however, be expected to occur; first, the hydroxyl splitting constant will decrease as the $p-\pi$ overlap between the oxygen and the ring decreases and second, hyperconjugative coupling to the ring will increase.[25] As the mechanism of coupling changes from spin polarization to hyperconjugation, the splitting constant is expected to change from a negative to a positive quantity. These two effects will each be approximately proportional to $\cos^2 \theta$, leading to an estimate for $\theta \cong 15°$. The observed temperature dependence of the hydroxyl splitting constant (*ca.* 5% in 100°) for duroquinol may be explained in terms of a change of θ with temperature. At low temperature, the mean value of θ might be expected to decrease, leading to an increased splitting constant. However, the hydroxyl splitting constant in hydroquinone is also temperature dependent[15] (*ca.* 2.7% in 100°). Since the steric effects are smaller, the temperature dependence may be caused by other effects such as a temperature-dependent Q_{OH} (compare also the temperature dependence of Q_{CH}, 1–2%/100° [26,27]). Moreover, the assumption implicit in the four-jump model, that the hydroxyl group spends a negligible amount of time out of plane, may only be approximately correct.

The conformation of dimethoxydurene can be considered in a related manner. The splitting of a methoxy group is expected to vary as $\cos^2 \theta$ and a comparison of the found (2.85) and predicted (3.20 gauss) values indicates that $\theta \cong 20°$. However, there is no evidence for *cis* and *trans* isomers as defined for duroquinol, nor for any line-width alternation. This may be due to the greater steric interactions which cause the potential barrier to rotation to be sufficiently small so that the lifetime of the conformations becomes relatively short thus giving a time-averaged spectrum. Alternatively, the methoxy group may be constrained to one side of the benzene ring plane and may oscillate rapidly between the two equilibrium positions with $\theta \cong 20°$. The temperature dependence of the methoxy splitting constant can be explained in a similar manner to that of the hydroxyl protons of duroquinol.

Acknowledgments. The author wishes to express his sincere thanks to Professor W. F. Forbes for his constant encouragement and valuable suggestions during all stages of this work. The author is also indebted to Mr. A. B. Barabas for help with the computer programs, to Dr. T. E. Gough for discussions, and to the National Research Council of Canada for a studentship and other financial assistance.

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Comparison of Chemical Exchange Rates Determined by Nuclear Magnetic Resonance Line-Shape and Equilibration Methods. Internal Rotation of N-Methyl-N-benzylformamide[1]

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Abstract: The rate of internal rotation about the C–N amide bond has been studied in N-methyl-N-benzylformamide between 170 and 90° by an nmr complete line-shape analysis method and between 20 and −2.5° by an equilibration technique. Exchange rates were calculated from the nmr spectra of the benzyl and formyl protons in the two rotational isomers by treating them as two separate, uncoupled, exchanging AB systems with unequal populations. The calculations for the formyl protons required inclusion of temperature dependence in the chemical shift. The equilibration studies were performed on samples in which the isomer with the methyl *cis* to the formyl proton was concentrated by complexing the equilibrium mixture with uranyl ion and stripping it off at low temperatures. The activation parameters obtained from the nmr studies agree well with those obtained by the classical equilibration method.

The various nmr techniques which may be employed to determine the nature and rate of fast exchange processes in liquids have been reviewed in several recent papers,[4-6] but there is one aspect which has received relatively little attention. This is the comparison of rates and/or activation parameters determined by nmr methods with those from more conventional approaches. Such comparisons are difficult because the 1 to 10^6 $\sec^{-1}$ exchange rates measured by nmr are too fast for most other methods applicable to liquids; moreover, many of the processes studied by nmr are con-

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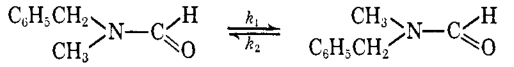
formational changes between "identical" forms indistinguishable by non-nmr methods. However, in some amides with two distinguishable isomers, the temperature dependence of the internal rotation about the C–N amide bond is great enough that one can measure the fast exchange rates at high temperatures by nmr[7–11] and the slow rates at low temperatures by a more conventional equilibration technique.[12,13] In this paper we report such a study of N-methyl-N-benzylformamide (MBF).

