Double Resonance Proton Spectra of Amides

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Several groups of workers have used a double resonance technique in NMR spectroscopy to eliminate the effect of the ^{14}N nucleus, which causes quadrupole broadening of the resonance signals from amide protons.[1,2] The structure of the amine proton spectrum, however, has not been completely resolved and a full analysis of the spectrum could not be performed. This presumably can be attributed to incomplete decoupling of the ^{14}N nucleus from the protons. The completely decoupled spectra of formamide (pure, in water, and in acetone solution), acetamide (in water solution), and *N*-methyl acetamide, have now been observed and are analyzed in this work.

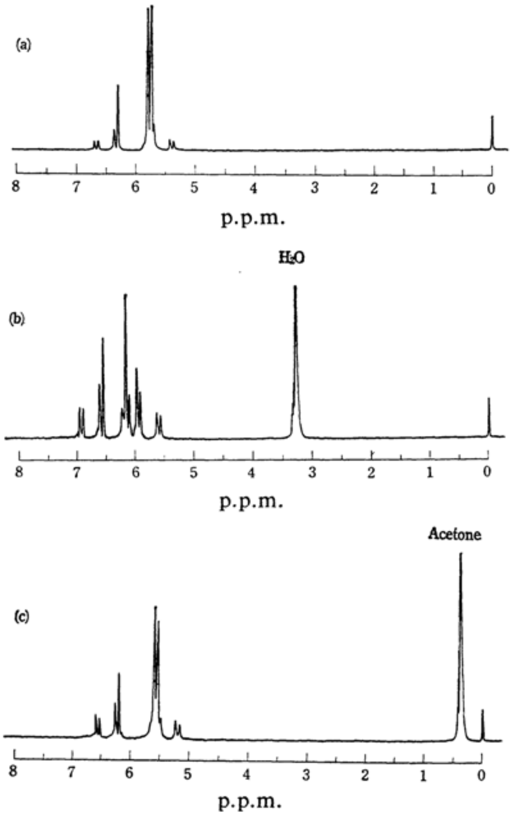
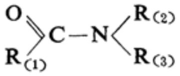


Fig. 1. Proton resonance spectra of ^{14}N decoupled formamide measured relative to cyclo hexane as external reference at 40 Mc./s. (a) pure liquid, (b) 18 mol.% in water, (c) 48 mol.% in acetone. The solvent resonances were recorded at lower amplifications.

Proton resonance spectra were recorded at 40 Mc./s. using a JEOL JNM-3 spectrometer equipped with a double resonance system.[3] The groups in the various amides are labeled as follows:



The decoupled spectra of formamide in different conditions are shown in Fig. 1. The signal due to the formyl proton, $H_{(1)}$, appears as a quartet at low field. In the spectrum of the neat liquid, the signal due to the amine protons, $H_{(2)}$ and $H_{(3)}$, contains six lines, whereas with the same sample in aqueous solution, the $H_{(3)}$ signal shifts to lower field and appears as a triplet, as shown in Fig. 1(b). In the case of the pure liquid, therefore, the $H_{(2)}$ signal

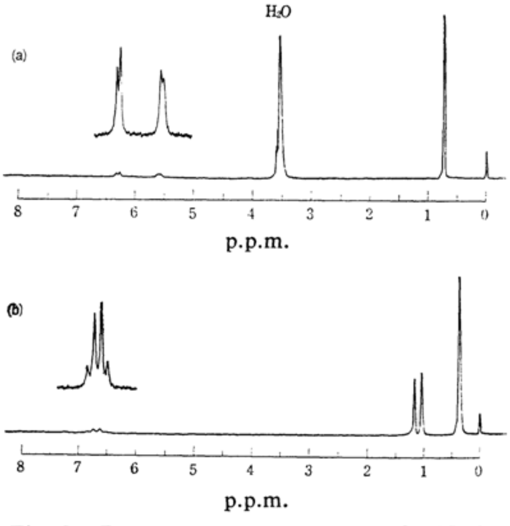


Fig. 2. Proton resonance spectra of ^{14}N decoupled (a) acetamide in 13 mol.% aqueous solution relative to external cyclohexane reference, and (b) *N*-methyl acetamide relative to internal cyclohexane reference at 40 Mc./s. The water resonance was recorded at a lower gain.

