beta) \log {}^{\mathrm{W}}\gamma_{\mathrm{B}^-}^{\mathrm{D}} \qquad (17)$$

Table VII. Solvent Activity Coefficients for the Transfer of Ions from Water to Me_2SO–Water Mixtures (log ${}^{\mathrm{W}}\gamma^{\mathrm{D}}$), from 50% Me_2SO to 70% Me_2SO (log ${}^{50}\gamma^{70}$), and from 50% Me_2SO to 90% Me_2SO (log ${}^{50}\gamma^{90}$) at 20 °C

ion	% Me_2SO	log ${}^{\mathrm{W}}\gamma^{\mathrm{D}}$	log ${}^{50}\gamma^{70}$	log ${}^{50}\gamma^{90}$
AcO^- [a]	50	3.08		
	70	≈4.50	≈1.42	
	90	≈6.50		≈3.42
$CH_3CH_2CH_2NH_3^+$ [a]	50	−1.81		
	70	≈−2.4	≈−0.6	
	90	≈−2.8		≈−1.0
 (7⁻) [b]	50			
	70		−1.93	
	90			<−2.7
9-CN-Fl⁻ (**10⁻**)[c]	50	−1.37[d]		
	90	−4.02[d]		−2.65
9-COOMe-Fl⁻ (**11⁻**)[c]	50			
	90			−2.12
 (12⁻) [c]	50	0.38[d]		
	70	0.76[d]	0.38	
	90	1.79[d]		1.41
$CH_3COCHCOCH_3^-$ (**13⁻**)	50	2.07		
	90	4.50		2.43
$PhCH{=}NO_2^-$ (**14⁻**)[c]	50	1.99		
	70	2.59	0.60	
	90	4.09		2.10
$CH_2{=}NO_2^-$ (**15⁻**)[c]	50	2.87		
	70	4.51	1.64	
	90	6.70		3.83

[a] Reference 10. [b] This work. [c] Reference 28. [d] W = 10% Me_2SO–90% water.

Equation 17 is analogous to eq 16 and is derived in a similar way, with $\alpha_{\mathrm{des}}^{\mathrm{B}^-}$ being a measure of the progress of the desolvation of B^- at the transition state. Since log ${}^{\mathrm{W}}\gamma_{\mathrm{B}^-}^{\mathrm{D}}$ is typically >0 (see B^- = AcO^- in Table VII) and advanced desolvation means $\alpha_{\mathrm{des}}^{\mathrm{B}^-} > \beta$, we have $\delta_{\mathrm{B}^-} > 0$.

When the ionizing agent is an amine, late development of the solvation of the incipient ammonium ion[3b,29] (NH^+) contributes to the solvent effect on k_0 by a term given by eq 18 in which $\alpha_{\mathrm{sol}}^{\mathrm{NH}^+}$ ($<\beta$) measures the progress in the solvation of the ammonium ion.

$$\delta_{\mathrm{NH}^+} \approx (\alpha_{\mathrm{sol}}^{\mathrm{NH}^+} - \beta)(-\log {}^{\mathrm{W}}\gamma_{\mathrm{NH}^+}^{\mathrm{D}}) \qquad (18)$$

This term is again derived in a similar manner as δ_{C^-} and δ_{B^-}. In contrast to δ_{B^-}, $\delta_{\mathrm{NH}^+} < 0$ because ammonium ions are better solvated by Me_2SO, i.e., $\log {}^{\mathrm{W}}\gamma_{\mathrm{NH}^+}^{\mathrm{D}} < 0$ (see NH^+ = $CH_3CH_2CH_2NH_2^+$ in Table VII).

The experimentally observed solvent effects on k_0 can now be approximated by eq 19 (deprotonation by oxyanions) and 20 (deprotonation by amines), respectively. These equations include

$$\delta \log {}^{\mathrm{W}}k_0^{\mathrm{D}}(\mathrm{CH/B}^-) \approx \delta_{\mathrm{C}^-} + \delta_{\mathrm{B}^-} + \delta_{\mathrm{SR}} \qquad (19)$$

$$\delta \log {}^{\mathrm{W}}k_0^{\mathrm{D}}(\mathrm{CH/N}) \approx \delta_{\mathrm{C}^-} + \delta_{\mathrm{NH}^+} + \delta_{\mathrm{SR}} \qquad (20)$$

an additional term, δ_{SR}, which accounts for possible effects that cannot be attributed to late solvation/early desolvation of the various ions. This δ_{SR} term may include a dynamic solvent reorganization (SR) effect[30-33] and/or some transition-state effects[8,33] that have no counterpart in the reactants or products.

