Nuclear Magnetic Resonance Study of Acetaldehyde Aqueous Solution

By Yuzuru FUJIWARA and Shizuo FUJIWARA

(Received December 28, 1962)

Acetaldehyde in aqueous solution has been the subject of spectroscopic and calorimetric investigations in regards to the equilibrium with hydrated molecules.

$$CH_3CHO + H_2O \rightleftarrows CH_3CH(OH)_2 \qquad (1)$$

In spectroscopic studies, the absorption band due to C=O double bond is the measure of concentration of aldehyde and its disappearance by formation of hydrated molecules has been investigated. Nuclear magnetic resonance (NMR) technique has the merit to measure all kinds of protons in both sides of Eq. 1 and enables us to investigate it more precisely than the spectroscopic method. From the view point of NMR, acetaldehyde shows characteristic features, for instance, aldehyde hydrogen gives the NMR signal in a very low field, and the spin coupling constant between methyl and aldehyde hydrogens is very small. These features of NMR spectra may be interpreted in correlation with the chemical activity of aldehyde hydrogen. Since NMR data such as chemical shift, spin coupling constant, and relaxation time can be interpreted in terms of electronic and structural configurations, and of motion of molecules, we planned to make an NMR investigation of acetaldehyde in aqueous solution.

Experimental

NMR spectra were obtained at 56.445 Mc./sec., using a Varian Associates spectrometer. Chemical shifts were measured by the side band method from the methyl proton signal of free acetaldehyde. Concentrations of various species of hydrogen were measured as the areas of the spectra obtained. This was actually practised by setting the condition that line width was so large that the transverse

---

1) R. P. Bell and J. C. Clunie, *Trans. Faraday Soc.*, **48**, 439 (1952); R. P. Bell and B. B. Darwent, ibid., **46**, 34 (1950).

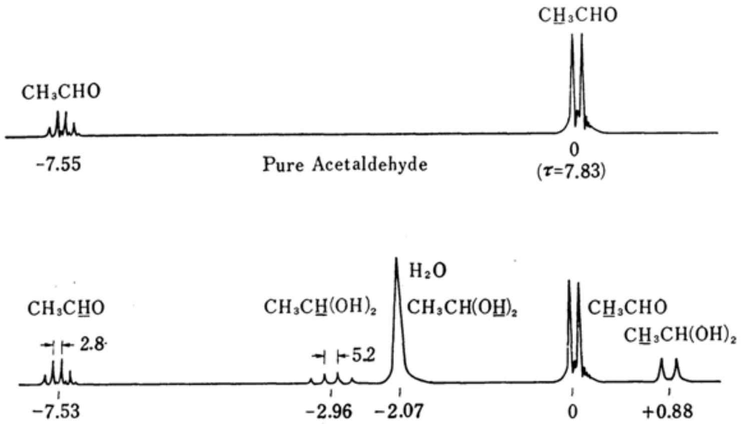
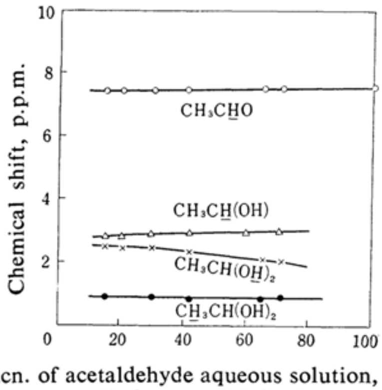


Fig. 1. NMR Spectra of acetaldehyde 42 mol. % aqueous solution.

relaxation times, T_2's, were predominated by the inhomogeneity of the external magnetic field. This method to determine the concentration is helpful to avoid the change of concentration on sealing the sample in the tubes, since acetaldehyde with boiling point 20.8°C volatilizes easily at room temperature. Acetaldehyde was prepared by the decomposition of commercial paraaldehyde using sulfuric acid as catalyst and was redistilled.

Results and Discussion

NMR spectra of acetaldehyde are shown in Fig. 1. Each component of the spectra is easily assigned unambiguously as shown in Fig. 1 with the consideration of the line shape and the intensity[3]. The hydrogens of water and OH radicals of hydrated aldehyde form a single broad line, and its position depends upon concentration (cf. Fig. 2). The width of this line increases as the temperature is lowered or as the concentration of acetaldehyde is increased. This suggests the existence of proton exchange between water and hydrated aldehyde and that of the rate of exchange is rather rapid. The magnitudes of chemical shift and spin-spin coupling constant, J, of all components except water coincide well with those in the literatures[2,3].