Insofar as related studies are concerned, the most relevant appears to be that of Mannschreck, Mattheus, and Rissmann,[14] who found that the activation parameters obtained from an equilibration study of N-benzyl-N-2,4,6-tetramethylbenzamide compare favorably with those for N,N-2,4,6-pentamethylbenzamide from an nmr line-broadening technique. However, the comparison is of two similar but nonetheless different compounds, so there remains the question of how much of an effect substituting an N-methyl group for an N-benzyl group has on the internal rotation rate and activation parameters.[15] Ollis and Sutherland have compared the thermodynamic parameters for the ring inversion of tri-*o*-thymotide from nmr studies with the polarimetry results for its racemization. However, as pointed out in their preliminary report,[16] it is yet to be established that the same conformational change is involved in the two processes. Finally, Curtin and co-workers[17] have determined the *syn–anti* isomerization rates for several substituted imines from the nmr coalescence temperatures and the slower rates for another imine by means of equilibration studies employing ultraviolet spectra. The two sets of rates are reduced to a common temperature, the substituent effects are calculated by a Hammett $\sigma\rho$ treatment, and the results are found to agree within the accuracy of the over-all method.

The extent to which we have avoided some of the limitations of the earlier work reflects the favorable properties of N-methyl-N-benzylformamide. The nonequivalence of the two isomers, I and II, makes it



$$(C_6H_5CH_2)(CH_3)N{-}CH{=}O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (CH_3)(C_6H_5CH_2)N{-}CH{=}O \qquad (1)$$

I II

possible to concentrate one of them (II) by complexing the equilibrium mixture with uranyl ion and stripping it off at low temperatures, and then to observe the return to equilibrium.[13] Also, the Gibbs free energy of I is only about 135 cal/mole less than that of II, and the difference is virtually temperature independent. Therefore, nearly equal amounts of I and II occur at thermal equilibrium, which greatly facilitate the nmr measurements. Furthermore, as may be seen in eq 1, the chemical shifts of four different sets of protons can be affected by the exchange, and it proved possible to use the formyl and benzyl proton resonances to obtain two independent sets of exchange rates and activation parameters from the nmr line-shape analyses.

Experimental Section

The N-methyl-N-benzylformamide (MBF) was prepared by the reaction of formic acid with N-methyl-N-benzylamine.[18] The MBF produced was isolated and purified by distillation under vacuum. For the proton high-resolution nmr line-shape studies, 5% by volume of *t*-butylbenzene was added to the MBF as a resolution standard, and the sample was degassed under vacuum by the usual freeze–thaw procedure. The proton spectra were obtained with a Varian Associates A-60 spectrometer using a variable-temperature probe. The reported temperatures are accurate to within ±2°.

The techniques used to prepare samples for equilibration study were very similar to those reported previously.[13] First, the uranyl nitrate adduct of MBF was formed and crystallized from dichloromethane. Then, the uranyl nitrate was stripped from the adduct at low temperatures, leaving MBF with a II/I isomer ratio about twice the equilibrium value of 0.8. In order to make the stripping easier, the adduct was initially partly redissolved in dichloromethane. The dichloromethane solution of the adduct was stripped rapidly three times with ice water, once with a cold sodium carbonate solution, and then with ice water again. The dichloromethane solvent was removed from the MBF by distilling it off under vacuum at −10°. This was the low-temperature limit as at still lower temperatures MBF set up as a solid that could not be transferred readily to a tube for the equilibration studies. An alternative method for separating solvent and MBF that is more convenient was also used. The solvent was pumped off at −25°, a sample of the solid was transferred to a small centrifuge cone, enough was melted rapidly at about +10° to centrifuge, and the clear supernatant liquid was transferred for the final study. In this case the clear liquid became a slushy solid below about −5°.

The return to equilibrium of the MBF samples with a nonequilibrium isomer ratio was followed by observing the time dependence of the proton spectrum in a Varian A-60 nmr spectrometer with the variable temperature probe at a preset value. The isomer ratio was obtained by measuring the areas under the nmr lines corresponding to the formyl protons in isomers I and II. The highest temperature at which equilibration studies could be made this way was around +25°; it was determined by the rate of approach to equilibrium compared with the time required for the sample to attain a uniform, stable temperature in the spectrometer and for enough spectra to be recorded to establish the equilibration rate. The low-temperature limit of about −5° was determined mainly by the freezing point of the sample, as mentioned above.

Results

Proton High-Resolution Spectrum of MBF. At room temperature the rate of rotation around the C–N bond in MBF is slow on the nmr time scale and therefore the proton spectrum is a combination of lines from isomers I and II. Nonetheless, the spectrum is relatively simple. The benzyl protons give rise to two lines separated by a chemical shift $\Delta\nu$ = 10.1 Hz, centered at τ 5.62 with the low-field line somewhat less intense (0.46 *vs.* 0.54). There is a similar pair of lines at τ 1.80 for the formyl protons, with $\Delta\nu$ = 12.8 Hz, except that the high-field peak is less intense. The spectra of the formyl and benzyl protons, measured at 40° and 60 MHz, are given in Figure 1. We also expected to find two peaks for the N-methyl groups, with a chemical shift of 5 to 10 Hz

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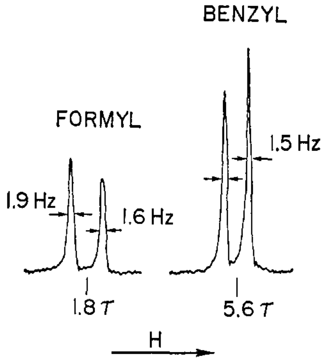

Figure 1. High-resolution spectra of formyl and benzyl protons, measured at 40° and 60 MHz.

between the two isomers;[19] however, only a broadened peak was found at τ 7.34, with a total width of 1.8 Hz at half-maximum intensity. The aromatic protons give a broad band around τ 3.1.

It is of interest to establish whether I or II is more stable. This assignment can be based on the finding in N,N-dimethylformamide[20] that the coupling J_t of the formyl proton to the *trans*-methyl group protons, as in I, is larger than the coupling J_c to the *cis*-methyl group protons as in II. Thus, if we assume the coupling of benzyl and formyl protons to be the same as that of the methyl, the width of the formyl proton resonance should be larger in I than in II, namely, $3J_t + 2J_c$ as compared to $2J_t + 3J_c$. And, in fact, the low-field component of the formyl resonance is observed to have a width of 1.9 Hz, whereas that at high field is narrower, 1.6 Hz. Thus, we attribute the low-field formyl line to I and, as it is more intense than the high-field line, we conclude that I is more stable than II.

Support of this assignment is provided by the N-methyl resonance which exhibits some partially resolved, temperature-dependent, fine structure. In particular, at temperatures where exchange broadening does not occur, a doublet splitting of about 0.5 Hz and a smaller one of 0.15 Hz are discernible and are presumably J_t and J_c. Furthermore, the line width decreased from 1.8 Hz at room temperature to 1.2 Hz at 166°. This high-temperature residual width indicates the probable importance of coupling with the benzyl protons as well as with the formyl. Such coupling would also explain our finding that both components of the benzyl resonance have about the same width, 1.5 Hz at temperatures of 65° or less where exchange broadening is unimportant.

The equilibrium constant $K = C_{II}/C_I$ was determined at several temperatures by measuring the relative areas under the two formyl proton lines. This pair of lines was used in all relative population determinations because it is better resolved than the benzyl or any other pair. In the low-temperature region -2.5 to 20°, K was found to be constant at 0.80 within an experimental error of ± 0.03. However, K was somewhat higher, 0.85, at temperatures about 100°. Thus, the standard Gibbs free energy of I is 135 cal/mole lower than that of II, and the difference is temperature independent within experimental error over the range investigated.

Exchange Rates from Nmr Line-Shape Analysis. In this portion of the study, the exchange rate was determined from the complete line shape using the equations derived for an uncoupled AB system with the exchanging sites unequally populated.[7] Because of the unequal populations, the exchange lifetimes τ_1 and τ_2 differ for the two sites, as do the corresponding rate constants k_1 and k_2, where $k_i = 1/\tau_i$. However, the line shapes are governed by a single exchange parameter defined originally[7] as $\tau = \tau_1\tau_2/(\tau_1 + \tau_2)$ which is related to the average exchange rate k as

$$k = 1/2\tau = (k_1 + k_2)/2 \qquad (2)$$

Individual values can of course be obtained for k_1 and k_2 by combining a determination of k with the results given for the equilibrium constant K in the preceding paragraph. But there seems to be little point in so doing, and all of our kinetic data are presented as the average rate constant k, defined in eq 2.

A FORTRAN program CURVE 4 was used to perform the line-shape analyses on an IBM 7094 computer. The over-all approach is very similar to that described in more detail in our previous paper dealing with a coupled AB system.[21] The input to CURVE 4 includes the chemical shift $\delta\nu$ and total line width W'' in the absence of exchange,[6] the relative population P_a of one site,[7] the observed spectrum as a set of about 50 digitized absorption intensities at stated intervals in frequency, and a "guessed" value for the exchange rate k. The program first normalizes the area of the experimental spectrum. It then calculates theoretical intensities for the abscissa values of the experimental points and normalizes the area of the theoretical spectrum; these calculations are made with the line-shape equations[7] employing the input values of $\delta\nu$, W'', P_a, and k. Next, SDEV, the sum of the squared deviations between theoretical and experimental intensities, is computed; and finally the best fit is obtained by a search routine which steps off the appropriate input parameter(s), ordinarily only k, to minimize SDEV. Also, a graphical output using a CALCOMP plotter provided a convenient visual check of the agreement between calculated and experimental shapes. Two comparisons of this type have been traced and consolidated in Figure 2.

Analyses as described above were made for both the formyl and the benzyl proton lines observed at temperatures between 62 and 166° and the results obtained are summarized in Table I. The analysis of the formyl proton line shapes was complicated by an appreciable temperature dependence of the intrinsic shift between the two isomers. The change in $\Delta\nu$ was directly apparent in the temperature interval 25 to 87° for which the exchange effects are negligible in comparison to the intrinsic temperature dependence of the shift. The latter is due probably to association effects, perhaps of an hydrogen-bonding variety; in any event, the observed dependence is fitted very well by the following equilibrium-type expression

$$\log \Delta\nu = (0.706 \pm 0.022) + (121.9 \pm 7.2)T^{-1} \qquad (3)$$

where T is in °K. The chemical shift $\Delta\nu(T)$ used to fit the formyl line shape at each temperature was obtained with eq 3. The accuracy of this procedure was

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[19] Chemical shifts of this magnitude are common for the rotational isomers of amides, but they are affected by a variety of factors, some quite subtle and poorly understood.

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Table I. Rate Constants Obtained for High Temperatures by Complete Line-Shape Analysis of the Benzyl and Formyl Proton Resonances

Temp, °C	Benzyl[a] k, sec^{-1}	Formyl[b] k, sec^{-1}	$\Delta\nu$, Hz	k_a, sec^{-1}
29	<0.01	<0.01	12.8_0	<0.01
44	<0.01	<0.01	12.3_3	<0.01
47	<0.01	<0.01	12.2_1	<0.01
62	<0.1	<0.1	11.6_7	1.1
77	<0.1	<0.1	11.4_2	2.7
87	<1.0	<1.0	11.0_0	4.2
97	1.8	2.2	10.8_3	8.0
103	4.0	4.6	10.7_1	11.8
108	8.2	5.6	10.5_9	20.0
113	12.0	10.0	10.5_0	24.6
122[c]	29	20	10.3_2	47
128	40	37	10.2_1	60
133	73	45	10.1_2	90
138	85	76	10.0_4	123
144	151	96	9.9_5	162
151	242	128	9.8_4	216
156	320	180	9.7_6	312
158	420	200	9.7_3	350
166	590	240	9.6_2	440

[a] The relative population P_a of the low-field site was taken to be 0.46, and the total line width W'' in absence of exchange, 1.5 Hz. [b] The values of k correspond to the temperature-dependent values given for the chemical shift $\Delta\nu$; the k_a's are approximate rate constants obtained by using a constant chemical shift of 12.80 Hz, the room-temperature value. For both sets of calculations, P_a was taken to be 0.54 and W'', 1.9 Hz. [c] This is the approximate coalescence temperature for both pairs of lines.

checked at temperatures below coalescence by minimizing SDEV with respect to $\Delta\nu$ as well as k. An example is given in Figure 2, in which the spectrum observed at 97° is compared with a "best-fit" spectrum calculated for $\Delta\nu = 12.8$ Hz and with *the best fit* found by adjusting *both* $\Delta\nu$ and k. The value of SDEV is 19.3 for the former and 4.8 for the latter; from this difference and also the visual comparison in Figure 2, it is clear that the temperature dependence of $\Delta\nu$ must be included in the analysis. The chemical shift becomes smaller at higher temperatures, so neglect of its temperature dependence leads to apparent rates k_a which are larger than the true rates k, as is shown by the two sets of values in Table I.

The benzyl results were analyzed using the room-temperature chemical shift of 10.1 Hz. There was no evidence of a temperature-dependent $\Delta\nu$ at higher temperatures where exchange effects were still negligible. Nor was the fit of calculated to experimental line shapes improved by changing the chemical shift at higher temperatures where the lines were partially coalesced.

Two approximations made in the line-shape analysis merit comment. It was assumed that the relative populations of the two sites were constant at 0.54 and 0.46 for the whole temperature range. This could be checked for partially coalesced lines below the coalescence temperature of 122° by using P_a as an adjustable parameter in fitting the line shape, but not at higher temperatures. Fortunately, the rate constants obtained from the line-shape analysis are not very sensitive to P_a; and therefore it seems that this approximation did not introduce appreciable error in our results. The matter of the line width in the absence of exchange is more serious.

The line-shape equations are in terms of the parameters T_2^0 which describe the natural line widths in the absence of exchange broadening.[6] But in addition there is the instrumental broadening and the substantial further broadening by unresolved fine structure resulting from coupling among the benzyl, formyl, and N-methyl protons, of which the coupling to the formyl protons is affected by the exchange. Also, there probably is some ^{14}N coupling which is temperature dependent because of the ^{14}N quadrupolar relaxation.[22] Proper allowance for or removal of all of these effects is difficult, so we simply used the total line width W'' observed at 29° as if it corresponded to T_2^0. This neglects the possible temperature dependences and limits the accuracy of our rate determinations, particularly in the slow and fast exchange regions.

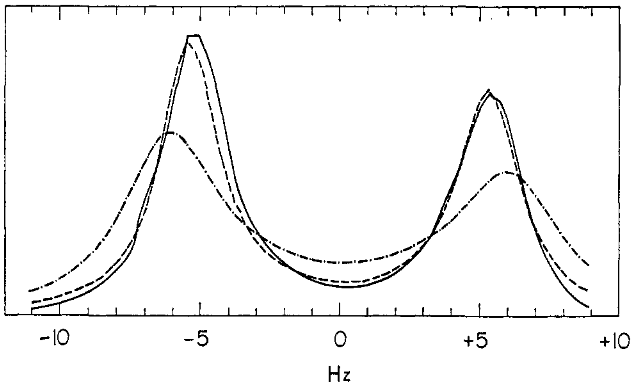

Figure 2. The observed and calculated line shapes of the formyl proton resonance in MBF at 97°. The solid line is the observed line shape and the broken lines are the shapes calculated for an uncoupled two-site system with unequal populations (0.54/0.46) undergoing exchange. The dotted line (- · - ·) is the best fit obtained with the low-temperature chemical shift of 12.8 Hz; it corresponds to $k = 8$ sec^{-1}. The dashed line (- - - -) is the best fit obtained using both the chemical shift and the exchange rate as adjustable parameters; it corresponds to a chemical shift of 10.83 Hz and $k = 2.20$ sec^{-1}. All line widths in the absence of exchange were taken to be 1.9 Hz.

Equilibration Rate Studies. At the start of the equilibration procedure, after stripping off the uranyl nitrate adduct of MBF, the ratio of isomers II/I was always greater than 1.7. This ratio R was determined from the formyl proton lines as a function of time t' at a given temperature. The average rate constant k was calculated from the slope of a semilog plot of the data by means of the equation

$$-2kt = -(k_1 + k_2)t = \ln[(R - K)/(1 + R)] \quad (4)$$

where K is the low-temperature equilibrium constant, 0.80. This equation is an adaptation for our purposes of the usual expression[23] for a reversible, first-order reaction, with initial conditions such that $R = \infty$, when $t = 0$; *i.e.*, C_I, the concentration of I, is zero at $t = 0$. The value of t' which corresponds to $C_I = 0$ is governed by the actual experimental procedure and is not readily measured. Nonetheless, a plot of ln $[(R - K)/(1 + R)]$ *vs.* the known, corresponding times t' gives a straight line, the slope of which establishes the value of $(k_1 + k_2)$. Useful results were obtained for the temperature interval −2.5 to 20° as listed in Table II.

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Table II. Rate Constants Obtained for Low Temperatures by the Equilibration Method

Temp, °C	Exchange rate,[a] k, sec^{-1}	Temp, °C	Exchange rate,[a] k, sec^{-1} $\times 10^4$
−2.5	0.6×10^{-4}	15	4.4
5	1.7	19.5	11.5
5[b]	1.4	20	11.0
9.5	3.4		

[a] The estimated standard error for these values is ±10%. [b] The rate was obtained from the relative intensities of the two benzyl lines in this case.

Discussion

Arrhenius plots of the rate constants found by the two methods are given in Figure 3. The three sets of data were fitted by least squares, which gave the lines in the figure and the activation parameters summarized in Table III. The rate constant k which is plotted is the average for the forward and reverse reactions, so the activation parameters are the corresponding averages. However, the errors in the average values are larger than the small differences in the individual values, so the latter are not given, especially as they can be calculated readily from our result that $\Delta G° = 0.135$ kcal/mole.

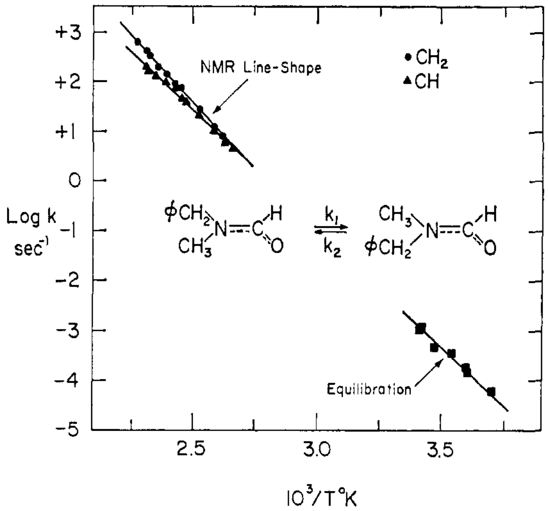

Figure 3. Arrhenius plots of the internal rotation rate as obtained by the nmr complete line-shape analyses and by the equilibration study. The rate constant k (sec^{-1}) is the average rate constant $(k_1 + k_2)2$.

Table III. Activation Parameters for the Internal Rotation of N-Methyl-N-benzylformamide[a]

Activation parameter	Nmr line-shape analysis Benzyl	Formyl[b]	Equilibration method
E_a, kcal/mole	25.0 ± 1.5	22.7 ± 1.5	20.0 ± 3
Log A	15.2 ± 1	13.9 ± 1	11.9 ± 1.6
$\Delta H^{\ddagger}$, kcal/mole	24.3 ± 1.5	22.0 ± 1.5	19.5 ± 3
$\Delta G^{\ddagger}$, kcal/mole	20.9 ± 0.4	21.0 ± 0.4	21.6 ± 0.7
$\Delta S^{\ddagger}$, eu	8.8[c]	2.4[c]	−6.5[c]

[a] The values of $\Delta H^{\ddagger}$, $\Delta G^{\ddagger}$, and $\Delta S^{\ddagger}$ were evaluated for 373.1°K. [b] These results, as well as those in Figure 3, are from the line-shape analysis with the temperature-dependent $\Delta\nu$. [c] The deviation in $\Delta S^{\ddagger}$ may be as large as the value given.

Inspection of Figure 3 and comparison of the data in Table III show that the nmr line-shape and equilibration methods give the same results within experimental error. The results from the two line-shape studies, of the benzyl and formyl resonances, agree better with one another than with the equilibration results. However, the latter only extend over 22.5°, at temperatures which are 100 to 150° removed from the line-shape studies. Therefore, we feel that the over-all agreement is sufficiently good to confirm the general validity of the theory describing the effects of chemical exchange upon nmr spectra.[6,7] The agreement and errors are particularly respectable for $\Delta G^{\ddagger}$, which is the parameter least susceptible to systematic errors.[6,24]

Originally, we had hoped that the line-shape analyses of the benzyl and formyl spectra, both of which are affected by the same exchange process, might give results in better agreement than those actually obtained. Nonetheless, the comparison does indicate the magnitude of the systematic errors which may be caused by neglecting the temperature dependence of broadening caused by unresolved fine structure. Further studies of this nature[25] could be helpful in improving the reliability of the nmr methods.

The activation parameters found for the internal rotation of MBF compare favorably with the values reported by Mannschreck, *et al.*,[12,14] for similar substituted amides. To be sure, Franconi and co-workers[26] gave earlier values of $E_a = 11.9 \pm 2$ kcal/mole and log $A = 7$ for MBF, which are much lower than ours. However, in a later, critical study of possible sources of error in nmr rate determinations, they arrived at higher values of E_a and log A for a number of N,N-dimethylamides,[11] which compare more favorably with ours. Neglect of the temperature dependence of the formyl proton shift introduces appreciable systematic error. For example, the rate constants in Table I, calculated by assuming $\Delta\nu$ to be constant at the low-temperature value, lead to $E_a = 19.3$ kcal/mole and log $A = 12.3$, both being substantially less than the respective, corrected values of 22.8 kcal/mole and 13.8 given in Table III.

It is rather surprising that so far little attention has been paid to this problem as, for example, Hatton and Richards[27] performed a thorough study of solvent effects in various amides, and one can expect these relatively large intermolecular interactions to be temperature dependent. Fryer, Conti, and Franconi[11] did observe a temperature-dependent chemical shift between the *cis*- and *trans*-methyl group protons in dimethylformamide and proposed an approximate procedure to account for this dependence in their nmr determinations of the exchange rate. The problem in general merits more serious consideration, and examples of exchanging coupled AB systems, with a temperature-dependent AB chemical shift, are under investigation.[28]

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