Internal Rotation in N,N-Dimethylacetamide-d_3 and a Structure–Reactivity Correlation for the Rotation Reaction of Amides[1]

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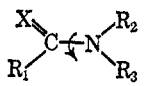
Abstract: Kinetic studies of internal rotation in N,N-dimethylacetamide-d_3 by high-resolution nmr spectroscopy using *total* line-shape analysis gave the activation parameters: (neat liquid) $E_a = 19.6 \pm 0.3$ kcal/mole, $\log A = 13.8 \pm 0.2$, $\Delta F^*_{298.2} = 18.2$ kcal/mole; (9.5 mole % in DMSO-d_6) $E_a = 20.6 \pm 0.3$ kcal/mole, $\log A = 14.3 \pm 0.3$, $\Delta F^*_{298.2} = 18.6$ kcal/mole. These results are compared with other previously available activation parameters for undeuterated DMA and the activation parameters resulting from treatment of the data by the peak-separation and intensity-ratio methods. Quantitative correlation of the rotation reaction using the two-parameter $\rho^*\sigma^* + SE_s$ equation has been attempted, and the approximate values of ρ^* and S obtained were -1 and -2, respectively.

Since the initial kinetic investigations of hindered internal rotation in amides (I, X = O) by high-resolution nmr spectroscopy,[2] a variety of similar studies have



I

been reported dealing with the effects of solvent and structural variation on the rotational barriers.[3] However, recent critical analyses[4-6] of the problems associated with the application of nmr to kinetic studies suggest that reliable data may only be available for the few systems (I) which have been recently studied by the spin-echo,[4,7] high-resolution *total* line shape,[1b,3b,e] or direct equilibration methods.[3b,c]

The majority of the kinetic investigations have dealt with compounds I containing the N,N-dimethyl group ($R_2 = R_3 = CH_3$). Although these cannot be studied by the direct equilibration method,[3b] they offer the advantages of possesssing energetically equivalent (and thus equally populated) rotational isomers, potentially simple line shapes for analysis, and the possibility of ready comparison and interpretation of solvent effects and the effects of structural variations of R_1 and X on the rotational barrier. Of this group, however, reliable kinetic data *may* only exist for the N,N-dimethylamides in which R_1 is CCl_3, CF_3, or Cl. Activation parameters for all three have been determined by spin-echo methods,[4,7] while the latter has been additionally studied by the high-resolution *total* line-shape analysis method.[1b]

These compounds were specifically chosen because the groups R_1 did not contain any hydrogen atoms. In spin-echo studies, the presence of nonexchanging hydrogens may lead to interpretational errors,[4] and in steady-state line-shape studies, α hydrogens in R_1 may unequally couple with each of the two N–CH_3 groups producing an asymmetric NCH_3 line shape.[2,5,6,8-10]

The two most frequently studied amides which are characterized by such unequal coupling are N,N-dimethylacetamide and N,N-dimethylformamide. Since these compounds, in which R_1 is CH_3 and H, respectively, would be important contributors to a general structure–reactivity correlation of amide rotational barriers, it seemed important to eliminate existing uncertainties in their activation parameters. In this regard, we have determined the activation parameters for hindered internal rotation in N,N-dimethylacetamide-d_3 ($R_1 = CD_3$, X = O) by high-resolution nmr spectroscopy using the method of total line-shape analysis. These data have been used with other available results to demonstrate a structure–reactivity correlation for the rotational reaction in amides.

While this work was in progress, Conti and von Philipsborn reported results of a high-resolution study of N,N-dimethylformamide-d_1 and a high-resolution double-resonance study on undeuterated DMF.[10] However, their spectral data were not analyzed using the total line-shape comparison method, but rather by a method involving a combination of approximate methods.

Results

The experimentally observed NCH_3 resonances for DMA and DMA-d_3 in DMSO-d_6 determined under similar conditions are shown in Figure 1. The slight asymmetry observed for DMA-d_3 in Figure 1 was also

(1) (a) Studies of Chemical Exchange by Nuclear Magnetic Resonance. III; (b) part II: R. C. Neuman, Jr., D. N. Roark, and V. Jonas, *J. Am. Chem. Soc.*, **89**, 3412 (1967); (c) support by the U. S. Public Health Service (National Institutes of General Medical Sciences) through Grant GM-13342 is gratefully acknowledged.