Reference CH_3CHO.
Fig. 2.

The methyl proton signal for the hydrated molecule shows smaller value of chemical

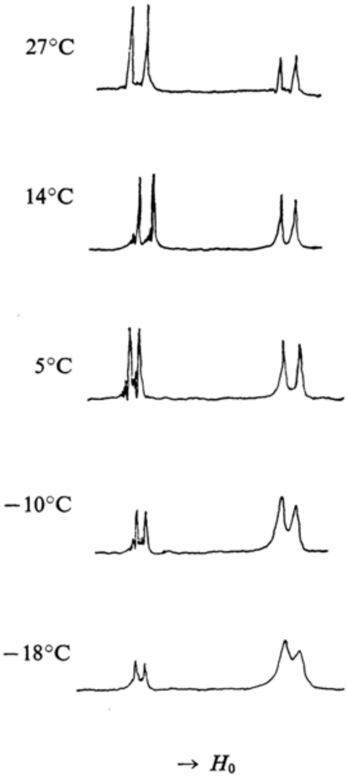


Fig. 3. Acetaldehyde 30 mol. % aqueous solution.

---

[2] G. V. D. Tiers, Private communication "Characteristic NMR Shielding Values for Hydrogen Organic Structures" (1958).

[3] E. Lombardi and P. B. Sogo, *J. Chem. Phys.* **32**, 635 (1960); M. Matsushima. Abstructs of the 15th Annual Meeting of The Chemical Society of Japan (1961).

shift and a larger coupling constant as compared with that for the free molecule. Moreover, the difference between the two J's as well as that between the two shift is conspicuous; $J=5.2$ and 2.8 c. p. s. and $\delta=2.96$ and 7.53 p. p. m. for hydrated and free molecules, respectively. Resonance positions of all hydrogens other than that in OH are almost constant and independent of the concentration. The spectra are temperature dependent as shown in Fig. 3. The line width of hydrated acetaldehyde increases as the solution becomes viscous in a lower temperature range, while that of free molecules does not vary so much. The intensity of the latter is much reduced at lower temperatures as the result of drift of the chemical equilibrium. Saturation curves for methyl protons in both hydrated and free molecules at two temperatures, 27°C and −14°C, are shown in Figs. 4 and 5, respectively. As seen in Fig. 4, the behaviors of the two lines are almost the same for both species of molecules at 27°C, whereas very different from each other at −14°C. In Table I, the relative relaxation times are shown, where T_1 for free molecule at room temperature was taken as unit. The T_1's obtained from saturation curves with the assumption that T_1 is equal to T_2, coincide fairly well with the T_2's which were obtained from the line width. Small discrepancies between the two sets of relaxation times may have been caused by the neglect of field inhomogeneity. T_1 diffrence between the two kinds of molecules at −14°C is due to the difference in correlation times for the Brownian motion of molecules. It is interesting that the correlation times are different between the free and the hydrated acetaldehyde molecules, namely, the molecules of similar size in homogeneous medium of liquid. T_1's of free molecules are almost equal to each other at 27°C and at −14°C inspite of a large difference in viscosity of the solution. This fact suggests that translational motion of the molecule does not effectively contribute to relaxation. On the other hand, T_1 of the hydrated molecule is much smaller than that of free molecule at the lower temperature and this may be attributed to the difference of rotational motions, since hydrated molecules are strongly hydrogen-bonded with surrounding water, receiving hindrance in both translational and rotational motions, whereas unhydrated ones are comparatively speaking, free and rotational motion remains. Measurements of T_1 values in two different temperature ranges made it possible to calculate the apparent activation energy as 7.1 and 1.3 kcal./mol. for the rotational motions of hydrated and unhydrated molecules, respectively. The strength of the hydrogen bond ranges around 5 kcal./mol. for water or ethanol. The fact that the value obtained here (3.5 kcal./mol.) is a little smaller than this value may be due to its structure which has two adjacent OH's, unfavorable to form hydrogen bonds.

