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# Nuclear Magnetic Double-resonance Study of the Hindered Internal Rotation in Formamide

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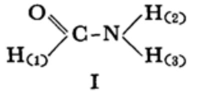
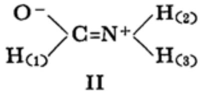
The nitrogen-14 quadrupole relaxation broadening effect on the proton spectrum of formamide was eliminated by a $^1H$-$\{^{14}N\}$ double resonance technique. The completely-decoupled proton spectra of formamide in the neat liquid and in acetone, dioxane, and water solutions were observed at several temperatures. The spectra observed at room temperature were analyzed on the basis of an ABC system, while the spectra at higher temperatures ($\sim$100°C) were analyzed on the basis of an $AB_2$ system. From the changes in the resonance lines of the formyl proton with the temperature, the values of the activation energy for the hindered internal rotation about the C–N bond, $E_a^{rot}$, and for the intermolecular proton exchange involving the amine protons, $E_a^{ex}$, were obtained. It has been found that the hydrogen-bond formation on the carbonyl oxygen of formamide increases the $E_a^{rot}$ value and the magnitude of the vicinal coupling constants, while it decreases the magnitude of the geminal coupling constant.

The hindered internal rotation in amides has been attributed to the partial double-bond character in the C-N bond resulting from a contribution from a resonance form such as II.



I



II

The stability of the II resonance form must be affected by the nature of the intermolecular interactions between amide and the solvent molecule. One would predict a solvent effect on the activation energy for rotation about the C–N bond. Such solvent effect has been demonstrated for *N,N*-disubstituted amides[1,2] and thioamides[3] using a nuclear magnetic resoance technique. Effects due to protonation[4] and complex formation[5] have also been observed. Such solvent effects are also found for unsubstituted amides. However, the resonance lines of the protons bonded directly to nitrogen are broadened, and a complete analysis of the spectrum is usually not possible. The broad nature of the lines is derived from the quadrupole coupling of the $^{14}N$ nucleus. The quadrupole broadening can be eliminated by a technique of

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1) J. C. Woodbrey and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 13 (1962).

2) A. G. Whittaker and S. Siegel, *J. Chem. Phys.*, **42**, 3320 (1965); **43**, 1745 (1965).

3) A. Loewenstein, A. Melera, P. Rigny, and W. Walter, *J. Phys. Chem.*, **68**, 1597 (1964).

4) G. Fraenkel and C. Franconi, *J. Am. Chem. Soc.*, **82**, 4478 (1960).

5) E. S. Gore, D. J. Blears, and S. S. Danyluk, *Can. J. Chem.*, **43**, 2135 (1965).

nuclear magnetic double resonance⁶⁾ and also by the substitution of the isotope, $^{15}$N. Sunners *et al.*⁷⁾ studied $^{15}$N-substituted formamide and found the activation energy for rotation, $E_a{}^{rot}$, to be 18±3 kcal/mol for formamide in a 10 mol% acetone solution.

In the present work the quadrupole broadening was eliminated by the nuclear magnetic double-resonance technique. The completely-decoupled proton spectra of formamide were then obtained under different conditions. The values of $E_a{}^{rot}$ have been determined in several solutions. The solvent effects on $E_a{}^{rot}$ and NMR parameters will be discussed.

## Experimental

**Measurements.** Double resonance experiments were carried out on a $^1$H-{$^{14}$N} double resonance spectrometer which made possible the complete decoupling of the $^1$H-$^{14}$N coupling by the irradiation of the large second radio-frequency field at about 2.9MHz and the observation of the proton resonance at 40MHz. Details of the spectrometer and associated equipments have been described elsewhere.⁸⁾

Double-resonance proton spectra were obtained for each sample at several temperatures. The accuracy of the sample temperature determinations was about ±1°C. The frequency and width of each resonance line were determined by a method of sideband audio modulation, with an accuracy of ±(0.5%+0.05)Hz. In order to monitor the homogeneity of the field, the line width of cyclohexane, which was used as a reference, was measured in each measurement.