(2) G. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(3) (a) A recent review of the literature has been given;[1b] (b) H. S. Gutowsky, J. Jonas, and T. H. Siddall, III, *J. Am. Chem. Soc.*, **89**, 4300 (1967); (c) A. Mannschreck, A. Mattheus, and G. Rissmann, *J. Mol. Spectry.*, **23**, 15 (1967); (d) J. Sandstrom, *J. Phys. Chem.*, 71, 2318 (1967); (e) D. J. Bertelli and J. T. Gerig, *Tetrahedron Letters*, 2481 (1967); (f) E. Lustig, W. R. Benson, and N. Duy, *J. Org. Chem.*, **32**, 851 (1967); (g) T. M. Valega, *ibid.*, **31**, 1150 (1966).

(4) A. Allerhand and H. S. Gutowsky, *J. Chem. Phys.*, **41**, 2115 (1964).

(5) C. W. Fryer, F. Conti, and C. Franconi, *Ric. Sci., Rend. A.*, **8**, 788 (1965).

(6) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Am. Chem. Soc.*, **88**, 3185 (1966).

(7) K. H. Abramson, P. T. Inglefield, E. Karkower, and L. W. Reeves, *Can. J. Chem.*, **44**, 1685 (1966).

(8) (a) M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962); (b) D. G. Gehring and W. A. Mosher, *J. Org. Chem.*, **31**, 3436 (1966).

(9) R. C. Neuman, Jr., and L. B. Young, *J. Phys. Chem.*, **69**, 1777, 2570 (1965).

(10) F. Conti and W. von Philipsborn, *Helv. Chim. Acta*, **50**, 603 (1967).

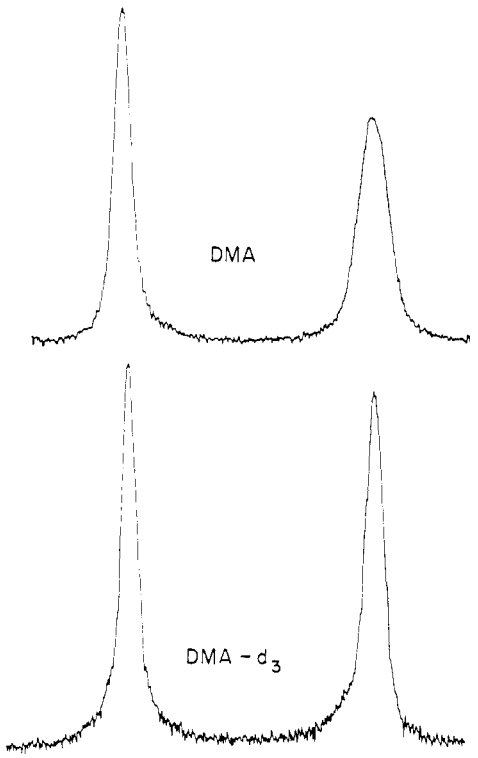


Figure 1. The experimentally observed NCH_3 resonance signals for 10% solutions of DMA (40°) and DMA-d_3 (44°) in DMSO-d_6; $\delta\nu = 9.6$ cps.

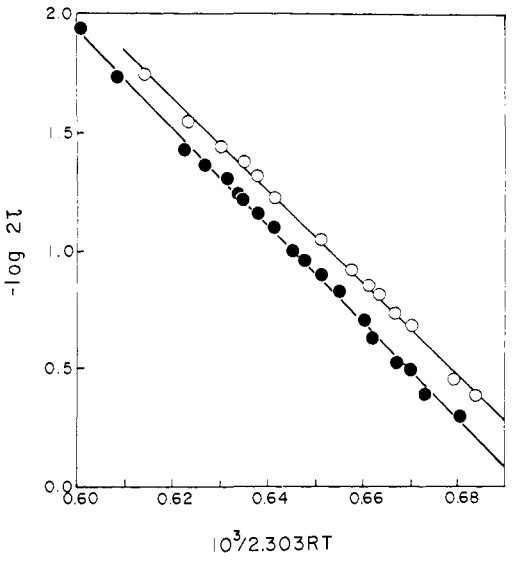


Figure 2. Arrhenius plots of the kinetic data (Table V, Experimental Section) for internal rotation about the central C–N bond in DMA-d_3: open points, neat DMA-d_3, $E_a = 19.6 \pm 0.3$ kcal/mole, log $A = 13.8 \pm 0.2$; solid points, 9.5 mole % DMA-d_3 in DMSO-d_6, $E_a = 20.6 \pm 0.3$ kcal/mole, log $A = 14.3 \pm 0.3$.

seen in spectra of neat DMA-d_3. This asymmetry prompted us to do separate line-shape analyses on each N–CH_3 resonance line in addition to a best-fit analysis of the whole line shape for neat DMA-d_3. These results and those obtained for a total line-shape analysis of DMA-d_3 in DMSO-d_6 are given in Table I.

distinct improvement in the time and accuracy of spectral analysis over those used in our previous study.[1b] The details of the analysis method and a discussion of our temperature calibrations are given in the Experimental Section. Temperature-dependent nonexchanging chemical shifts ($\delta\nu_\infty$) and inhomogeneity corrections were included in the calculations (see Experimental Section).