TABLE I. RELATIVE RELAXATION TIME

Temp., °C		CH_3CHO	$CH_3CH(OH)_2$
27	T_1/T_{20}	$\bar{1}.00$	$\bar{0}.771$
	T_1/T_{10}	1.0	0.91
−14	T_1/T_{10}	0.724	0.115
	T_2/T_{10}	0.715	0.22

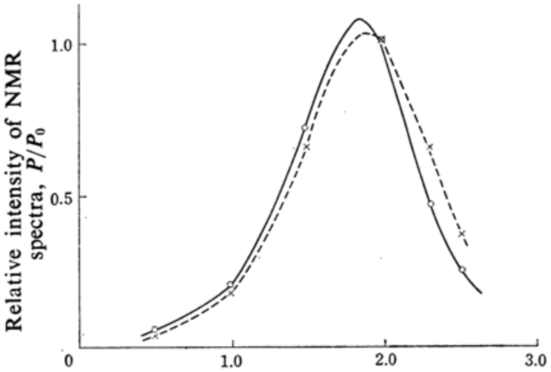


Fig. 4. Saturation carves of CH_3CHO at 27°C.

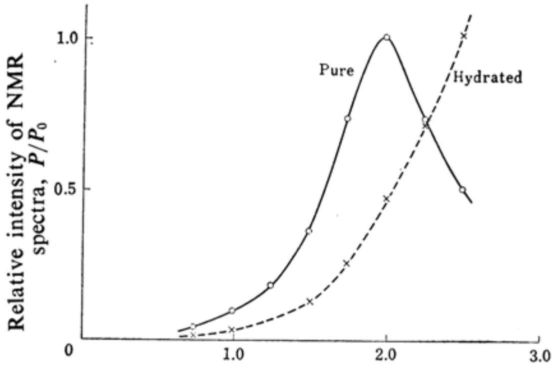


Fig. 5. Saturation curves of CH_3CHO at −14°C.

Configurations of hydrated and free acetaldehyde will be discussed in regard to the large difference of J's. The value of J, 5.2 c. p. s., for the hydrated molecule may be interpreted by simple application of the electronegativity $-J$ rule which was empirically obtained by Glick et al. for isopropyl derivatives[4]. Equation 2 correlates the coupling constants with

---

[4] R. E. Glick and A. A. Bothner-By, *J. Chem. Phys.*, **25**, 362 (1956).

the Huggins' electronegativity scale, E[5], of the substituent, X for $(CH_3)_2CHX$.

$$J(\text{c. p. s.})=8.0-0.55\times E \qquad (2)$$

If we modify this relation to replace the methyl radical in isopropyl by OH, Eq. 2 leads to 5.6 c. p. s. as J value for hydrated acetaldehyde, which is a fairly good approximation. This result suggests that the electron density around protons is reduced by this replacement. Provided that this substitution only affects the electron density in such a way that it is reduced homogeneously throughout the molecule, the electron density of aldehyde hydrogen is reduced by 16% from that of propane, by using Karplus calculation of J by the valence bond method[6] and by comparing the J, 5.2 c. p. s. with the J for propane which has been reported as 7.26 c. p. s.[7] If we assume that the electron densities around C–H protons in pure and hydrated molecules are mainly determined by the polarization of C–O bonds, then the electron densities of C–H protons should be very different between the two molecules, since J's are different. Pure aldehyde has one C=O bond and the hydrated molecule has two C–OH bonds. The ionicity of C–O single bond has been reported as about 22%[8] and that of C=O double bond of acetaldehyde as 47%[9] by the measurement of the electric dipole moment[10]. In so far as the polarization is concerned the aldehyde hydrogen can not make any sizable difference between the two molecules. This result contradicts the observed difference of J's for pure and hydrated acetaldehyde, since Glick's rule stands for linear relationship between J and electron density which is determined by the electronegativity of the substituent. The observed difference may be attributed partly to that of hybridization of carbon orbitals; sp^3 and sp^2 structures for hydrated and pure aldehyde, respectively. Comparing propane ($J=7.26$) with propylene ($J=6.4$)[7] the orbital effect can be estimated and the expected value for pure acetaldehyde should be 4.6 c. p. s. which is still larger than the experimental value of 2.8 c. p. s. In order to analyze the results more precisely, further investigations would be necessary for many other factors such as difference of excitation energy, bond length[11], and angle[11,12], and electronic configurations. The low value of aldehyde-hydrogen shift could be interpreted in terms of (1) the effect of electric field due to the dipole moment of C=O, (2) the anisotropic magnetic screening of C=O double bond and (3) the reduction of electronic screening associated with the decrease of electron density. The magnetic effect 2 will be of the order of 4.57 p. p. m. which was obtained as the difference between the hydrated and the unhydrated aldehyde. The electronic effect is calculated as 2.8 p. p. m. by using the Lamb's screening constant for hydrogen atom[15] and the electron density obtained from the discussion of J. The electric field effect was estimated to be 4.4 p. p. m. comparing the shifts of ethane and acetaldehyde[2]. The sum of these effects is 11.77 p. p. m. which is reasonable and proves that the above estimations are correct.