The measurements were made at a constant second radio-frequency field. The frequency was 2.88950 MHz, while the amplitude, $H_2$, was 4.3 gauss. The value of $H_2$ was determined from the Bloch-Siegert shift,⁹⁾ $\delta_B \sim \gamma^2 H_2{}^2/2\Delta\omega$, where $\Delta\omega$ is the frequency difference between the proton resonacne and the second radio-frequency field. Figure 1 shows typical spectrum of cyclohexane with the bracketing side-band signals. When the second radio-frequency field is supplied, the resonance shifts to a lower field (from A to B). A plot of $\sqrt{\delta_B}$ *vs.* the voltage of second radio-frequency, to which $H_2$ is proportional, resulted in a straight line, as is shown in Fig. 2. Thus, $H_2$ can be determined precisely from the Bloch-Siegert shift in the hetero-nuclear double resonance.

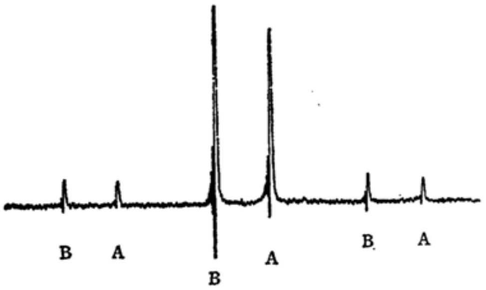

Fig. 1. Bloch-Siegert shift in cyclohexane resonance. A, normal resonance; B, $H_2$ supplied

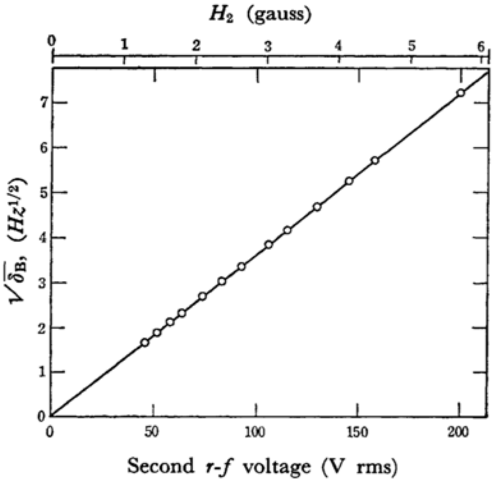

Fig. 2. Plot of $\sqrt{\delta_B}$ *vs.* the voltage of the second *r-f* field.

**Preparation of Samples.** Formamide was purified as follows: With bromothymol blue as an indicator, reagent-grade formamide was neutralized with solid sodium hydroxide. Sodium formate was added to the neutral liquid, and formamide was fractionally distilled under reduced pressure by passing dry argon through. All the solvents were reagent-grade quality and were dried and doubly-distilled prior to use. The samples were degassed and sealed *in vacuo*. The compositions of the samples were determined by means of their weight.

## Results and Discussion

**Chemical Shifts and Coupling Constants at Room Temperature.** The double-resonance proton spectra of formamide in the neat liquid and in water, acetone, and dioxane solutions at 27°C are shown in Fig. 3. The spectra can be assigned on the basis of three nonequivalent protons. This indicates that the rotation about the C–N bond is very slow at room temperature. The assignment of the spectra has been described previously.¹⁰⁾ The spectra have been analyzed on the basis of an ABC system, employing the Castellano-Waugh method.¹¹⁾ Details of the method of spectrum analysis have been described elsewhere.¹²⁾

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7) B. Sunners, L. H. Piette, and W. G. Schneider, *Can. J. Chem.*, **38,** 681 (1960).

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10) H. Kamei, This Bulletin, **38,** 1212 (1965).

11) S. Castellano and J. S. Waugh, *J. Chem. Phys.*, **34,** 295 (1961).

12) M. Shibuya, H. Kamei, and T. Yonemoto, *Shizuoka-daigaku Denshikogaku-kenkyujo Kenkyuhokoku (Bull. Research Institute of Electronics, Shizuoka Univ.)*, **1,** 131 (1966).

