

Nuclear Magnetic Resonance Studies of Hydrogen Bonding in Ethanol

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The proton magnetic resonance of ethanol in CCl_4 solution has been studied as a function of concentration over the range pure ethanol (17 M) to 0.03 M. The shift of the OH proton frequency with concentration is interpreted in terms of hydrogen bonding between alcohol molecules, and an equilibrium constant for dimer formation is reported. The OH proton resonance of the ethanol monomer occurs slightly to the high field side of the CH_3 resonance. The value of the characteristic OH resonance frequency of the dimer (deduced from the NMR results and pertinent infrared data) suggests that the dimer is structurally different from higher polymers.

The utility of nuclear magnetic resonance (NMR) in studies of hydrogen bonding (H-bonding) has been demonstrated in several investigations (1-3). The effect of H-bonding in shifting the OH proton resonance frequency was first recognized for ethanol about six years ago (4, 5), but only recently (6) has the NMR spectrum of alcohols been examined in solutions sufficiently dilute to prevent most intermolecular H-bonding. In connection with recent infrared studies of H-bonding in alcohols (7)¹ we have investigated the variation of the proton resonance of ethanol with change of concentration in CCl_4 solution.

EXPERIMENTAL

A Varian V4300B high resolution NMR spectrometer was used, together with associated 12-inch magnet system and super stabilizer. A fixed frequency of 40 Mc/sec and a magnetic field of approximately 9400 gauss were employed. Sample tubes of 5-mm outer diameter (containing about 0.3 ml) were used with

¹ This article contains references to many earlier infrared investigations.

TABLE I
CHEMICAL SHIFT AS A FUNCTION OF ALCOHOL CONCENTRATION*

X	δ	X_n	Δ_b
0	-0.41	1.000	—
0.0027	-0.325 \pm 0.05	0.964	2.44
0.0047	-0.260	0.935	2.35
0.0071	-0.188 \pm 0.05	0.899	2.23
0.0095	-0.013 \pm 0.05	0.861	2.88
0.0134	+0.425	0.785	3.90
0.0174	0.895	0.696	4.30
0.0382	1.905	0.435	4.10
0.072	2.715	0.279	4.34
0.099	2.860	0.213	4.16
0.292	3.573	0.076	4.31
0.518	3.845	0.034	4.41
0.73	4.010	0.027	4.55
0.94	4.135	—	—
1.00	4.155	0	4.57

* X is the mole fraction of alcohol; δ , the chemical shift of the OH proton, referred to the central peak of the ethanol CH_3 triplet; x_n , the fraction of OH protons that are not H-bonded (from the infrared measurements of ref. 7); and Δ_b , the average chemical shift of the H-bonded OH protons. See text for exact definitions of δ and Δ_b .

a sample spinner for all solutions except the most dilute studied, 0.028 M. At this low concentration a tube of 8-mm outer diameter was used without a spinner. The resultant loss of resolution renders the datum from this sample less accurate than the remaining data.

The sideband technique, as described previously (2-4), was used to measure chemical shifts, using as reference the CH_3 proton resonance of ethanol, or the proton resonance of benzene, which was added to the solvent in a concentration of one percent. For each sample the average was taken of three or more measurements of the audiofrequency necessary to cause superposition of a sideband of the reference signal on the main band of the OH proton signal. The accuracy of the measurement should be within ± 0.4 cps, corresponding to 0.01 ppm. In some cases, which are noted in Table I, interference from adjacent CH_3 or CH_2 peaks caused a decrease in accuracy. The sideband technique was not used for the 0.028 M solution; in this case the chemical shift was determined from an average of eight measurements of the OH- CH_3 shift. The known spin-spin splitting of the CH_3 resonance (8) was used as an internal calibration.

Reagent grade ethanol, benzene and carbon tetrachloride were used without purification, except that the CCl_4 was dried by a method described previously (7). The sample tubes were dried just before use by flaming them out on a

vacuum line. Solutions were made up with pipettes or micropipettes. The relative concentrations are known to approximately $\pm 3\%$.

All experiments were conducted at room temperature. The temperature of the sample was estimated to be $27^\circ \pm 3^\circ\text{C}$.

RESULTS

In agreement with work on other H-bonding systems (1-6), we observed only one line that could be attributed to the OH proton. This resonance showed a marked concentration dependence, which is to be expected if the line arises from a rapid exchange of protons between two or more species (free and bonded OH) whose resonance frequencies differ by an amount that is small compared with the rate of exchange (1). The NMR spectrum is shown in Fig. 1. The variation of the resonance with concentration furnishes a means of studying changes in the relative amounts of the different species.

The "chemical shifts" are expressed in terms of the dimensionless function δ , defined in accordance with previous usage (1, 3), as follows:

$$\delta = \frac{H_r - H}{H_r} \times 10^6 = \frac{\nu_r - \nu}{\nu_r} \times 10^6,$$

where H and H_r are the resonance fields for sample and reference, respectively, ν_r is the known resonance frequency of the reference proton (~ 40 Mc/sec) and

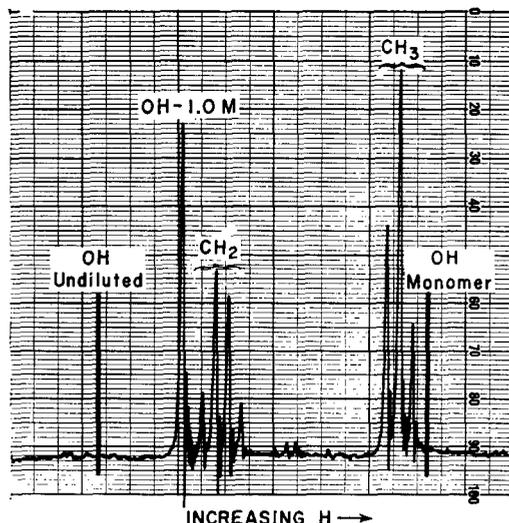


FIG. 1. NMR spectrum of ethanol in CCl_4 . The spectrum shown is for a mole fraction of alcohol $X = 0.01$. The positions of the OH resonance for $X = 1.0$ and $X \sim 0.003$ are indicated by vertical bars.

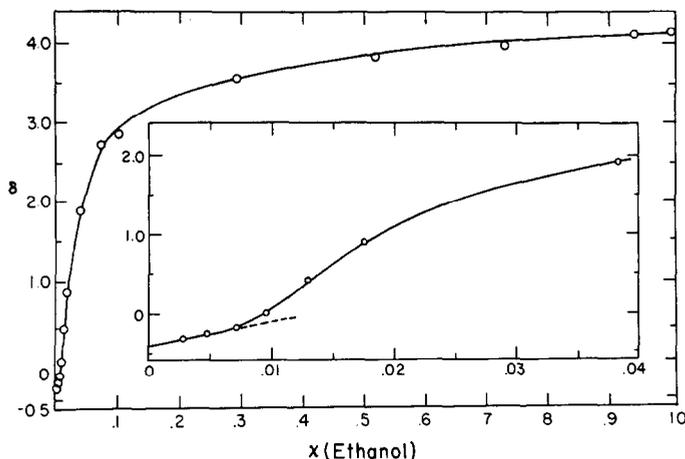


FIG. 2. Chemical shift of the OH proton resonance, δ , vs mole fraction of alcohol, X .

$\nu_r - \nu$ is obtained by the sideband technique. All shifts are referred to the central peak of the CH_3 triplet in ethanol. (The benzene resonance used as reference in some experiments then has a δ of 6.112.) The variation of δ with concentration is shown in Fig. 2, where the composition of the solution is expressed² in terms of mole fraction ethanol, X . A curve of this general shape, including the reversal of curvature at $X \sim 0.015$, is in accord with expectations for a system consisting of monomers, dimers, and higher polymers. The curve was extrapolated to $X = 0$ with the assumption that δ is a linear function of X (as required by the theory discussed later) below $X = 0.005$. The value of δ thus obtained for the infinitely dilute solution, -0.41 , is assumed to be the true δ for the monomer and is designated δ_m .

At high alcohol concentrations ($X \geq 0.94$) the OH resonance is split into a triplet by spin interactions with protons of the CH_2 group. This splitting is not in conflict with the appearance of only one OH resonance frequency, rather than one for each polymeric species present. The spin coupling is believed to arise through an interaction of the nuclei transmitted by the electrons in the intervening covalent bond (9). This OH bond need not be ruptured in order to average the chemical shifts to a single value. Instead, the H-bonds can break and re-form rapidly to accomplish this averaging, leaving any given proton bonded to an oxygen atom long enough to permit observation of the coupling with the adjacent CH_2 group. The slow variation of δ over a rather wide range of concentrations suggests, however, that most of the polymeric species have approximately

² Below $X = 0.1$ the concentration of ethanol in moles/liter is given approximately by $C = 10 X$.

the same value of δ , designated δ_p . We shall use for δ_p the value of δ in undiluted ethanol, 4.155.