In order to compare our results using the complete Gutowsky–Holm line-shape equation with those obtainable from the same data using the approximate peak-separation and intensity-ratio modification of this equation,[2,4,8] we have determined the activation parameters resulting from these two approximate methods (Table II) using our nmr spectral data for DMA-d_3 in DMSO-d_6.

Table I. Activation Parameters for Hindered Internal Rotation in DMA-d_3 by Total Line-Shape Analysis

Solvent, mole %	E_a, kcal/mole[a]	Log A[a]	$\Delta F^*_{298.2}$, kcal/mole[a]	$\Delta H^*_{298.2}$, kcal/mole[b]	ΔS^*, eu[c]
Neat	19.6 ± 0.3[d]	13.8 ± 0.2	18.2	19.0	+2.7
	(19.5 ± 0.3)[e]	(13.8 ± 0.2)	(18.2)	(18.9)	(+2.3)
	(19.8 ± 0.3)[f]	(13.9 ± 0.2)	(18.2)	(19.2)	(+3.4)
DMSO-d_6 (9.5%)	20.6 ± 0.3[d]	14.3 ± 0.3	18.6	20.0	+4.7

[a] Caiculated using the usual equations. [b] $\Delta H^* = E_a - RT$. [c] $\Delta S^* = (\Delta H^* - \Delta F^*)/T$. [d] Complete NCH_3 line shape. [e] High-field half of the NCH_3 line shape. [f] Low-field half of NCH_3 line shape.

Table II. Activation Parameters for Hindered Internal Rotation in DMA-d_3 in DMSO-d_6 by Total Line-Shape, Peak-Separation, and Intensity-Ratio Methods

Method[a]	E_a, kcal/mole[b]	Log A[b]	$\Delta F^*_{298.2}$, kcal/mole[b]	$\Delta H^*_{298.2}$, kcal/mole[b]	ΔS^*, eu[b]
PSEP	16.2 ± 0.4	11.6 ± 0.3	17.9	15.6	−7.7
IR	19.5 ± 0.6	13.6 ± 0.4	18.3	18.9	+2.0
TLS	20.6 ± 0.3	14.3 ± 0.3	18.6	20.0	+4.7

[a] PSEP, peak separation; IR, intensity ratio; TLS, total line-shape analysis. [b] See Table I.

Arrhenius plots for the best-fit analyses of the whole line shapes are shown in Figure 2, and the kinetic data corresponding to these plots are given in the Experimental Section (Table V). The computer programs used in this study were based on an analysis method recently outlined by Gutowsky, *et al.*,[11] and represent a

(11) J. Jonas, A. Allerhand, and H. S. Gutowsky, *J. Chem. Phys.*, 42, 3396 (1965).

Table III. Activation Parameters for Hindered Internal Rotation in Undeuterated DMA

No.	Solvent	E_a, kcal/mole[a]	Log A[a]	$\Delta F^*_{298.2}$, kcal/mole[a]	$\Delta H^*_{293.2}$, kcal/mole[a]	ΔS^*, eu[a]	Ref
1	Neat	10.6	7.8	17.4	10.0	−24.8	8a
2		12.0	8.5	17.8	11.4	−25.5	2
3		20.2	16.1	15.7	19.6	+13.1	8b
4		23.0	16.0	18.7	22.4	+12.4	5
5	Formamide	24.7	16.4	19.8	24.1	+14.4	9

[a] See Table I.

Discussion

Dimethylacetamide-d_3. A comparison of the spectra in Figure 1 indicates that deuterium substitution in the CH_3CO group significantly sharpens the NCH_3 resonance signals.[12] The slight asymmetry remaining in the DMA-d_3 spectrum may be the result of residual unequal CD_3–NCH_3 coupling or perhaps unequal quadrupole broadening by the ^{14}N nucleus. In any case, while the data for neat DMA-d_3 (Table I) indicate that separate analyses of the two NCH_3 lines lead to slightly different activation parameters, they are within experimental error. Thus we do not feel that our results are significantly affected by this factor.

A comparison of the values of $\Delta F^*_{298.2}$ for the neat sample and that in DMSO-d_6 suggests a possible solvent effect. Dimethyl sulfoxide should be capable of strong dipolar association with an amide, and the higher values of ΔH^* and ΔS^* seem to indicate that this is stronger than dipolar association between amide molecules. Evidence for association equilibria between amide molecules has been inferred from observed temperature dependence of the nonexchanging chemical shift $\delta\nu_\infty$ between the two N–CH_3 lines.[1b,4,6,13] Rather large changes in $\delta\nu_\infty$ as a function of temperature have been observed for dilute solutions of amides and thioamides in nonpolar solvents.[1b,13] The relatively small effect of temperature on $\delta\nu_\infty$ for DMA-d_3 in neat solution and in DMSO-d_6 (Table V, Experimental Section) is no doubt a reflection of the large concentration of solvating molecules masking the temperature dependence of the association equilibrium constants. The positive values of ΔS^* (Table I) agree with previous predictions concerning the expected changes in solvation in proceeding from the ground state to the rotational transition state.[1b,9]

The choice of method for analyzing a given set of nmr spectral data clearly influences the resulting activation parameters (Table II). As has been previously observed,[1b,4] values of $\Delta F^*_{298.2}$ are less sensitive than the other activation parameters, but they yield the least amount of interesting information. Adequate discussion of the possible errors associated with these various line-shape methods has been given.[6] Although the limiting factor in all cases is the quality of the basic nmr spectral data, it is agreed that the method of *total* line-shape analysis rests on much firmer ground than the others.[6] For this reason, we feel that this method should be used for these types of high-resolution steady-state nmr kinetic studies. Arguments may be presented is support of the use of approximate methods in special cases, but we do not think that such data will merit the same level of confidence as those obtained from the *total* line shape.

Previously available activation parameters for undeuterated DMA (Table III) are characterized by significant discrepancies. The spread in values of $\Delta F^*_{298.2}$ is particularly surprising considering the relative constancy of this parameter between laboratories for other amides.[1b,4] Interestingly, none of these other amides gave asymmetric NCH_3 line shapes due to spin–spin coupling (*vide supra*), and it would be expected that differences in instrumental resolution would lead to greater discrepancies in such a case. Although all of the data in Table III represent the use of approximate methods, the set of parameters listed as number 4 was obtained from the combined use of several approximate methods and thus represents the result of a partial approach to total line-shape analysis.[5] The similarity of this value of ΔF^* to our data for DMA-d_3 suggests that set number 4 may represent the best previously available parameters. The activation parameters listed as sets number 1 and 2 seem grossly out of line based on the large negative values of ΔS^*, while the suspiciously low value of ΔF^* in set number 3 casts doubt on these results. The high activation parameters for DMA in formamide (number 5) have been rationalized on the basis of special hydrogen-bonding solvent effects associated with formamide;[9] however, the use of the intensity-ratio analysis leaves this question open.

The activation parameters for hindered rotation in DMA should not be the same as those for DMA-d_3. The rotation reaction for N,N-dimethylamides (I) is presumably influenced by inductive, resonance (and hyperconjugation), and steric effects associated with the group R_1, and the magnitude of these various interactions is most certainly modified by substitution of CD_3 for CH_3. Although we felt that differences in these effects due to isotopic substitution would be small, and activation parameters for DMA-d_3 would be a good approximation to those of undeuterated DMA, an attempt to place this feeling on a more quantitative basis has been made. The results of the analysis outlined below indicate that within experimental error this assumption appears to be correct.

Structure–Reactivity Correlation. Various reactions of aliphatic systems have been correlated by one-parameter equations using either the polar substituent constants σ^* or the so-called steric substituent constants E_s, or by a two-parameter equation using both constants.[14,15] If such a linear free-energy correlation

(12) The spectrum for DMA-d_3 in Figure 1 was determined at a slightly higher temperature than that for DMA. The resonance lines in the former spectrum are actually somewhat broader than they would appear at the lower temperature since truly nonexchanging spectra are only obtained below 25°.

(13) A. G. Whittaker and S. Siegel, *J. Chem. Phys.*, 42, 3320 (1965).

(14) See J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 219–235.

(15) The polar substituent constant σ^* presumably is a measure of the

Table IV. Selected Rotational Barriers for Amides of the Structure $RCON(CH_3)_2$ and the Corresponding Substituent Parameters for R

R	E_a, kcal/mole	Log A	$\Delta F^*_{298.2}$, kcal/mole	σ^*[a]	E_s[a]	Ref
H	22.0	13	21.7	0.5	1.24	10
CF_3	20.6	14.3	18.6	(2.8)[b]	−1.16	7
CCl_3	14.6	12.5	15.0	2.65	−2.06	4
(CH_3)[c]	(19.6)	(13.8)	(18.2)	0.0	0.0	c

[a] From the compilation given in ref 14. [b] Obtained by extrapolation of the available data.[a] [c] Our data for neat DMA-d_3; see text.

existed for the rotational reaction of N,N-dimethylamides (I, $R_2 = R_3 = CH_3$; X = O), it might be possible to quantitatively predict the magnitude of the difference between DMA and DMA-d_3. In addition, such a correlation would indicate the relative importance of steric, inductive, and resonance effects on the rotational barrier.[15] Although qualitative statements[1b,3c,g,5,8] have been made concerning the operation of these various effects on internal rotation in amides, no general quantitative correlation has been attempted.

Unfortunately, very few appropriate data are available to which a reasonably high confidence level can be attached. Careful consideration led to the choices shown in Table IV. The two halogenated systems were studied by the spin-echo method;[4,7] the values for DMF represent those recently obtained by a high-resolution double-resonance method using a combined approximate analysis method,[10,16] and those for R = CH_3 represent our data for neat DMA-d_3 (Table I). Although this requires the assumption that the activation parameters for DMA-d_3 and DMA are virtually identical, we felt that such an assumption was more appropriate to a first approximation than the choice of a previously reported value of ΔF^* (Table III) for undeuterated DMA. A striking aspect of these data is the close grouping of the values of log A about the value 13 (Table IV).

Using the one-parameter equations, it was found that a plot of $(-\Delta F^*_R + \Delta F^*_{CH_3})$ *vs.* σ^* gave virtually no correlation, whereas a plot of $(-\Delta F^*_R + \Delta F^*_{CH_3})$ *vs.* E_s did show a crude correlation indicating a negative value of the reaction constant S.[15] The two-parameter equation[14] (eq 1) involving both interaction mechanisms was rearranged to give eq 2, and a plot of σ^*/Δ *vs.* E_s/Δ gave

$$\Delta = (-\Delta F^*_R + \Delta F^*_{CH_3})/2.3RT = \rho^*\sigma^* + SE_s \quad (1)$$

$$\sigma^*/\Delta = 1/\rho^* - (S/\rho^*)(E_s/\Delta) \quad (2)$$

the approximate values −1 and −2 for ρ^* and S, respectively. A plot of eq 1 using these values and the data in Table IV is shown in Figure 3 (solid points). The line shown represents the theoretical plot of slope 1 and zero intercept.

Although the resulting correlation between the data and the theoretical line is not exceptional, we feel that these results do lead to some useful conclusions. In particular, the magnitudes of ρ^* and S indicate that inductive, resonance, and steric effects are all significant, but that the combination of the latter two effects (reflected in S) is more important than the inductive effect (ρ^*).[15] Further, the negative values of both ρ^* and S confirm qualitative observations that increasing steric size,

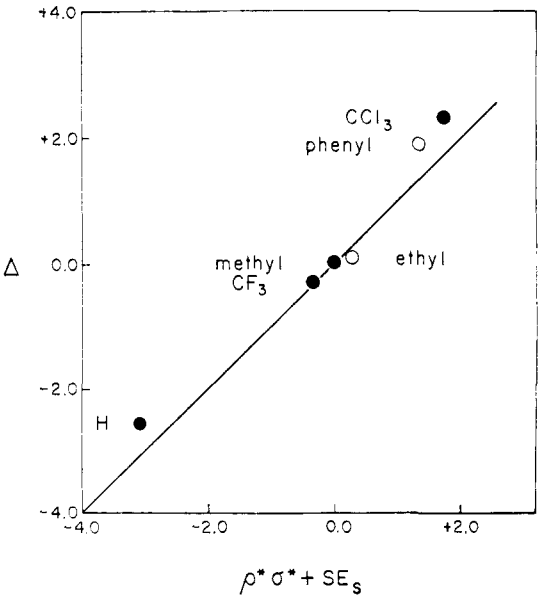


Figure 3. A plot of $(-\Delta F^*_R + \Delta F^*_{CH_3})/2.3RT$ (abbreviated as Δ) *vs.* $\rho^*\sigma^* + SE_s$ for the substituent groups R_1 shown ($\rho^* = -1$, $S = -2$, $T = 298.2°$). The *theoretical* line has a slope of 1 and a zero intercept. See text for differences between open and solid points.

increasing resonance electron donation, and increasing inductive electron donation due to R_1 in simple N,N-dimethylamides all lower the rotational barrier.[17] Sufficient data are available to test this correlation on N,N-dimethylbenzamide and N,N-dimethylpropionamide[18] although these amides were not chosen to develop the correlation because their activation parameters were considered less reliable than those in Table IV. The results are shown by the open points in Figure 3.