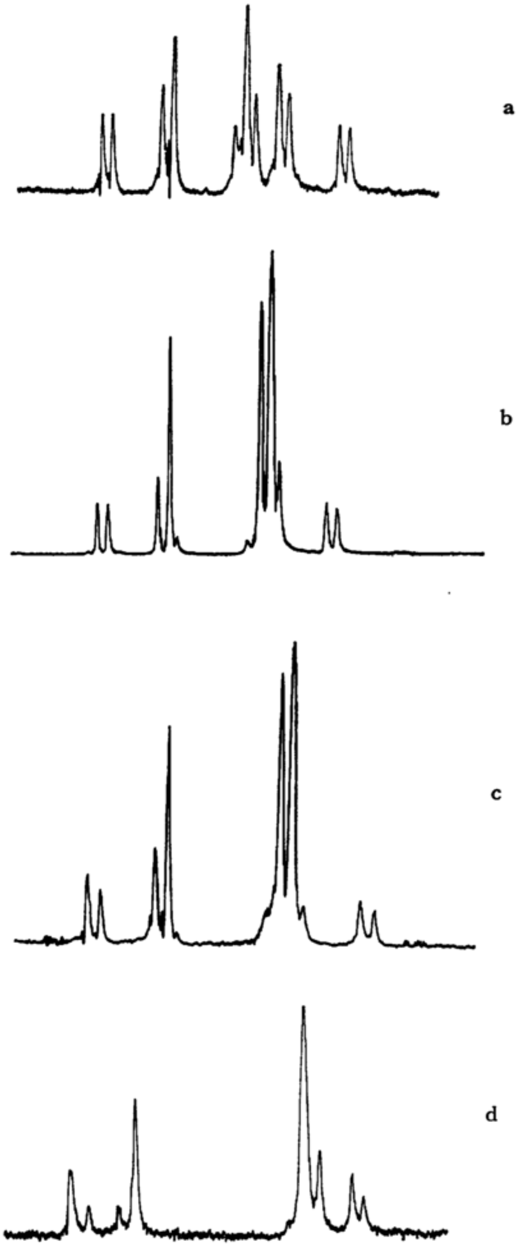

Fig. 3. $^{14}N$ decoupled proton spectra of formamide a) in the neat liquid, and in the solutions with b) water, c) acetone, and d) dioxane at 27°C.

Table 1. NMR Parameters (in Hz) of ABC type spectrum of formamide at 27°C

| Solvent | Neat | Water | Acetone | Dioxane |
|---|---|---|---|---|
| Concentration mol% | 100 | 22.8 | 22.2 | 24.6 |
| $\delta_1$ | $-266.8$*1 | $-264.7$*1 | $-266.4$*2 | $-262.7$*2 |
| $\delta_2$ | $-232.1$*1 | $-228.9$*1 | $-221.5$*2 | $-215.8$*2 |
| $\delta_3$ | $-239.9$*1 | $-242.2$*1 | $-229.4$*2 | $-219.3$*2 |
| $J_{12}$ | ±13.6 | ±13.8 | ±13.5 | ±13.5 |
| $J_{13}$ | ±2.0 | ±2.2 | ±1.7 | ±1.4 |
| $J_{23}$ | ±2.4 | ±2.2 | ±2.7 | ±2.7 |

*1 Relative to cyclohexane as external reference and corrected for bulk diamagnetic susceptibility, $\chi_v$. The values of $\chi_v(\times 10^6)$ for formamide, water, and cyclohexane at 27°C are taken to be $-0.549$, $-0.717$, and $-0.626$, respectively.

*2 Relative to cyclohexane as internal reference.

The chemical shifts and coupling constants are given in Table 1. All the coupling constants have the same sign. The same results have been obtained for formamide-$^{15}N$ by Bourn and Randall using a proton-proton double-resonance technqiue.[13]

A solvent effect on the chemical shift and the coupling constant is observed. This may arise from the different natures of the hydrogen-bond interactions in the different systems. Amine protons engage in the intermolecular hydrogen bond and the chemical shift is strongly dependent on the nature of the interactions with the solvent. No remarkable solvent dependence is found in the chemical shift of the formayl proton.

The coupling constant also shows a solvent dependence. This indicates that the molecular geometry or the electronic structure is affected by the intermolecular interactions.