A few measurements were made of the CH_2 proton resonance as a function of alcohol concentration. δ for CH_2 varied only from 2.47 at $X = 0.01$ to 2.42 at $X = 1.0$. The small shift may be due to change in the dielectric environment or to a small perturbation in CH_2 electron density caused by the formation of H bonds (10).

DISCUSSION

DIMER ASSOCIATION CONSTANT

A solution of alcohol in a relatively inert solvent such as CCl_4 almost certainly consists of a mixture of several types of H-bonded species, as well as nonbonded monomers. It is reasonable to attempt an interpretation of the NMR data in terms of equilibria between such species. Gutowsky and Saika (1) have shown that when rapid proton exchange occurs among several molecular species the observed δ is the average of the δ 's for each of the species, weighted according to the fraction of the molecules present in each form. This average carries the implicit assumption that the value of δ_m obtained above is independent of concentration. In support of this assumption we can cite the approximate constancy of the proton resonance of the CH_2 group in ethanol, which as we have seen varies only slightly even though subject both to the solvent perturbation as well as an indirect H-bond perturbation.

Huggins, Pimentel, and Shoolery (3) have shown that with these assumptions, plus an assumed δ_d for the dimer which is also concentration independent, the equilibrium constant for dimer formation is related to the limiting slope of the δ vs X plot by the equation

$$(d\delta/dX)_{X=0} = 2K\Delta_d,$$

where $K \equiv x_d/x_m^2$, $\Delta_d \equiv \delta_d - \delta_m$, and x_d , x_m are mole fractions of dimer and monomer, respectively. Δ_d is then independent of the chosen reference. From the data of Fig. 2 we obtain a limiting slope of 31 and a value for K of $15/\Delta_d$. An estimate of the value of Δ_d depends upon the structure of the dimer. Both an open form, with one H-bonded and one free proton, and a cyclic form, with two H-bonded protons, have been suggested (7). Using a similar line of argument to that given in ref. 3 we conclude that a reasonable range for Δ_d is approximately $\frac{1}{4}\Delta_p$ to $\frac{1}{2}\Delta_p$ (1.1-2.3) for an open dimer, and $\frac{1}{2}\Delta_p$ to Δ_p (2.3-4.6) for a cyclic dimer³. ($\Delta_p \equiv \delta_p - \delta_m$). K is thus in the range 10 ± 4 (open dimer) or 5 ± 2 (cyclic dimer) in reasonable agreement with the infrared results (7), 15 ± 3

³ This estimate for Δ_d depends on an assumed linear relation between the NMR H-bond shift, Δ , and the infrared OH stretching frequency H-bond shift (from ref. 7).

(open dimer) or 7.5 ± 1.5 (cyclic dimer). These results are not in agreement with those of Cohen and Reid (6), whose curve of NMR frequency vs concentration shows almost zero limiting slope. They conclude that their data are "consistent with a model in which trimers and tetramers are more stable than dimers. . . ." We have not obtained equilibrium constants for formation of trimers and higher polymers, which would be necessary for a quantitative comparison of dimer and polymer stabilities.

It must be emphasized that the values of K calculated from the NMR data are critically dependent on the limiting slope. The shape of the curve indicates that the inclusion of data at lower concentrations might result in a decrease in the slope but is unlikely to cause any significant increase. Since alcohols have been shown to form weak H-bonded complexes with aromatics (11), we have calculated the effect on the limiting slope of a weak interaction between ethanol and the benzene added as reference. The small amount of benzene present in our solutions can change the limiting slope by only five percent at most. We consider this effect negligible. We have also computed the effect of the possible presence of a small amount of water. Since the CCl_4 was dried by a method that reduces the water content to less than a mole fraction of 0.0001 (ref. 7), we find that the possible error introduced in this way is also negligible in the concentration range of ethanol that we have studied.

The value of Δ_d cannot be far outside the range that we have estimated. In the following section we shall determine Δ_d by another method and further restrict the probable range of K .

Determination of Δ_d . Since there are too many parameters (δ 's for each species and at least two independent equilibrium constants) to be determined from the limited number of NMR data, we have attempted to use some of the information previously obtained by infrared studies (7) to aid in the interpretation of the NMR results. The important quantity to be taken from the infrared work is the value of ϵ_m/ϵ_m^0 at each concentration corresponding to an NMR measurement. [ϵ_m is the apparent absorption coefficient of the monomer OH band at 3635 cm^{-1} , $\epsilon_m \equiv (1/Cd) \log_{10} I_0/I$; and ϵ_m^0 is the true absorption coefficient of the monomer, obtained by extrapolating ϵ_m to zero concentration (7).] If only monomer absorbed at 3635 cm^{-1} , ϵ_m/ϵ_m^0 would be equal to the fraction of alcohol molecules in the monomeric form. However, it has been suggested (7) that nonbonded hydrogen atoms at the end of polymeric chains (or of open dimers) absorb also at this frequency, thus making ϵ_m/ϵ_m^0 greater than the fraction of monomer. Provided that the absorption coefficient of the "end group" hydrogens is the same (or nearly the same) as that of the monomer, namely ϵ_m^0 , then ϵ_m/ϵ_m^0 represents the fraction of OH protons that do *not* participate in H-bonds. We shall assume that this is the case and use the values of ϵ_m/ϵ_m^0 given in Table I as the fraction of nonbonded OH protons, designated x_n . Furthermore, we shall

assume that all of these protons have substantially the same NMR resonance frequency, namely that of the monomer, δ_m .

With these assumptions, we can now calculate from the NMR datum at each concentration an average characteristic resonance frequency for all *bonded* OH protons, δ_b . The observed value of δ is the weighted average of the δ 's for the bonded and nonbonded protons (1),

$$\begin{aligned}\delta &= x_n\delta_m + (1 - x_n)\delta_b \\ &= \delta_m + (1 - x_n)\Delta_b.\end{aligned}$$

Here $\Delta_b \equiv \delta_b - \delta_m$. The values of Δ_b obtained from the measurements of δ by NMR and of x_n by infrared are listed in Table I. It is apparent that Δ_b decreases gradually from 4.57 to ~ 4.2 over the concentration range $X = 1.0$ (undiluted alcohol) to about $X = 0.02$. Below this latter concentration Δ_b drops sharply to the range 2.2–2.4. The calculated values of Δ_b at very low concentrations of ethanol are subject to considerable error because of the uncertainties in the small difference $(1 - x_n)$. Nevertheless, the abrupt change in Δ_b in the region of $X \approx 0.01$ is real and reflects the presence of a considerable fraction of the bonded OH groups in molecules where their characteristic Δ is considerably lower than Δ_p . Since this is the region where infrared studies show that dimers are the predominant bonded species (7), this distinctly different characteristic Δ almost certainly belongs to the dimer. Δ_d is therefore concluded to be about 2.3 for a cyclic dimer. For an open dimer Δ_d would be the average of this value (for the bonded hydrogen) and 0 (for the nonbonded hydrogen), or 1.2. These values are near the lower limit of the possible range previously assumed for Δ_d . With the new values of Δ_d we obtain equilibrium constants for dimer formation of 13 (open dimer) or 6.5 (cyclic dimer).

The relatively constant value obtained for Δ_b above $X \sim 0.02$ indicates that the higher polymers (probably all polymers above dimers) have approximately the same Δ_p for all bonded protons. The slight decrease in Δ_b with decreasing concentration of alcohol might result from the presence of small and varying amounts of dimer, from the failure of the intensity of the infrared band at 3635 cm^{-1} to represent adequately the number of nonbonded protons in polymers, or from a gradual change in Δ_p caused by variation in Δ 's for either the nonbonded or bonded H atoms with polymer size.

With regard to the structure of the dimer—cyclic or open—the NMR data provide equilibrium constants and values of Δ_d consistent with either structure. As in the case of the infrared frequencies (7), however, the observation that the characteristic Δ_d for the bonded H atom (or atoms) in the dimer is considerably different from that found for all higher polymers furnishes a basis for argument that the H-bonds of the dimer are structurally different from those of the higher

polymers. Thus the NMR results are consistent with the conclusion drawn previously (7, 12) that the alcohol dimer is probably cyclic with two nonlinear H-bonds, contrasted with the linear H-bonds expected for higher polymers.

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