C_3H_7O), 288 (1.9, M − $HCOOC_3H_7$), 181 (66.7, 3,4,5-trimethoxybenzyl), 131 (25, $C_3H_7OCHOC_3H_7$), and 89 (100, $HOCHOC_3H_7$).

2-Cyano-2-(diethoxymethyl)-3-(3,4,5-trimethoxyphenyl)propionamide (18). 2-Cyano-2-(diethoxymethyl)-3-(3,4,5-trimethoxyphenyl)propionitrile (10 g, 28.7 mmol) was combined with 200 mL of ethanol–water (1:1) containing 3.6 g of potassium hydroxide. The solid dissolved upon warming, and the solution was heated at reflux for 35 min. The mixture was cooled and concentrated in vacuo to dryness. The residue was triturated with water and filtered. The solid was slurried in water, filtered, and dried to yield 7.1 g (67.5%) of a buff-colored solid: mp 125–127 °C; NMR ($CDCl_3$) δ 1.26, 1.33 (t's, 6, $J = 7$ Hz, $CH_2\mathbf{CH_3}$), 3.11, 3.22 (ABq, 2, $J = 13$ Hz, benzyl CH_2), 3.74, 3.77 (q's, 4, $J = 7$ Hz, $O\mathbf{CH_2}CH_3$), 4.74 (s, 1, $CH(OEt)_2$), 5.59, 6.24 (br s, 2, $CONH_2$), and 6.59 (s, 2, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity, assignment) 366 (2, M), 323 (11.7, M − CONH), 277 (8.2, M − NH_2CO_2Et), 181 (55, 3,4,5-trimethoxybenzyl), and 103 (100, $C_2H_5OCHOC_2H_5$).

Methyl 2-Cyano-2-(diethoxymethyl)-3-(3,4,5-trimethoxyphenyl)propionimidate (19). 2-Cyano-2-(diethoxymethyl)-3-(3,4,5-trimethoxyphenyl)propionitrile (2.5 g, 7.2 mmol) was dissolved in 27 mL of dry methanol, and the solution was heated at reflux for 1 h. A 2-mL aliquot was concentrated in vacuo to an oil: NMR ($CDCl_3$) δ 1.14 and 1.25 (t's, 6, $J = 7$ Hz, $CH_2\mathbf{CH_3}$), 3.07 (s, 2, benzyl CH_2), ~3.6 (q's, 4, $\mathbf{CH_2}CH_3$), ~3.8 (s, 12, OCH_3), 4.65 (s, 1, $CH(OEt)_2$), 6.40 (s, 2, aromatic H), and 7.7 (s, 1, NH (exchanges with D_2O)); IR bands at 2255 ($C{\equiv}N$) and 1505, 1509, and 1610 cm^{-1} ($C{=}NH$); mass spectrum (70 eV), *m/e* (relative intensity, assignment) 380 (1.8, M), 334 (1.3, M − C_2H_5OH), 277 (7.4, M − $C_2H_5OC(NH)OCH_3$), 181 (23, 3,4,5-trimethoxybenzyl), and 103 (100, $C_2H_5OCHOC_2H_5$).

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Registry No. 3, 55474-40-3; **4**, 71870-92-3; **66**, 71870-93-4; **9**, 65430-22-0; **10**, 65743-11-5; **11**, 65743-12-6; **12a**, 29958-02-9; **12b**, 57941-89-6; **12c**, 37389-84-7; **13a**, 65708-35-2; **13b**, 71870-94-5; **13c**, 65708-36-3; **14a**, 738-70-5; **15**, 2531-80-8; **16**, 71870-95-6; **17**, 71870-96-7; **18**, 71870-97-8; **19**, 71870-98-9; **20**, 71870-99-0; **21**, 71871-00-6; **22**, 71885-39-7; **23**, 71871-01-7; **24**, 7391-29-9; **25**, 759-65-9; **26**, 609-08-5; **27**, 83-13-6; **28**, 685-87-0; **29**, 71870-80-9; **30**, 40988-36-1; **31**, 86-29-3; **32**, 3699-66-9; **33**, 50-29-3; **34**, 71870-81-0; **35**, 7402-30-4; ethyl 2-(diethoxymethyl)-2-nitropropanoate, 71870-82-1; 2-cyano-2-(diisopropoxymethyl)-3-(3,4,5-trimethoxyphenyl)propionitrile, 71870-83-2; ethyl 2-acetyl-2-(diethoxymethyl)-3-(3,4,5-trimethoxyphenyl)propanoate, 71870-84-3; 2-benzoyl-2-(diethoxymethyl)-3-(3,4,5-trimethoxyphenyl)propionitrile, 71870-85-4; 2-(diethoxymethyl)-2-tosyl-3-(3,4,5-trimethoxyphenyl)propionitrile, 71870-86-5; methyl 2-(*m*-chlorobenzoyl)-2-(diethoxymethyl)propanoate, 71870-87-6; 2-benzoyl-2-(dimethoxymethyl)propionitrile, 71870-88-7; ethyl 2-oxo-2-ethoxycarbonyl-2-(diethoxymethyl)butanoate, 71870-89-8; diethyl 2-(diethoxymethyl)-2-methylpropanedioate, 40364-91-8; diethyl 2-(diethoxymethyl)-2-phenylpropanedioate, 71870-90-1; diethyl 2-bromo-2-(diethoxymethyl)propanedioate, 71870-91-2; diethyl ethoxymethylenemalonate, 87-13-8; 1,1-bis(*p*-chlorophenyl)-2,2-dichloroethane, 72-54-8; TMOF, 149-73-5; TEOF, 122-51-0; DEMA, 14036-06-7; TiPOF, 4447-60-3; guanidine, 113-00-8; 3,4,5-trimethoxybenzylcyanoacetic acid, 42864-52-8; 3,4,5-trimethoxybenzaldehyde, 86-81-7; malonitrile, 109-77-3; 2-cyano-3-(3,4,5-trimethoxyphenyl)acrylonitrile, 5688-82-4.

Rates of Ionization of 1,1-Dinitroethane in 50% Dimethyl Sulfoxide–50% Water. Solvent Effect on Proton Transfer

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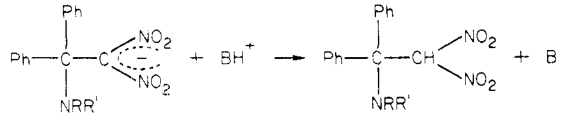
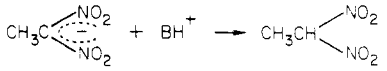
The rates of ionization of 1,1-dinitroethane have been measured in 50% Me_2SO–50% water (v/v) in the presence of various buffers. For a given p*K* difference between 1,1-dinitroethane and the buffer, the rates are up to ten times higher than those in pure water. This increase is consistent with the notion that solvational reorganization is at least partly responsible for the slow rates of proton transfer involving nitroalkanes, but it also shows that the rate enhancing effect of Me_2SO is relatively small as long as there is a significant protic component in the solvent. The data refute the hypothesis that the recently reported high rate of protonation of 1 on carbon by the hydronium ion is due to a solvent effect and support the notion of an intramolecular proton transfer 5 → 2.

While studying nucleophilic additions of amines to 1,1-dinitro-2,2-diphenylethylene in 50% Me_2SO–50% water (v/v), we also measured the rates of proton transfer to the carbon of the amine–olefin addition complex 1.[1] With BH^+ = piperidinium ion, morpholinium ion, *n*-$BuNH_3^+$, $PhNH_3^+$, and cacodylic acid, the rate constants are of the same order of magnitude as the rate constants for the protonation of the anion of 1,1-dinitroethane (3) in aqueous solution by general acids of comparable pK_a.[2]



(1)

1 2



(2)

3 4

On the other hand, the rate constant for protonation of 1 by the *hydronium ion* is about 10^4 times higher than that for the protonation of 3. This high rate was explained by initial protonation of 1 on *nitrogen*, followed by an intramolecular proton switch to form 2[1] (eq 3).

In view of the known rate enhancing effect of Me_2SO on proton transfers involving carbon acids,[3-5] the possibility

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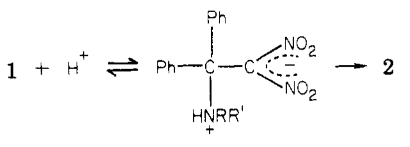
(1) C. F. Bernasconi and D. J. Carré, *J. Am. Chem. Soc.*, **101**, 2698 (1979).

(2) R. P. Bell and R. L. Tranter, *Proc. R. Soc. London, Ser. A*, **337**, 518 (1974).

0022-3263/79/1944-4829$01.00/0



5

(3)

that the much higher rate with 1 is due to the reaction being conducted in 50% Me$_2$SO–50% water instead of pure water had to be considered. A serious difficulty with this alternative explanation is that protonation of 1 by all other acids is *not* dramatically enhanced; hence this explanation would require that only the reaction with the hydronium ion is subject to a very large solvent effect.

Even though unlikely, we decided to test—and hopefully discard—this hypothesis by measuring the rates of protonation of 3 in 50% Me$_2$SO–50% water (v/v). The data obtained are also of interest in the much broader context of solvent effects on proton transfers involving carbon acids.[3-9]

Results

Rates of proton transfer were measured in buffer solutions, under pseudo-first-order conditions with the nitro compound as the minor component. The reactions can be represented by

$$\underset{\mathbf{4}}{CH_3CH(NO_2)_2} \underset{k_{-1}^{H}a_{H^+} + k_{-1}^{BH}[BH] + k_{-1}^{w}}{\overset{k_1^{w} + k_1^{B}[B^-] + k_1^{OH}a_{OH^-}}{\rightleftharpoons}} \underset{\mathbf{3}}{CH_3\bar{C}(NO_2)_2} \qquad (4)$$

The following buffers were used: HCl, dichloroacetic, chloroacetic, and acetic acid, formic acid, *p*-cyanophenol, and phenol. The ionic strength was kept constant at 0.5 M with KCl. The rates were measured in the stopped-flow apparatus by following the changes in the absorption of 3 at 381 nm. At pH >p$K_a^{NO_2}$,[10] the equilibrium was approached in the direction 4 → 3 by mixing a slightly acidic solution of the nitro compound with the appropriate buffer. At pH <p$K_a^{NO_2}$, the equilibrium was approached from the opposite direction by mixing a slightly basic solution of the substrate with the appropriate buffer.

The reciprocal relaxation time for reaction 4 is given by

$$1/\tau = k_1^{w} + k_1^{B}[B^-] + k_1^{OH}a_{OH^-} + k_{-1}^{H}a_{H^+} + k_{-1}^{BH}[BH] + k_{-1}^{w} \qquad (5)$$

$1/\tau$ was measured as a function of buffer concentration and pH; the data are summarized in Table I. Depending on the pH range, several terms in eq 5 become negligible, which allows relatively straightforward evaluation of the various rate constants as shown below.

The *p$K_a^{NO_2}$* of 4 was determined by standard spectrophotometric procedures to be 5.13 ± 0.02 at 20 °C and μ = 0.5 M. The pK_a values of the buffers were determined potentiometrically; they are summarized in Table II.

Evaluation of Rate Constants. In HCl solution, eq 5 simplifies to

$$1/\tau = k_{-1}^{H}a_{H^+} \qquad (6)$$

and k_{-1}^{H} = 315 M^{-1} s^{-1} is obtained from a plot of $1/\tau$ vs. a_{H^+}.[11] This allows calculation of $k_1^{w} = K_a^{NO_2}k_{-1}^{H} = 2.34 \times 10^{-3}$ s^{-1}.

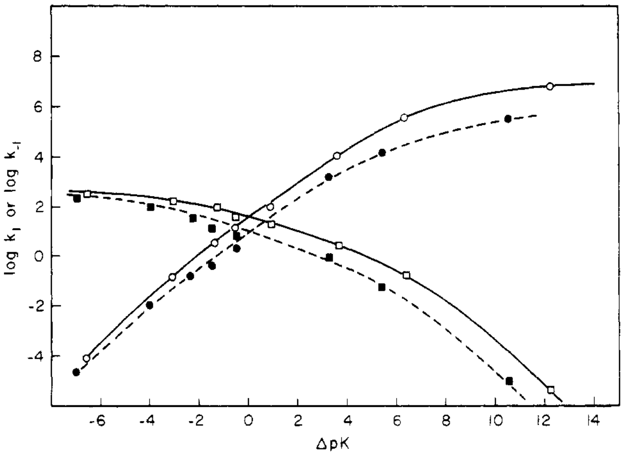


Figure 1. Eigen plot for reaction 4: circles, k_1; squares, k_{-1}; open symbols, 50% Me$_2$SO–50% water (v/v), 20 °C; closed symbols, water, 25 °C.

In dichloroacetic acid buffer, eq 5 becomes

$$1/\tau = k_{-1}^{H}a_{H^+} + k_{-1}^{BH}[BH] \qquad (7)$$

and k_{-1}^{BH} = 178 M^{-1} s^{-1} is obtained from a plot of $1/\tau$ vs. [BH]; $k_1^{B} = k_{-1}^{BH}K_a^{NO_2}/K_a^{BH}$ is calculated to be 0.14 M^{-1} s^{-1}.

In chloroacetic, formic, and acetic acid buffers, eq 5 takes on the form

$$1/\tau = k_1^{w} + k_{-1}^{H}[H^+] + (k_{-1}^{BH} + k_1^{B}K_a^{BH}/a_{H^+})[BH] \qquad (8)$$

where the slope of a plot of $1/\tau$ vs. [BH] is $k_{-1}^{BH} + k_1^{B}K_a^{BH}/a_{H^+}$. In the case of chloroacetic acid, k_1^{B} was substituted by $k_{-1}^{BH}K_a^{NO_2}/K_a^{BH}$ so that the slope is $k_{-1}^{BH}(1 + K_a^{NO_2}/a_{H^+})$ from which k_{-1}^{BH} = 91.3 M^{-1} s^{-1}, and then k_1^{B} = 4.07 M^{-1} s^{-1} could be obtained. In the case of formic and acetic acids, the slopes were determined at two different pH values which provided two simultaneous equations for k_{-1}^{BH} and k_1^{B}. The following rate constants were obtained: k_{-1}^{BH} = 33.0 M^{-1} s^{-1} and k_1^{B} = 12.2 M^{-1} s^{-1} for formic acid and k_{-1}^{BH} = 18.2 M^{-1} s^{-1} and k_1^{B} = 95.2 M^{-1} s^{-1} for acetic acid. With formic acid k_1^{B}/k_{-1}^{BH} = 0.37 determined kinetically compares very well with $K_a^{NO_2}/K_a^{BH}$ = 0.30 from pK measurements; in the case of acetic acid, the two ratios are 5.2 and 8.14, respectively.

In *p*-cyanophenol buffer, eq 5 simplifies to

$$1/\tau = k_1^{B}[B^-] \qquad (9)$$

with $k_1^{B} = 1.22 \times 10^4$ M^{-1} s^{-1}; $k_{-1}^{BH} = k_1^{B}K_a^{BH}/K_a^{NO_2}$ is calculated to be 2.92 M^{-1} s^{-1}.