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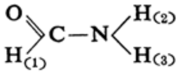
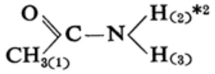
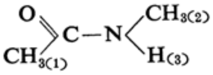
[1] L. H. Piette, J. D. Ray and R. A. Ogg, *J. Mol. Spectroscopy*, **2**, 66 (1958).

[2] E. W. Randall and J. D. Baldeschwieler, ibid., **8**, 365 (1962).

[3] H. Kamei, *Bull. Electrotechnical Lab.*, **28**, 591 (1964) H. Kamei, *Japanese J. Appl. Phys.*, **4**, 212 (1965).

TABLE I. CHEMICAL SHIFTS (in p.p.m., relative to cyclohexane)*1 AND COUPLING CONSTANTS (in c./s.) OF SOME AMIDES

	 $\mathrm{O{=}C(H_{(1)})-N(H_{(2)})(H_{(3)})}$	18 mol.% $HCONH_2$ in water	48 mol.% $HCONH_2$ in acetone	 $\mathrm{O{=}C(CH_{3(1)})-N(H_{(2)})(H_{(3)})}$*2	 $\mathrm{O{=}C(CH_{3(1)})-N(CH_{3(2)})(H_{(3)})}$
δ_1	−6.71	−6.63	−6.70	−0.61	−0.55*3
δ_2	−5.78	−5.70	−5.67	−5.36	−1.29*3
δ_3	−6.01	−6.05	−5.90	−6.14	−6.74*3
J_{12}	13.4	13.4	13.8		
J_{13}	2.2	2.1	2.0		
J_{23}	2.4	2.2	2.5	2.4	4.7

*1 Corrected for bulk diamagnetic susceptibility, χ_v. The values of $\chi_v(\times 10^6)$ for formamide, acetamide, water, acetone, and cyclohexane are taken to be −0.551, −0.618, −0.721, −0.460, and −0.631, respectively (Fujiwara et al., "Kōbunkainō Kakujikikyōmei, Kagaku eno Ōyō," Maruzen, Tokyo (1962); Hodgman et al., "Handbook of Chemistry and Physics," The Chemical Rubber Publishing, Cleveland (1963)).

*2 In 13 mol.% aqueous solution.

*3 Relative to cyclohexane as internal reference.

apparently consists of a quartet whose line at lowest field overlaps the highest field component of the $H_{(3)}$ triplet. The assignment of the lines is indicated in Fig. 1. Analysis of the spectra has been carried out on the basis of an ABX system and the estimated values of the chemical shifts and the coupling constants are shown in Table I. The values of these NMR parameters are in good agreement with those obtained for ^{15}N-substituted formamide.[4] The variation in the chemical shifts and the coupling constants which occurs with change of solvent, may arise from the different natures of the hydrogen bonding interactions in the three systems.

Figure 2(a) shows the spectrum of acetamide in 13 mol.% aqueous solution, and Fig. 2(b) shows the spectrum of *N*-methyl acetamide at 30°C. The signal of the amine protons of acetamide appears as an AB type quartet which must be due to nonequivalence of the two protons, $H_{(2)}$ and $H_{(3)}$. By analogy with formamide the low-field doublet is assigned to the proton, $H_{(3)}$, which is in the cis position relative to the methyl group. Broadening of the line width may be caused by spin coupling with the protons of the methyl group. The amine proton of *N*-methyl acetamide appears as a quartet due to spin coupling with the *N*-methyl protons. The results of the analysis of the spectra are shown in Table I. The internal chemical shift between $R_{(1)}$ and $R_{(3)}$, δ_{13}, in *N*-methyl acetamide is 0.66 p.p.m. greater than that observed in the case of acetamide. Substitution of an *N*-methyl group in formamide was observed to cause δ_{13} to decrease by 0.48 p.p.m.

The ^{14}N resonance frequency for the amides considered above has been found to be 2889500 ±25 c./s.

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