**Temperature Effects on the Spectrum.** The spectra of formamide in the neat liquid at several temperatures are shown in Fig. 4. On raising the temperature, the rate of the hindered internal rotation about the C–N bond is increased,

Table 2. NMR parameters (in Hz) of $AB_2$ type spectrum of formamide at higher temperatures

| Solvent | Neat | Water | Dioxane |
|---|---|---|---|
| Concentration mol% | 100 | 22.8 | 24.6 |
| Temperature °C | 102 | 93 | 101 |
| $\delta_1$ | $-268.2$*1 | $-265.3$*1 | $-263.8$*2 |
| $\delta_{2,3}$ | $-221.0$*1 | $-221.1$*1 | $-198.6$*2 |
| $J$ | 7.5 | 7.5 | 7.3 |
| $\bar{\delta}$*3 | $-236.0$ | $-235.5$ | $-217.3$ |
| $\bar{J}$*3 | 7.8 | 8.0 | 7.5 |

*1 Relative to cyclohexane as external reference and corrected for bulk diamagnetic susceptibility, $\chi_v$. The values of $\chi_v(\times 10^6)$ for formamide (93°C), formamide (102°C), water (93°C), cyclohexane (93°C), and cyclohexane (102°C) are taken to be $-0.522$, $-0.519$, $-0.694$, $-0.572$, and $-0.564$, respectively.

*2 Relative to cyclohexane as internal reference.

*3 $\bar{\delta}=(\delta_2^{27}+\delta_3^{27})/2$ and $\bar{J}=(J_{12}^{27}+J_{13}^{27})/2$.

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[13] A. J. R. Bourn and E. W. Randall, *Mol. Phys.*, **8**, 567 (1964).

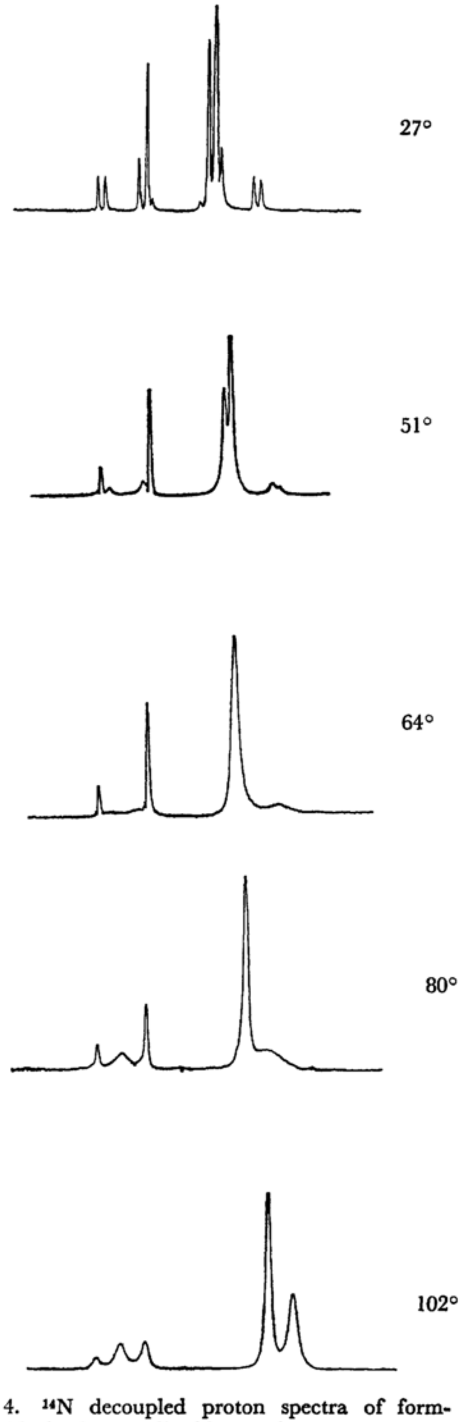

Fig. 4. $^{14}$N decoupled proton spectra of formamide in the neat liquid at various temperatures.

and the spectrum is changed. At higher temperatures the rate of rotation becomes very rapid, so the amine protons are indistinguishable one from the other and the spectrum changes to an $AB_2$-type pattern. The coupling constants and the chemical shifts of the $AB_2$-type spectrum are given in Table 2, along with the average chemical shifts and the coupling constants at 27°C, $\bar{\delta}=(\delta_2^{27}+\delta_3^{27})/2$ and $\bar{J}=(J_{12}^{27}+J_{13}^{27})/2$. The signal of the amine protons is progressively shifted toward higher field with the increase in the temperature. This higher-field shift can be attributed to the increasing dissociation of the hydrogen bond involving these protons.

**Hindered Internal Rotation and Intermolecular Proton Exchange.** The signal shapes are influenced not only by the hindered internal rotation, but also by the intermolecular proton exchange involving the amine protons. As the temperature is raised, the rate of these rate processes increases and the lines broaden and coalesce. It is not possible to obtain the information concerning the hindered internal rotation separately from the information concerning changes in the signal of the amine protons. Although the formyl proton does not participate in the rate processes, its signal is affected by the rate processes through the spin-spin interaction. To the first-order approximation, the two outer lines of the $H_{(1)}$ quartet are unaffected by the internal rotation, and the line width and the separation between the two lines are not altered. Since the intermolecular proton exchange influences all the lines in the spectrum, the broadening of the two outer lines is attributable to the intermolecular proton exchange. The two inner lines broaden and ultimately coalesce. Changes in the separation between the two outer lines have not been observed up to 80°C.

The mean lifetime, $2\tau$, of the intermolecular proton exchange was evaluated from the broadening of the two outer lines in the $H_{(1)}$ quartet by employing the following relation:[14]

$$1/2\tau = \pi(\Delta'-\Delta) \qquad (1)$$

where $\Delta'$ (in Hz) is taken as the half-line width of the broadened line and where $\Delta$ is the line width in the absence of exchange. From 15°C to 30°C, changes in the line width have been lost in the experimental error. At lower temperatures a line broadening has been observed; this may arise from the increase in the viscosity of the sample. The line width at 27°C has been used as $\Delta$. The values of the activation energy, $E_a{}^{ex}$, for the intermolecular proton exchange have been obtained from the plots of log $1/2\,\tau$ *vs.* $1/T$; the results are shown in Table 3. The value for the neat liquid is in good agreement with the value of $10\pm3$ kcal/mol reported by Sunners *et al.*[7] for formamide-$^{15}$N at higher temperatures, where internal rotation is already rapid.

In view of the above facts, it is possible to deal with the $H_{(1)}$ quartet by means of the approximation presented above.

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14) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y. (1959), p. 218.

TABLE 3. ACTIVATION ENERGY AND FREQUENCY FACTOR*

| Solvent | Neat | Water | Acetone | Dioxane |
|---|---|---|---|---|
| Concentration mol% | 100 | 22.8 | 22.2 | 24.6 |
| $E_a^{rot}$ (kcal/mol) | 18.9±1.0 | 21.3±1.3 | 16.9±1.9 | 16.8±1.0 |
| log $A^{rot}$ | 12.9±0.6 | 14.9±1.3 | 12.1±1.3 | 11.9±0.7 |
| $E_a^{ex}$ (kcal/mol) | 12.1±2.5 | 14.5±5.5 | | 11.7±1.3 |
| log $A^{ex}$ | 7.6±1.5 | 9.3±3.5 | | 7.1±0.8 |

* The errors quoted are 95% confidence limits.

At a given temperature the mean lifetime, $2\tau$, of the protons at the $H_{(2)}$ and $H_{(3)}$ positions was evaluated from the relation (1) (at lower temperatures) and the following relation[14] (at higher temperatures):

$$1/2\tau = \pi(\delta\nu)^2/2(\Delta'-\Delta) \qquad (2)$$

where $\delta\nu$ (in Hz) is the separation between two inner lines in the absence of rotation. The values of $E_a{}^{rot}$ were obtained from the plots of log $1/2\,\tau$ *vs.* $1/T$. The results are given in Table 3, with the frequency factors.

The observed changes in $E_a{}^{rot}$ with the solvent may be associated with the effects of the solvent on the partial double-bond character in the C–N bond. The predominant effect is a hydrogen-bonding effect. The hydrogen-bond formation on the carbonyl oxygen in the formamide molecule tends to favor the contribution of the II resonance form, and it increases the double bond character in the C–N bond. In acetone and dioxane solutions, the amine protons may be strongly bonded to the oxygen atoms in the acetone or dioxane molecule, while the carbonyl oxygen in the formamide molecule is left relatively free. Thus, the double-bond character in the C–N bond decreases and the activation energy is lowered compared to that in the neat liquid. In a water solution, the hydrogen bond between formamide and water is stronger than that of amide with itself, and a higher activation energy is found.