In phenol buffer, eq 5 becomes

$$1/\tau = k_1^{OH}a_{OH^-} + k_1^{B}[B^-] \qquad (10)$$

Plots of $1/\tau$ vs. [B$^-$] provide $k_1^{B} = 3.55 \times 10^5$ M^{-1} s^{-1} from the slopes; the intercepts of these plots at three different pH values are $k_1^{OH}a_{OH^-}$ and yield $k_1^{OH} = 7.33 \times 10^6$ M^{-1} s^{-1}. Finally, $k_{-1}^{w} = k_1^{OH}K_w/K_a^{NO_2} = 1.25 \times 10^{-4}$ s^{-1} is obtained, where $K_w = 1.26 \times 10^{-16}$ is the ionic product of the

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(3) (a) C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **90**, 3415 (1968); (b) C. D. Ritchie, *ibid.*, **91**, 6749 (1969).

(4) B. Cox and A. Gibson, *J. Chem. Soc., Chem. Commun.*, 638 (1974).

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

(6) E. F. Caldin, *J. Chem. Soc.*, 3345 (1959).

(7) J. E. Crooks in "Proton Transfer Reactions", E. Caldin and V. Gold, Eds., Wiley, New York, 1975, p 153.

(8) F. Hibbert, *Compr. Kinetics*, 8, 354 (1977).

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

(10) p$K_a^{NO_2}$ stands for the pK_a of 4.

(11) The linearity of $1/\tau$ with a_{H^+} at pH as low as 1.66 shows that protonation of 3 on oxygen to form the aciform of 1,1-dinitroethane in a preequilibrium is insignificant and indicates that the pK_a of the aciform is <1 in 50% Me$_2$SO–50% water (v/v). Similarly, Bell and Tranter's[2] data indicate that pK_a^{aci} < 2 in pure water. These results suggest that the reported pK_a^{aci} = 4.0[12] must be erroneous; a similar conclusion is implied by spectral data.[13]

(12) J. S. Belew and L. G. Hepler, *J. Am. Chem. Soc.*, 78, 4005 (1956).

(13) S. S. Novikov, V. I. Slovetskii, V. A. Tartakovskii, S. A. Shelev, and A. A. Fainzil'berg, *Dokl. Akad. Nauk SSSR*, **146**, 104 (1962); *Chem. Abstr.*, **58**, 3289g (1963).

Table I. Rates of Ionization of 1,1-Dinitroethane in 50% Me_2SO-50% Water (v/v) at 20 °C

buffer	pH	$10^2[B^-]$, M	$10^2[BH]$, M	$1/\tau$, s^{-1}
HCl	2.76		0.25	0.625
	2.42		0.50	1.39
	2.08		1.00	2.81
	1.89		1.50	4.07
	1.66		2.50	6.64
$Cl_2CHCOOH$	2.74	0.136	0.050	0.847
	2.75	0.341	0.126	0.914
	2.74	0.682	0.251	1.21
	2.75	1.36	0.502	1.59
	2.74	2.05	0.753	2.08
	2.75	2.73	1.00	2.51
	2.74	3.41	1.26	2.96
$ClCH_2COOH$	3.77	0.098	0.103	0.19
	3.75	0.246	0.258	0.32
	3.76	0.493	0.516	0.54
	3.77	0.986	1.033	1.00
	3.76	1.48	1.55	1.47
	3.76	1.97	2.07	1.88
	3.76	2.47	2.58	2.30
HCOOH	4.58	0.099	0.106	0.070
	4.57	0.248	0.265	0.147
	4.57	0.495	0.530	0.26
	4.57	0.990	1.06	0.49
	4.57	1.48	1.59	0.73
	4.57	1.98	2.12	0.97
	4.56	2.47	2.65	1.21
	5.06	0.104	0.0395	0.040
	5.00	0.260	0.0988	0.086
	5.02	0.520	0.198	0.144
	5.01	1.04	0.395	0.277
	5.02	1.56	0.593	0.389
	5.03	2.08	0.791	0.526
	5.01	2.56	0.988	0.670
CH_3COOH	5.39	0.024	0.106	0.054
	5.38	0.061	0.264	0.103
	5.39	0.121	0.529	0.217
	5.40	0.242	1.06	0.425
	5.40	0.363	1.59	0.611
	5.40	0.484	2.12	0.850
	5.41	0.606	2.64	1.065
	6.00	0.0954	0.105	0.118
	6.02	0.191	0.209	0.215
	5.99	0.239	0.261	0.280
	5.99	0.477	0.523	0.510
	6.00	0.954	1.046	1.02
	6.03	1.91	2.09	2.14
	5.99	2.39	2.61	2.55
4-CN-C_6H_4OH	8.69	0.093	0.107	11.0
	8.68	0.233	0.267	28.0
	8.70	0.465	0.535	56.9
	8.70	0.698	0.802	84.1
	8.69	0.93	1.07	109
C_6H_5OH	10.74	0.0034	0.0166	60.7
	10.74	0.0051	0.0249	70.9
	10.74	0.0068	0.0332	78.9
	10.79	0.0102	0.0498	93.6
	10.73	0.0169	0.0831	125
	10.74	0.0203	0.0997	138
	11.12	0.0064	0.0136	132
	11.11	0.0128	0.0272	147
	11.12	0.0191	0.0409	167
	11.12	0.0255	0.0545	187
	11.12	0.0319	0.0681	215
	11.38	0.0141	0.0159	306
	11.39	0.0188	0.0211	334
	11.42	0.0236	0.0264	347
	11.41	0.0283	0.0317	357
	11.40	0.0330	0.0370	394