A value of σ^* for the CD_3 group can be calculated from the ionization constants[19] of CD_3COOH and CH_3COOH since the ionization equilibria of aliphatic carboxylic acids are correlated by the one-parameter $\rho^*\sigma^*$ equation ($\rho^* = 1.72$).[14] The resulting value of σ^* is

inductive property of the substituent group, while the "steric" substituent constant E_s is a combined measure of the steric size and resonance effect (including hyperconjugation) of the substituent group.[14] The corresponding reaction constants are ρ^* and S, respectively.

(16) Although the activation parameters chosen for DMF were derived from an approximate analysis, the value of ΔF^* obtained is very similar to other available values.[10] Even if it is not exactly correct, it will be useful for indicating a trend since it appears to be so much larger than that for DMA.

(17) The lowering of rotational barriers due to increasing size of R_1 in simple systems of the type discussed (I) is explained by relief of steric strain in proceeding from the planar ground state to the rotational transition state. However, several unusual amides have been recently studied by Mannschreck,[3c] in which steric considerations suggest that strain in the ground state should be less than that in the rotational transition state. His data seem to bear out this conclusion.

(18) Values of σ^* for the phenyl and ethyl groups are +0.60 and −0.10, respectively; the corresponding values of E_s are −0.90 and −0.07, respectively.[14] The most recent values of ΔF^* for DMBz (15.6 kcal/mole) and DMP (18.0 kcal/mole) were chosen.[5] They were obtained from the combination of several approximate methods.

(19) See E. A. Halevi, *Progr. Phys. Org. Chem.*, 1, 109 (1963).

either −0.015 or −0.011, depending on whether the ionization constant data of Halevi or Streitwieser are used.[19] Since it is not clear which data are correct, we will use the average value $\sigma^* = -0.013$. Calculation of a value of E_s for CD_3 is less straightforward. The definitions of σ^* and E_s lead to eq 3 in which the ratio

$$E_s = \log (k/k_0)_B - 2.48\sigma^* \quad (3)$$

$(k/k_0)_B$ can be chosen as the relative rate of base-catalyzed hydrolysis of CD_3COOEt and CH_3COOEt.[14] Using the data of Bender and Feng ($(k/k_0)_B = 1.11$)[20] and our calculated value of σ^*, a value of +0.08 for E_s was obtained. These substituent constants, qualitatively, reflect the anticipated increased electropositivity of CD_3 ($\sigma^*_{CH_3} - \sigma^*_{CD_3} > 0$) and the reduced hyperconjugation and/or smaller effective size associated with CD_3 ($E_s(CH_3) - E_s(CD_3) < 0$).[19,21] Their absolute magnitudes also seem consistent with experience.[19,21]

Substitution of these constants and the values of ρ^* and S previously determined into eq 1 indicates that $\Delta F^*_{CD_3}$ should be about 0.2 kcal/mole greater than $\Delta F^*_{CH_3}$. Since this difference is within the experimental error of our activation parameters (Table I), the initial prediction that the activation parameters for DMA-d_3 should represent a good approximation to those of DMA seems to be reasonable.

The activation free energies determined for DMF and DMF-d_1 by Conti and von Philipsborn are 21.7 and 23.0 kcal/mole, respectively.[10] Although these authors do not discuss this difference, it might be interpreted as a reflection of a deuterium isotope effect. Using the values of ρ^* and S obtained by us and a value of $\sigma^*_D = -0.022$ calculated from the ionization constants of DCOOH and HCOOH, we calculate that a value of $E_S(D) = +1.7$ is necessary to account for this difference. Compared to $E_S(H) = +1.24$, this value seems somewhat large and suggests that the difference should not be casually assumed to reflect the isotope effect.