The equilibrium constant K for 1, defined as

$$K=(H)/(A-H)(W-H)$$

where W, A and H refer to concentrations of water, free, and hydrated acetaldehyde, respectively. K is plotted against the concentration of acetaldehyde in Fig. 6. The equilibrium constant decreases with the increase of concentration. This may be attributed partly to the experimental error in the measurements of concentration where we neglected effects of relaxation times and activities. For dilute solutions, however, the errors mentioned above are small and K approaches to 0.021 l./mol. This value coincides well with the UV and NMR results by other authors[1,3]. The temperature dependence of the equilibrium constant is also shown in Fig. 7 and the heat of hydration was calculeted as 4.9 kcal./mol., which also agrees well with the data already reported[1], within the experimental errors.

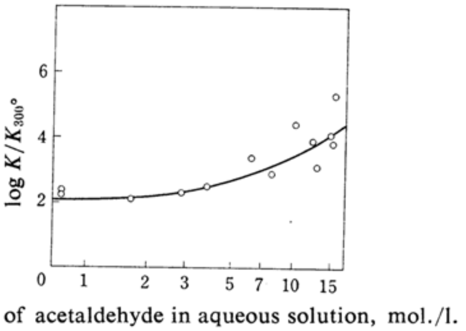


Fig. 6.

---

5) M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123 (1953).

6) M. Karplus, *J. Chem., Phys.*, **30**, 11 (1959).

7) D. R. Whitman, ibid., **32**, 67 (1960).

8) C. A. Coulson, "Valence", Oxford Univ. Press, (1951).

9) L. Pauling, "The Nature of Chemical Bond", Cornell Univ. Press, N. Y. (1940).

10) L. G. Wesson, "Tables of Electric Dipole Moments", The Technology Press, M. I. T., Mass. (1948).

11) L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions", The Chem. Soc., London (1958).

12) H. S. Gutowsky, M. Karplus and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959).

13) A. L. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961).

14) S. Fujiwara, N. Nakagawa and H. Shimizu, "High Resolution NMR", Maruzen, Tokyo (1962).

15) W. E. Lamb, *Phys. Rev.*, **60**, 817 (1941).

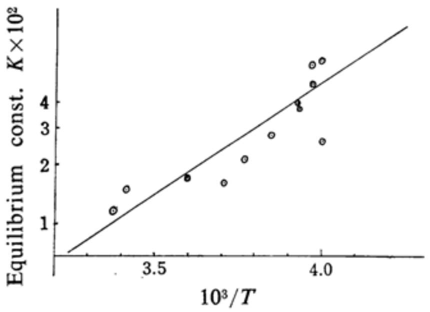


Fig. 7. Temperature dependence of the equilibrium constants.

Conclusion

In aqueous solution of acetaldehyde the hydrated and unhydrated molecules have different relaxation times, since the interaction with the solvent, mainly the formation of hydrogen bonding, is different. Relaxation is dominated mainly by rotational motion of the molecule. The hydrogen bond between the hydrated acetaldehyde and water has the energy about 3.6 kcal./mol. and these hydrogens exchange with each other rapidly.

Small J of acetaldehyde may be attributed to the smallness of electron density around protons and also to the bond angle, the bond length, and the cxcitation energy. The NMR signal of aldehyde hydrogen locates in a low field because of the electron density, the anisotropic magnetic screening of the C=O and the electric field produced by the dipole moment of the C=O and these effects were estimated to be 2.8, 4.6 and 4.4 p. p. m., respectively.

The equilibrim constant and the heat of hydration are determined by the NMR method more accurately than by other conventional methods and the obtained values are in good agreement with the values in the literatures.

The authors thank Mr. Naohiro Hayakawa of the Japan Atomic Energy Research Institute for the help to obtain the NMR spectra. They are grateful to Dr. Hiroshi Shimizu of Chiba University for valuable discussions.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo