An NMR Study of Acetaldehyde Methanol Solutions

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Aqueous solutions of acetaldehyde have been investigated utilizing the technique of nuclear magnetic resonance (NMR). The heat of hydration, the equiliblium constants, the chemical shifts, the spin-spin coupling constants, the relative relaxation times and the activation energies for Brownian motions of the molecules have been determined. The probable electronic structures and proton exchange between water and hydrated acetaldehyde have been discussed.[1]

NMR posseses a considerable advantage for the investigation of the states of such chemically unstable substances as hemiacetal, which forms when acetaldehyde and methanol are mixed. Hemiacetal is difficult to detect by means of other than NMR.

In the present investigation solutions of methanol and acetaldehyde were compared with solutions of water and acetaldehyde. Where no catalyst is used, the rates of the formation of hemiacetal and acetal are so low that measurement of the equilibrium constants for the systems of aldehyde-hemiacetal and aldehyde-acetal are precluded, while the rates of formation are measurable.

Experimental

NMR spectra were obtained at 60 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 determined by measuring the area under the curves with consideration of the power saturation. Acetaldehyde was prepared by the decomposition of commercial para-aldehyde, using sulfuric acid as a catalyst, and by redistillation.

Results and Discussion

It is well known that acetaldehyde and methanol react as follows:

$$CH_3CHO + CH_3OH \rightarrow CH_3CH(OH)(OCH_3)$$

$$CH_3CH(OH)(OCH_3) + CH_3OH \rightarrow CH_3CH(OCH_3)_2 + H_2O$$

The NMR spectra of these solutions are shown in Fig. 1, where the signals for all species of hydrogen appear at separate positions and are unambiguously assigned to their respective curves through such NMR features as fine structure, chemical shift, line width, the concentration dependence of the line intensity, and a comparison of these spectra with the spectra of pure and aqueous solution of dimethylacetal. Three kinds of methoxy methyl hydrogen appear separately in acetal, hemiacetal, and methanol, and three kinds of methyl hydrogen also appear separately in acetal, hemiacetal and acetaldehyde. These phenomena can be explained in terms of the electron density and the long-range magnetic shielding of the C–C and C–O bonds. The anisotropic magnetic effect of C=O on the shift of the methine proton is estimated to be 5.0 p.p.m. on the basis of the difference between the shift of free and that of solvated acetaldehyde; this is not so different from the value of 4.6 p.p.m. obtained from an aqueous solution of acetaldehyde.[1]

Three kinds of OH hydrogen in water, methanol and hemiacetal form a single broad line in a 60 mol. % solution; its position depends on the concentration (cf. Fig. 2). This suggests a rapid hydrogen exchange, the shift corresponding to the variation of the concentration of each component. In a 10 mol. % solution, these OH hydrogens are separated and have different line widths, i. e., 5.8 c. p. s. for water, 5.3 c. p. s. for hemiacetal, and 6.8 c. p. s. for methanol. If we assume that exchanges are slow[2] and that the ratios

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[1] Y. Fujiwara and S. Fujiwara, This Bulletin, 36, 574 (1963).

[2] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, N. Y. (1958). p, 225.

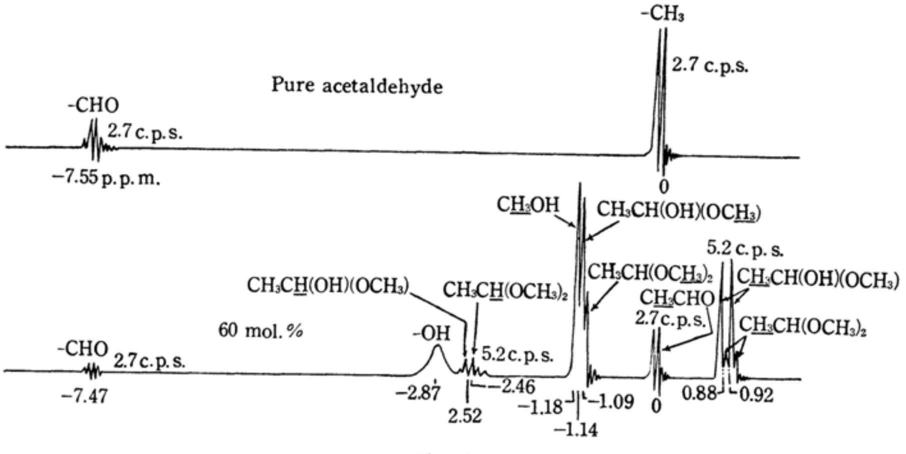

Fig. 1—a

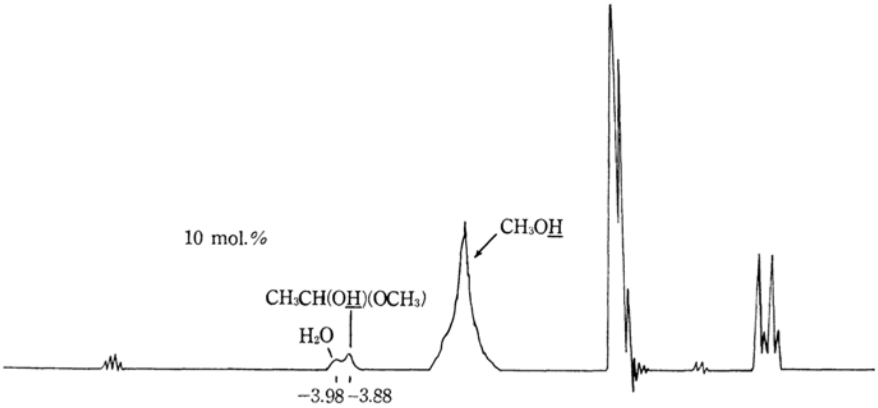

Fig. 1—b NMR spectra of acetaldehyde methanol solution

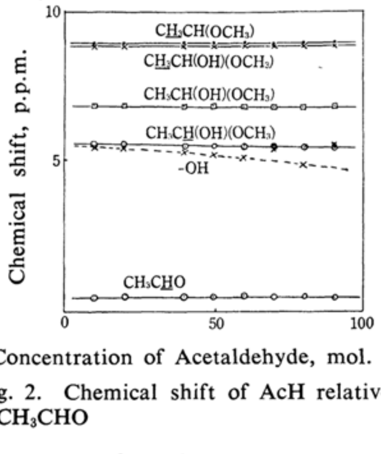

Fig. 2. Chemical shift of AcH relative to CH_3CHO

TABLE I. RATE OE HYDROGEN EXCHANGE

		l./mol./sec.
H_2O	— H_2O	$k_{11}=1.6$
MeOH	— MeOH	$k_{22}=0.58$
$\underset{\text{OMe}}{\text{MeCH(OH)}}$	— $\underset{\text{OMe}}{\text{MeCH(OH)}}$	$k_{33}=0.35$
H_2O	— MeOH	$k_{12}=0.97$
H_2O	— $\underset{\text{OMe}}{\text{MeCH(OH)}}$	$k_{13}=0.76$
MeOH	— $\underset{\text{OMe}}{\text{MeCH(OH)}}$	$k_{23}=0.45$

of the rates of exchange are constant for common species, one may estimate the exchange rates as in Table I. The order of the values in Table I corresponds to the order of the size of molecules and appears reasonable. Moreover, a comparison of these data with the exchange rate for pure water obtained by Meiboom[3] shows that the corresponding value obtained in this laboratory is 0.63 times that of Meiboom. Since his data refer to solutions catalyzed by acid or base, a correction was made to adjust the concentration for this comparison. This can be regarded as a good agreement; the slight discrepancy may be attributed to the role of diffusion due to the different concentration of water. In the present

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[3] S. Meiboom, *J. Chem. Phys.*, **34**, 375 (1961).

case, the diffusion is somewhat a rate determinant. Arnold[4] has also reported a hydrogen exchange rate for pure ethanol which was about one-third of the value obtained in the present investigation for the exchange between methanol and methanol. This difference undoubtedly results from differences in molecular size.

Molecular motion can be investigated by the measurement of relaxation time, since it depends on the correlation time of the Brownian motion of the molecule. In this case the relative relaxation times were measured by the power saturation method (Fig. 3), assuming an extremely narrow case.[5] The results are shown in Table II, where the temperature dependence of relaxation times is also given. From these data, estimation of the activation energies for the molecular motions was made. Hemiacetal has the largest activation energy; this may be attributed to the restricted motion resulting from the hydrogen bonding with other OH's and is consistent with the case of hydrated acetaldehyde. Hydrated acetaldehyde has a larger value than hemiacetal; this may be explained by the greater tendency of hydrated acetaldehyde to undergo hydrogen bonding than hemiacetal. The activation energy for free acetaldehyde in a methanol solution is estimated to be 1.3 kcal./mol., which agrees quite well with that in an aqueous solution (1.27 kcal./mol.). The small temperature dependence of dimethylacetal may be ascribed to its spherical molecular shape, which hinders rotation very little, to the molecular structure, which has no group which can interact strongly with the surrounding molecules, and to the intermolecular motion, which may considerably contribute to the relaxation.