[a] $\mu = 0.5$ M (KCl).

Table II. Rate and Equilibrium Constants of the Ionization of 1,1-Dinitroethane (Reaction 4) in 50% Me_2SO-50% Water (v/v) at 20 °C[b]

rate constant, M^{-1} s^{-1}	pK_a^{BH}[b]	ΔpK[c]	k (ΔpK)[c] in water at 25 °C[d]
$k_1^{w}/[H_2O] = 2.34 \times 10^{-3}/27.6$	-1.44	-6.57	$1.33 \times 10^{-3}/55.5$ (-6.99)
$k_{-1}^{H} = 3.15 \times 10^2$	-1.44	6.57	2.32×10^2 (6.99)
$k_1^{Cl_2CHCOO^-} = 0.14$	2.02	-3.11	1.08×10^{-2} (-3.98)
$k_{-1}^{Cl_2CHCOOH} = 1.78 \times 10^2$	2.02	3.11	1.03×10^2 (3.98)
$k_1^{ClCH_2COO^-} = 3.65$	3.78	-1.35	*e*
$k_{-1}^{ClCH_2COOH} = 81.8$	3.78	1.35	*e*
$k_1^{HCOO^-} = 12.2$	4.60	-0.53	4.16×10^{-1} (-1.49)
$k_{-1}^{HCOOH} = 33$	4.60	0.53	12.9 (1.49)
$k_1^{AcO^-} = 95.2$	6.04	0.91	2.16 (-0.49)
$k_{-1}^{AcOH} = 18.2$	6.04	-0.91	6.70 (0.49)
$k_1^{CNC_6H_4O^-} = 1.22 \times 10^4$	8.75	3.62	*e*
$k_{-1}^{CNC_6H_4OH} = 2.90$	8.75	-3.62	*e*
$k_1^{C_6H_5O^-} = 3.55 \times 10^5$	11.45	6.32	*e*
$k_{-1}^{C_6H_5OH} = 0.17$	11.45	-6.32	*e*
$k_1^{OH} = 7.33 \times 10^6$	17.34	12.21	3.6×10^5 (10.51)
$k_{-1}^{w}/[H_2O] = 1.25 \times 10^{-4}/27.6$	17.34	-12.21	$6.28 \times 10^{-4}/55.5$ (-10.51)