Equations 19 and 20 account quite satisfactorily for the solvent effects observed for **10**–**15**, at least in a qualitative sense. (1) $\delta \log {}^{\mathrm{W}}k_0^{\mathrm{D}}$ (numbers in parentheses in Table V) is largest for car-

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(27) These approximate equalities do not require that $\alpha_{\mathrm{sol}}^{\mathrm{C}^-}$ and β individually are solvent independent, only that their difference is insensitive to the solvent change.

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Table VIII. Estimates for δ_{B^-} and δ_{NH^+} for **10–15** from Reference 8

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

Table IX. Estimates for δ_{C^-} and $\delta_{SR}(CH/N)$ for **10–15**, from Reference 8

	δ_{C^-}		$\delta_{SR}(CH/N)$	
CH acid	0% → 90% Me_2SO	50% → 90% Me_2SO	0% → 90% Me_2SO	50% → 90% Me_2SO
Fl-CN (**10**)	−0.60[a]	−0.40	0.77[a]	0.30
Fl-COOMe (**11**)		−0.32		0.66
1,3-indandione (**12**)	0.27[a]	0.21	0.83[a]	0.60
acetylacetone (**13**)	0.68	0.36	0.61	0.62
$PhCH_2NO_2$ (**14**)	0.61	0.32	2.61	1.77
CH_3NO_2 (**15**)	1.01	0.57	2.81	1.85

[a] 10% → 90% Me_2SO.

banions that have large positive log ${}^{W}\gamma_{C^-}^{D}$ values (Table VII), and becomes very small or even slightly negative for carbanions with log ${}^{W}\gamma_{C^-}^{D} \approx 0$ or <0, respectively.

(2) δ log ${}^{W}k_0^{D}$ for the amine reactions is smaller than for the carboxylate ion reactions, reflecting the fact that $\delta_{B^-} > 0$ (eq 19) but $\delta_{NH^+} < 0$ (eq 20).

(3) In the reactions of 9-cyanofluorene the combination of a strongly negative δ_{C^-} and a somewhat negative δ_{NH^+} should add up to a substantial decrease in k_0 in 90% Me_2SO. The fact that log k_0 is essentially solvent independent suggests that a positive δ_{SR} term contributes significantly to δ log ${}^{W}k_0^{D}(CH/N)$, eq 20. A similar conclusion may be drawn for the reaction of 9-carbomethoxyfluorene with amines where a slightly negative δ log ${}^{W}k_0^{D}(CH/N)$ would have been predicted on the basis of δ_{C^-} and δ_{NH^+} alone, but a slightly positive value is observed.

Is the Behavior of 7 Anomalous? Turning now to **7** we note that log k_0 for both the amine and the carboxylate ion reactions is lower in the Me_2SO-richer solvents. This is consistent with the negative log ${}^{W}\gamma_{C^-}^{D}$ values (Table VII) which lead to $\delta_{C^-} < 0$. The rather large decrease in log k_0 requires that log ${}^{W}\gamma_{C^-}^{D}$ is strongly negative, more so than for 9-cyanofluorene. This is borne out by our measurements, e.g., log ${}^{50}\gamma_{C^-}^{90} < -2.56$, which is probably significantly more negative than log ${}^{50}\gamma_{C^-}^{90} = -2.65$ for 9-cyanofluorene. What is puzzling, though, is that δ log ${}^{W}k_0^{D}(CH/N)$ and δ log ${}^{W}k_0^{D}(CH/B^-)$ are, within experimental error, the same. To some extent this result may be an artifact caused by the rather large experimental uncertainty. This uncertainty allows for the possibility that log ${}^{70}k_0^{90}(CH/N)$ could be as much as 0.23 log units more negative than log ${}^{70}k_0^{90}(CH/B^-)$, in qualitative agreement with expectation.

Experimental error cannot be the entire explanation, though. Added insight can be gained from a semiquantitative analysis of the relative contributions of δ_{C^-}, δ_{B^-}, δ_{NH^+}, and δ_{SR}. Such an analysis has recently been carried out for **10–15**,[8] with the results summarized in Tables VIII and IX. According to eq 19 and 20 the difference in the solvent effects between the carboxylate ion and amine reactions is given by

$$\delta\delta = \delta \log {}^{W}k_0^{D}(CH/B^-) - \delta \log {}^{W}k_0^{D}(CH/N) \approx \delta_{B^-} - \delta_{NH^+} + \delta_{SR}(CH/B^-) - \delta_{SR}(CH/N) \quad (21)$$

For the change from 50% to 90% Me_2SO the parameters in Tables VIII and IX ($\delta_{SR}(CH/B^-) - \delta_{SR}(CH/N) \approx 0.22$)[8] yield $\delta\delta \approx 0.31 + 0.09 + 0.22 \approx 0.62$. Since δ_{B^-}, $|\delta_{NH^+}|$, and δ_{SR} are expected to be smaller for the change from 70% to 90% Me_2SO (only comparison available for carboxylate ions), $\delta\delta$ is expected to be <0.62, perhaps 0.40 to 0.50. Two factors that would tend to decrease $\delta\delta$ below this estimate are the following.

The δ_{B^-} values summarized in Table VIII are estimated based on the assumption that in a first approximation $\alpha_{des}^{B^-} - \beta$ and $\alpha_{sol}^{NH^+} - \beta$ are independent of the carbon acid. In view of the similar β values for **10–15** in any given solvent (Table VI) this seemed a reasonable assumption. However, since β for **7** is significantly higher than for the other carbon acids, especially for the carboxylate ion reactions, and for the amine reactions in the more aqueous solvents, it is likely that $\alpha_{des}^{B^-} - \beta$ and $\alpha_{sol}^{NH^+} - \beta$ for **7** are significantly different than for **10–15**. With respect to $\alpha_{des}^{B^-} - \beta$, since β is close to unity and $\alpha_{des}^{B^-}$ cannot possibly exceed unity, $\alpha_{des}^{B^-} - \beta$ is bound to be quite small and probably significantly smaller than the value of 0.09[8] estimated for **10–15**. This will make δ_{B^-} very small and, δ_{B^-} being the largest contributor to $\delta\delta$, this feature will reduce $\delta\delta$ substantially.

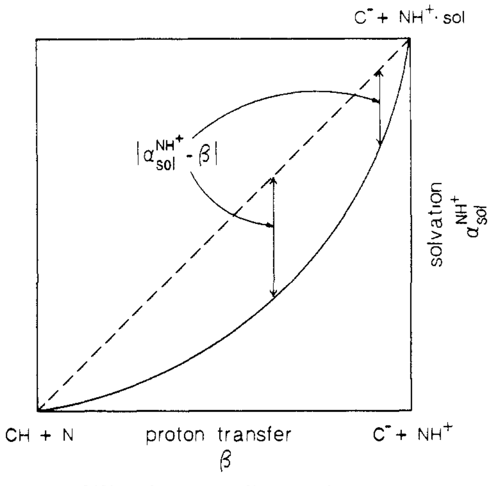

Figure 6. More O'Ferrall–Jencks diagram for the deprotonation of a carbon acid (CH) by an amine (N) showing separate axes for proton transfer (β) and solvation of the ammonium ion ($\alpha_{sol}^{NH^+}$). The curved reaction coordinate indicates that solvation lags behind proton transfer.

The effect of large β-values on $\alpha_{sol}^{NH^+} - \beta$ and thus on δ_{NH^+} is not as easily predicted. In principle, a larger β allows $|\alpha_{sol}^{NH^+} - \beta|$ to become larger, since the limiting value of $\alpha_{sol}^{NH^+}$ is zero. In reality it seems more plausible that $|\alpha_{sol}^{NH^+} - \beta|$ will remain about the same or even become *smaller*. Figure 6 shows a More O'Ferrall[34]–Jencks[14,35] type diagram in which proton transfer (β) and solvation of the ammonium ion ($\alpha_{sol}^{NH^+}$) are represented by separate axes. The dashed line refers to a hypothetical situation where solvation and proton transfer are completely synchronous, whereas the curved solid line shows the reaction coordinate with solvation trailing proton transfer. $|\alpha_{sol}^{NH^+} - \beta|$ is seen to be given by the distance between the dashed and the solid line. What this diagram demonstrates is that for a given reaction coordinate $|\alpha_{sol}^{NH^+} - \beta|$ goes through a maximum for β values slightly higher than 0.5, but decreases sharply when β approaches 0 or unity. According to this picture the relatively high β values for **7** are not expected to enhance $|\alpha_{sol}^{NH^+} - \beta|$ compared to **10–15**, but to either leave it unaffected or to even reduce it.

In conclusion, the significant decrease in δ_{B^-} coupled with an unchanged or slightly less negative δ_{NH^+} and the large experimental uncertainty in $\delta\delta$ appear sufficient to explain our results. In other words, **7** is only anomalous with respect to its high β values, but not with respect to how k_0 is affected by solvent changes. We do not know the reason for the high β values although we note that carbon acids that are activated by cyano groups usually have larger β values.[3d,17,22,36]

Conclusions

1. The intrinsic rate constant for the ionization of **7** by secondary amines in 50% Me_2SO–50% water (log k_0 = 3.29) lies between that for 4-nitrophenylacetonitrile (log k_0 = 3.95) and that for 2,4-dinitrophenylacetonitrile (log k_0 = 2.90). Even if k_0 for **7** is assumed to be depressed 10-fold by a steric effect, the corrected k_0 (log $k_0 \approx 4.3$) would still be suggestive of a resonance effect in the carbanion that is substantial and comparable to that in the reaction of **8**.

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(36) For **8** β = 0.74 but for **9** β = 0.50 in 50% Me_2SO–50% water with piperidine/morpholine.[16]

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2. log k_0 for **7** decreases with increasing Me_2SO content of the solvent. This is consistent with the large negative log $^{W}\gamma^{D}_{C^-}$ values determined from partition experiments with **7**.

3. The solvent effect on log k_0 is about the same for amine and for carboxylate ion reactions, in spite of expectations that log k_0 for the amine reactions should decrease more than for the carboxylate ion reactions, because $\delta_{NH^+} < 0$ (eq 20) but $\delta_{B^-} > 0$ (eq 19). This behavior, which is unique among all systems studied so far, is attributed to the very large Brønsted β values, particularly for the carboxylate ion reaction, which should make δ_{B^-} very small and possibly δ_{NH^+} less negative than in other systems.

Experimental Section

Materials. (α-Cyanodiphenylmethane)bis(tricarbonylchromium(0)) was prepared according to a previously reported method,[37] mp 166 °C (lit. mp 166 °C).[37]

The purification of the amines and carboxylic acids, where needed, has been described previously.[11a] Me_2SO was stored over a 4-Å molecular sieve prior to use.

Kinetic Measurements. The methods used were basically the same as described before.[11a] The reaction was monitored at 414 nm which corresponds to one of three maxima in the spectrum of the carbanion. In some of the experiments where the equilibrium was approached from the carbanion side the carbanion was generated in a multimixing Durrum-Gibson stopped-flow apparatus by reaction of the substrate with 0.002 or 0.01 M KOH. The acidic buffer solution was then added in the same apparatus a few seconds later and the decay of the carbanion monitored in the usual way. This technique was used in those cases where the carbanion solution was unstable which was a most serious problem in 50% Me_2SO.

Solvent Activity Coefficients. The solvent activity coefficients for the transfer of 7 from 50% to 70% Me_2SO ($^{50}\gamma^{70}_{CH}$) and from 50% to 90% Me_2SO ($^{50}\gamma^{90}_{CH}$) were determined by measuring partition coefficients for 7 between *n*-heptane and the various Me_2SO–water mixtures. The partition coefficients were measured as described previously;[28] they are defined as $^{50}p^{H} = [CH]_H/[CH]_{50}$, $^{70}p^{H} = [CH]_H/[CH]_{70}$, and $^{90}p^{H} = [CH]_H/[CH]_{90}$, respectively, with $[CH]_H$ being the equilibrium concentration of the carbon acid in *n*-heptane, and $[CH]_{50}$, $[CH]_{70}$, and $[CH]_{90}$ being the equilibrium concentrations of the carbon acid in the respective Me_2SO–water mixtures.

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Capacity of Quadricyclane Frameworks Related to *syn*-Sesquinorbornatriene for Excited-State Rearrangement

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Abstract: By means of a sequence of reactions involving sequential below-plane Diels–Alder cycloaddition to tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene, sensitized irradiation to transform the norbornadiene part structure into a quadricyclane, and introduction of a double bond into the noncyclopropanated bridge, it is possible to arrive efficiently at hexacyclic systems typified by **6**, **12**, and **18**. When the unsaturated center is substituted with an electron-withdrawing group, direct and sensitized irradiation results in quantitative translocation of the two cyclopropane rings. The pair of quadricyclane-containing valence isomers can be thermolyzed to the same *syn*-sesquinorbornatriene, irradiation of which in turn delivers only the photostable quadricyclane derivative. Monodeuteriated compound **18** undergoes excited-state isomerization only when directly irradiated. In contrast, *syn*-sesquinorbornatriene-*1-d* (**20**) engages in ring closure when sensitized (efficient ring closure) or directly irradiated (competitive polymer formation). Mechanistic analyses of this chemical behavior are provided, along with quantitative measurements of selected processes.

The structural uniqueness of the quadricyclane ring system has prompted many researchers to elucidate methods for its construction and to understanding its chemical reactivity. The parent hydrocarbon is available by the direct[2] or preferably sensitized photoisomerization[3] of norbornadiene. Substitution of one of the norbornadiene double bonds by one or two electron-withdrawing groups facilitates the valence isomerization.[4] While it is possible to reverse the light-induced ring closure by heating at 140–190 °C,[5] the cycloreversion occurs rapidly at ambient temperature in the presence of transition metals.[6] As a consequence of this reversible electrocyclization, the norbornadiene–quadricyclane couple has been intensively investigated as a promising tool for solar light energy conservation.[7]

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