Experimental Section

N,N-Dimethylacetamide-d_3. A 50-g sample of acetonitrile-d_3 (99.5%; Stohler Isotope Chemicals Co.) was slowly added to 187 g of cold concentrated hydrochloric acid. After addition the mixture was warmed to room temperature and then refluxed for 4 hr. The solution was filtered and neutralized with concentrated aqueous sodium hydroxide. After evaporation of the water, the solid sodium acetate-d_3 was dried at 155° for 30 hr. A 210-ml sample of phosphorus oxychloride was slowly added to the dried solid with cooling, the mixture was heated cautiously, and the resulting acetyl chloride-d_3 was collected by distillation (bp 51° at 750 mm) during the course of the reaction. A solution of the acetyl chloride-d_3 in 200 ml of ether was slowly added to a cooled solution containing 90 g of dimethylamine in 300 ml of anhydrous diethyl ether. The resulting mixture was filtered to remove dimethylammonium chloride, the ether was evaporated from the liquid phase, and the crude dimethylacetamide-d_3 was shaken with potassium hydroxide pellets and distilled: bp 71–74° (29 mm), 36.4 g (35.6% yield); nmr (DMSO-d_6): τ 7.03, 7.19; relative area 1:1; deuterium enrichment >95%; (CCl_4): 1655 (C=O); *undeuterated* DMA (CCl_4) 1662 cm^{-1} (C=O).

Dimethyl sulfoxide-d_6 was prepared by treatment of commercial dimethyl sulfoxide with sodium hydroxide in deuterium oxide (99.5%). The material resulting from six exchanges was distilled and dried over molecular sieves.

(20) M. L. Bender and M. S. Feng, *J. Am. Chem. Soc.*, **82**, 6318 (1960).
(21) D. D. Traficante and G. E. Maciel, *ibid.*, **87**, 4917 (1965).

Kinetic Studies. Details of our methods for obtaining the experimental spectra have been reported.[1b] Rate data were extracted from the experimental spectra using a different computer procedure from that previously reported.[1b] Intensity values as a function of frequency were taken from each experimental spectrum for 30 frequency values. These were then normalized and compared by least-squares procedures with normalized intensity values for the same frequencies calculated for a range of values of τ and $\delta\nu_\infty$ using the Gutowsky–Holm total line-shape equation. The values of τ and of $\delta\nu_\infty$ giving the smallest standard deviation between the experimental and calculated intensities were then used to calculate a line shape for visual comparison by methods previously reported. In all cases the agreement between the calculated line shape and the experimental spectrum was as good or better than that obtained using the methods previously outlined.[1b] In addition, we feel that the values of $\delta\nu_\infty$ obtained in this way are better than those obtained by using only the visual comparison method.

The values of T_2 for each experimental spectrum were determined from the line width of an internal sample of 1,1,2,2-tetrachloroethane. Low-temperature spectra of DMA-d_3 showed that the line widths of the NCH_3 resonance signals under nonexchanging conditions were essentially the same as those of the internal standard used for T_2 determinations. The spectra were calibrated using an audio side-band oscillator. The resultant kinetic data are given in Table V.

Table V. Kinetic and Spectral Data for DMA-d_3

Solvent	Temp, °K	$\delta\nu_\infty$, cps[a]	2τ, sec
Neat	319.6	10.00	0.413
	321.8	10.05	0.348
	326.1	10.00	0.208
	327.8	9.98	0.182
	329.5	9.85	0.152
	330.6	9.85	0.138
	332.4	9.95	0.119
	335.7	9.88	0.0888
	340.7	9.80	0.0584
	342.7	9.85	0.0474
	344.2	9.90	0.0414
	346.9	9.90	0.0356
	350.7	9.90	0.0280
	355.7	9.88	0.0179
DMSO-d_6 (9.5 mole%)	321.3	9.55	0.502
	324.8	9.45	0.406
	326.2	9.50	0.317
	327.7	9.40	0.296
	330.2	9.35	0.232
	331.1	9.40	0.194
	333.7	9.38	0.147
	335.7	9.35	0.126
	337.4	9.42	0.109
	338.8	9.20	0.0984
	340.9	9.40	0.0784
	342.7	9.40	0.0683
	344.4	9.40	0.0594
	344.8	9.10	0.0572
	346.2	9.40	0.0483
	348.8	9.40	0.0425
	351.2	9.40	0.0367
	359.2	9.40	0.0182
	363.8	9.40	0.0115

[a] Nonexchanging chemical shift used in the final line-shape calculation.

Temperature Calibration. Temperature measurements corresponding to each experimental spectrum were performed as previously reported.[1b] The Varian ethylene glycol "thermometer" was calibrated at six points between 45 and 95° by comparing the observed chemical shift between the CH_2 and OH proton resonances with temperatures measured by insertion of a thermocouple into a spinning sample tube. Comparison of the calibrated temperature to the temperatures obtained from the Varian manual indicated that the Varian temperatures were about 2.5° too low at the extremes of the measurement range, and about 1° too low in the center. The temperature calibration curve was continuous.

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The Crystal Structure of a Carbanion. Potassium 4,4-Dinitro-2-butenamide

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Abstract: The crystal structure of the potassium salt of the 4,4-dinitro-2-butenamide carbanion has been determined by X-ray diffraction. The entire carbanion is essentially planar. The N–C–N bond angle is 120° in spite of an O–O distance of only 2.51 Å between the nitro groups. The carbanions lie in planar layers 3.0 Å apart and are doubly hydrogen bonded into chains within these layers. The potassium cations lie 0.7 Å above and below the anion planes.

Nitromethane is a much stronger carbon acid than methane. However, unlike other acidifying groups, the effects of a second and third nitro group are not additive (see Table I). This lack of additivity has been attributed to steric repulsions which prevent all the atoms of the resulting carbanion from lying in the same plane.[2]

Table I. pK_a in Water at 25°[a]

CH_3NO_2	11	CH_3CN	25	$CH_3SO_2CH_3$	23
$CH_2(NO_2)_2$	4	$CH_2(CN)_2$	12	$CH_2(SO_2CH_3)_2$	14
$CH(NO_2)_3$	0	$CH(CN)_3$	−5[b]	$CH(SO_2CH_3)_3$	0

[a] See ref 2. [b] R. H. Boyd, *J. Phys. Chem.*, **67**, 737 (1963).

The thermodynamic acidity of a carbon acid (measured by the pK_a) is a function of the relative stability of the undissociated molecule and of the carbanion which results from deprotonation. A nitro group increases the acidity of methane both by stabilizing the carbanion and by decreasing the stability of the neutral molecule. Its stabilizing effect on the methide ion is due chiefly to delocalization of the charge by p-orbital interaction. Maximum interaction requires that the p orbitals of the carbon and nitrogen atoms be parallel, that is, that the sp^2 hybrid orbitals be coplanar. Therefore, two or three nitro groups can exert their full stabilizing effects only if the entire carbanion is coplanar.

Nitro groups make methane less stable toward deprotonation by withdrawing electrons from the carbon atom and thus weakening the C–H bond. Trinitromethane (nitroform) should be less stable than carbomethoxydinitromethane (methyl dinitroacetate) because the nitro group has a stronger electron-withdrawing effect than the carbomethoxy group. This estimate is based on the σ^* values of 2.00 listed by Taft[3] for carbomethoxy and 3.9 which can be derived for nitro from other values given by Taft.[3] From other values given in this compilation,[3] we estimate a σ^* value of 0.6 for the carbomethoxyvinyl group; therefore, carbomethoxyvinyldinitromethane (methyl 4,4-dinitro-2-butenoate) should be more stable than methyldinitroacetate and much more stable than nitroform.

As would be predicted from the proposed stabilities of the neutral molecules, nitroform is about 1.0 pK unit stronger an acid than methyl dinitroacetate.[4] However, 4,4-dinitro-2-butenoic acid derivatives are as strong or stronger acids than nitroform (see Table II). This would indicate that these compounds form more stable carbanions than either nitroform or methyl dinitroacetate.

Table II. pK_a in Methanol[4]

$(NO_2)_2CHCH{=}CHCOOCH_3$	3.15
$(NO_2)_2CHCH{=}CHCN$	1.91
$(NO_2)_3CH$	3.22

As stated above, a major factor in carbanion stability is delocalization of the charge from its formal location on the carbon atom. The reactivity of a carbanion toward an α,β-unsaturated system in a Michael-type addition gives an indication of the extent of such delocalization because the nucleophilicity of the carbanion is a function of the charge remaining on the carbon atom. Both trinitromethide and carbomethoxydinitromethide react readily with methyl acrylate in a Michael-type addition, but carbomethoxyvinyldinitromethide is totally unreactive.[4,5] This is additional evidence for the greater stability of the carbomethoxyvinyldinitromethide carbanion and indicates that the reason for its stability is extensive charge delocalization.

An obvious explanation for this carbanion stability (due to efficient charge delocalization) would be that 4,4-dinitro-2-butenoic acid derivatives form planar carbanions permitting maximum resonance interaction by

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