[a] $\mu = 0.5$ M (KCl). [b] pK_a^{BH} or $pK_a^{H_3O^+}$, $pK_a^{H_2O}$. [c] In the direction $4 \longrightarrow 3$ $\Delta pK = pK_a^{BH} - pK_a^{NO_2}$; in the direction $3 \longrightarrow 4$ $\Delta pK = pK_a^{NO_2} - pK_a^{BH}$. [d] Data from ref 2; $pK_a^{NO_2} = 5.24$ in water. [e] $k_1^{2\text{-Cl-}C_6H_4COO^-} = 1.62 \times 10^{-1}$ (-2.33); $k_{-1}^{2\text{-Cl-}C_6H_4COOH} = 34.7$ (2.33); $k_1^{2\text{-Cl-}C_6H_4O^-} = 1.60 \times 10^3$ (3.24); $k_{-1}^{2\text{-Cl-}C_6H_4OH} = 0.92$ (-3.24); $k_1^{CO_3^{2-}} = 2.88 \times 10^3$ (5.09); $k_{-1}^{HCO_3} = 1.85 \times 10^{-2}$ (-5.09); $k_1^{2,6\text{-}Me_2\text{-}C_6H_3O^-} = 1.47 \times 10^4$ (5.39); $k_{-1}^{2,6\text{-}Me_2\text{-}C_6H_3OH} = 5.98 \times 10^{-2}$ (-5.39).

solvent determined as $pK_w = pH - \log [OH^-]$ in 10^{-2} and 10^{-3} M KOH solutions.

Discussion

Table II summarizes the various rate constants for proton transfer in 50% Me_2SO-50% water as well as in pure water. k_{-1}^{H} for protonation of **3** is seen to be almost identical for the two solvents, thus definitely eliminating the hypothesis that the abnormally high rate of protonation of **1** by the hydronium ion (1.6×10^6 M^{-1} s^{-1})[1] is due to an effect of Me_2SO as the cosolvent. In fact, it is the rate of protonation of **3** by the *buffer acids* which are somewhat enhanced in the Me_2SO containing medium.

In order to accurately assess the effect of adding Me_2SO on the rate constants for the various acid–base pairs, one has to take into consideration the influence of the solvent on the equilibrium constants of the reactions (ΔpK) as well. This is best done by displaying the data in the form of an Eigen plot,[14] as shown in Figure 1. The Eigen plot in 50% Me_2SO is slightly displaced upward from the one in pure water. If one defines $k_1 = k_{-1} = k_{int}$ at $\Delta pK = 0$ as the intrinsic rate constant of the reaction, we note that k_{int} increases about fivefold in 50% Me_2SO. If the lower temperature in 50% Me_2SO is taken into account, the true increase in the intrinsic rate constant is probably closer to a factor of 10.

This increase is consistent with similar findings by others.[3-5] It supports the notion that solvational reorganization is at least part of the reason[3-7] why proton transfers in water involving carbon acids are frequently much slower than those involving "normal"[14] acids. Note, however, that the effect of adding 50% Me_2SO is quite small compared to the effect of changing from water to pure Me_2SO. For example, the rate of deprotonation of arylnitromethanes by phenoxide ion in pure Me_2SO is, for a given ΔpK, about 10^5 times faster than that in water.[5]

On the other hand, our results compare well with the 14-fold increase in the deprotonation rate of nitroethane by acetate ion in ~50% aqueous Me_2SO (mole fraction = 0.20), a solvent in which ΔpK is virtually the same as in water.[4] The smallness of the effect in 50% Me_2SO indicates that, as long as the solvent contains a significant mole fraction of water, its properties with respect to solvational reorganization are mainly governed by the protic component. This is consistent with the well-known dominance of the protic component of mixed protic–dipolar aprotic solvents on other solvational properties, particularly anion solvation as manifested by H_- functions for hydroxide and alkoxide ions.[9]

Another interesting point is that the difference between the rates in 50% Me_2SO and in pure water increases with increasing ΔpK. A possible reason for this trend is that with increasing acidity of the buffer (decreasing ΔpK), hydrogen bonding between the buffer acid and Me_2SO, which is known to be a better hydrogen bond acceptor than water,[15] becomes stronger. If it is necessary to break this hydrogen bond prior to proton transfer to the carbanion, this could lead to an increased activation energy for proton transfer which would become larger for more acidic buffers, thereby partially compensating for the rate enhancing effect of Me_2SO.

Experimental Section

Materials. 1,1-Dinitroethane was prepared by the method of Kaplan and Schechter.[16] The spectrum of the 1,1-dinitroethane anion has a λ_{max} of 381 nm in 50% Me_2SO–50% water (v/v); ϵ was determined to be 1.57×10^4 on a Gilford spectrophotometer.

The buffers were all reagent grade materials and were used without further purification. Reagent grade Me_2SO was stored over molecular sieves.

Solutions: pH and pK_a Measurements. The solutions were prepared by adding the appropriate amounts of aqueous buffer and/or KCl stock solutions to a measured amount of Me_2SO that would correspond to 50% of the final solution volume. To solutions containing the substrate was added 1 equiv of KOH or HCl, respectively, depending on whether the anionic or the neutral form was desired. The pH of the reaction solutions was measured and, where necessary, adjusted to a desired value by doing mock experiments which simulated the conditions in the stopped-flow apparatus. The pH measurements were performed on a Corning Digital 110 pH meter, using a salt bridge containing 50% aqueous Me_2SO saturated with KCl. The pH meter was calibrated with buffers described by Hallé et al.[17]

The pK_a values of the buffers were determined by standard potentiometric procedures, while the pK_a of 1,1-dinitroethane was obtained by standard spectrophotometric procedures.

Rate Measurements. The rates were determined in a Durrum-Gibson stopped-flow spectrophotometer. $1/\tau$ was determined by standard graphical evaluation of the oscilloscope traces.

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Registry No. 1,1-Dinitroethane, 600-40-8; Me_2SO, 67-68-5.

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[14] M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).

[15] (a) M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, **98**, 377 (1976); (b) H. H. Szmant in "Dimethyl Sulfoxide", Vol. 1, S. W. Jacob, E. E. Rosenbaum, and D. C. Woods, Eds., Marcel Dekker, New York, 1971, p 1.

[16] R. B. Kaplan and H. Schechter, *J. Am. Chem. Soc.*, **83**, 3535 (1961).

[17] J.-C. Hallé, R. Gaboriaud, and R. Schaal, *Bull. Soc. Chim. Fr.*, 2047 (1970).

Kinetics of the Aminolysis and Hydrolysis of *p*-Nitrophenyl Carboxylates in the Presence of Dodecylammonium Propionate and Aerosol-OT Aggregates in Benzene

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Kinetics of the reaction of *p*-nitrophenyl carboxylates with alkylamines (RNH_2; R = butyl, octyl, dodecyl and hexadecyl) and with *N*-alkylimidazoles (RImz; R = methyl, butyl, octyl, dodecyl and hexadecyl) were studied spectrophotometrically in the presence of dodecylammonium propionate (DAP) and bis(2-ethylhexyl) sodium sulfosuccinate (Aerosol-OT or AOT) reversed micelles in benzene. In the pure solvent, aminolysis of *p*-nitrophenyl acetate (NPA) is a function of the amine chain length. In the presence of 0.2 M DAP the reaction is ca. 39 to 50 times faster than that in the absence of the surfactant, due to bifunctional catalysis by the latter. Rates of diazole-catalyzed ester aminolysis (DAP concentration = 0.2 M) decrease with increasing alkyl chain length of both the diazole and/or the ester. Addition of water decreases the observed rates due to hydration of the DAP head groups. In the presence of AOT, the rates of MeImz-catalyzed ester hydrolysis decrease with increasing chain length of the ester alkyl group and increase as a function of added water. This reflects the importance of the substrates distribution between the bulk solvent and the micellar water "pool".

In nonaqueous solvents, several detergents aggregate to form reversed micelles.[1-3] These species have their polar head groups packed around a micellar "core" with the hydrophobic tails in contact with the solvent. Reversed