TABLE II. RELATIVE RELAXATION TIMES

Temp.	Relative relaxation time			*E*ac kcal./mol.
	+86°C	+30°C	−16°C	
CH_3CHO	1.3	1.0	0.74	1.3
$CH_3CH\langle^{OH}_{OCH_3}$	1.3	0.91	0.51	2.2
$CH_2CH(OCH_3)_2$	1.1	0.91	1.0	~0

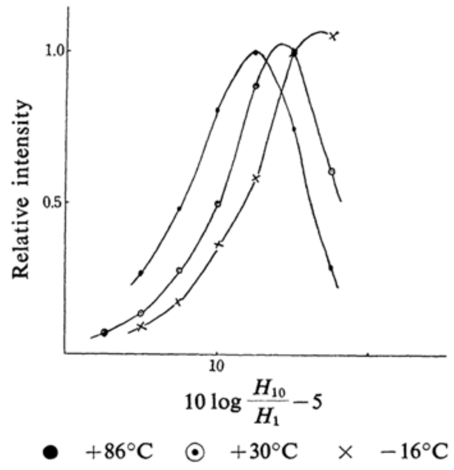
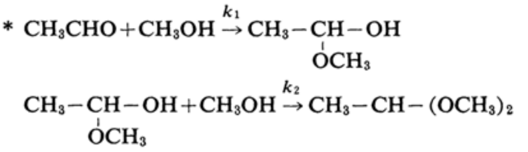


Fig. 3. Power saturation of $CH_3CH(OH)$-(OCH_3)

The formation of hemiacetal and acetal from the mixture of acetaldehyde and methanol is very slow when the system is free from a catalyst such as acid or salt. Nevertheless, measurements of their formation rates were made in the case where no catalyst was added. This was necessary in order to avoid the possible disturbance to the system which might be caused by the catalyst and to ascertain the direct interaction of aldehyde with alcohol. The values in Table III were calculated on the assumption that the reverse reactions are negligible and that the methanol content does not vary appreciably during the reaction. The validity of the first assumption was confirmed by observing that the reaction proceeds more rapidly and more extensively in the presence of a catalyst. That of the second was confirmed by measuring the methanol concentration before and after the reaction, which proceeded for 70 days. The agreement of the values obtained at various concentrations is satisfactory and suggests that the calculation based on the above assumption is correct.

TABLE III. REACTION RATE OF AcH-MeOH

Concn., mol./l. AcH	MeOH	$k_1 \times 10^5$* l./mol./hr.	$k_2 \times 10^5$* l./mol./hr.
14.4	6.2	9.0	1.9
12.8	8.5	8.1	2.4
9.2	13.7	8.1	1.9
4.7	18.1	8.7	0.30
Average		8.5 ± 1	2.1 ± 0.5



$$* \; CH_3CHO + CH_3OH \xrightarrow{k_1} CH_3-\underset{\displaystyle OCH_3}{\underset{|}{CH}}-OH$$

$$CH_3-\underset{\displaystyle OCH_3}{\underset{|}{CH}}-OH + CH_3OH \xrightarrow{k_2} CH_3-CH-(OCH_3)_2$$

Summary

By the NMR method, the methanol solution of acetaldehyde was studied; in this solution all the species of hydrogen of each molecule are measurable, and a kinetic study of the system was readily performed. This could be

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[4] J. T. Arnold, *Phys., Rev.*, 102, 136 (1956).

[5] N. Bloembergen, E. M. Purcell and R. V. Pound, ibid., 73, 672 (1948).

compared with any other conventional methods, by which some of the species usually present in the system are directly measured. The formation rates of hemiacetal and acetal were measured as $(8.5 \pm 1) \times 10^{-5}$ and $(2.1 \pm 0.5) \times 10^{-5}$ l./mol./hr., respectively, in the absence of a catalyzer. The hydrogen exchange rates for three kinds of OH's were also obtained. When compared with the related values in the literature, agreement is satisfactory. The relaxation times show a difference in the molecular motion corresponding to molecular structure and in the interaction with surrounding molecules.

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