On the Hydroxy Proton Multiplicity in the ^{1}H Nuclear Magnetic Resonance Spectra of 2-Chloroethanol in Inert Solvents

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The hydroxy proton multiplicity of 2-chloroethanol has been studied in inert solvents. It has been found that only a singlet is observed in fully dehydrated sample solutions from neat to 0.02M concentration at room temperature. A trace of water present in the sample solutions causes a multiplet structure at lower alcohol concentrations. The singlet can be explained in terms of proton exchange within the associated species of the alcohol as a result of the increased acidity of the hydroxy proton due to chlorine substitution. The triplet is interpreted as the result of the reduction in proton exchange within the associated species caused by water molecules which are incorporated into the associated species of the alcohol.

THE influence of intramolecular hydrogen bonding on the multiplicity of the hydroxy proton has been investigated for 2-chloroethanols.[1] It was concluded that intramolecular hydrogen bonding is responsible for the hydroxy proton multiplicity observed at lower concentrations, while the influence of proton acidity becomes important at higher concentrations as shown by the observation of the broad singlet structure. In this paper, we present experimental results showing that the hydroxy proton multiplet of 2-chloroethanol at lower concentrations is caused by a trace amount of water remaining in the solutions.

EXPERIMENTAL

2-Chloroethanol, carbon tetrachloride, and cyclohexane were all Wako Chemicals guaranteed reagents. Tetramethylsilane (TMS) was purchased from Merck. To obtain fully dehydrated sample solutions, dehydration and purification of the alcohol, the solvents, and TMS, and the preparation of the sample solutions were all carried out carefully in a grease-free vacuum line. The alcohol and solvents, dried over $MgSO_4$, and TMS were put into ampoules on the vacuum line with a small amount of $MgSO_4$, and dried thoroughly by magnetic stirring overnight. The fore-run of the reagents was taken off by vacuum distillation for each preparation. To prepare sample solutions, the alcohol and solvent were condensed into an ampoule by vacuum distillation, to which an i.r. cell and a ^{1}H n.m.r. tube were connected. In addition, volumetric sample preparation was also carried out. Each sample solution thus prepared was submitted to both ^{1}H n.m.r. and i.r. measurements. TMS, condensed into the n.m.r. tube during sample preparation, was used as internal reference. In several cases, to confirm the absence of water in the solutions containing TMS, the alcohol, solvent, and TMS were condensed into the ampoule and then i.r. and n.m.r. measurements were made. The n.m.r. spectra were obtained with a JEOL model 4H-100 100Mc spectrometer. I.r. spectra were obtained with a JASCO model A-3 spectrometer with fused silica cells having 0.5, 2.0, 20, and 100 mm pathlengths. I.r. spectra in the wavenumber region 4 000—2 800 cm^{-1} were utilized to obtain information about alcohol concentrations, the degree of alcohol association, and the presence of water. Alcohol concentrations were determined by using calibration curves constructed for the alkyl part of the alcohol. The absence of water in carbon tetrachloride was confirmed from the i.r. spectra obtained with a 100 mm cell.

RESULTS AND DISCUSSION

The experimental results obtained for 2-chloroethanol in carbon tetrachloride can be summarized as follows. (1) As shown in Table 1, the multiplet for the hydroxy proton depends upon the degree of dehydration of the sample solutions. (2) At room temperature, only a singlet is observed in the sample solutions prepared on the vacuum line, the concentration range being from neat to 0.02M. For our n.m.r. measurements, 0.02M is the lowest concentration used. At this concentration the monomer fraction is found to be *ca.* 0.84 from the OH band of the monomer alcohol in the i.r. spectrum. (3) With an increase in temperature, the singlet observed at the lower concentrations changes to a broad singlet and then to a triplet in the sample solutions prepared in the vacuum line. This is also the case for the sample solutions of lower concentrations prepared volumetrically with freshly distilled reagents. The temperature at which a triplet appears becomes higher as the alcohol concentration increases and at concentrations greater than 0.1M the singlet remains unchanged even at 100 °C. Table 2 illustrates some of these results. (4) A similar change in the multiplicity, *i.e.* from a singlet to a broad singlet and then to a triplet, was produced at 21 ± 0.5 °C by the stepwise addition of water to the sample solutions prepared on the vacuum line (Table 3). (5) The sharp singlet of neat 2-chloroethanol changes to a broad singlet upon addition of water at 21 ± 0.5 °C. (6) The i.r. spectra of the samples in result (4) show an increase in the absorbance of the OH band of the self-associated

TABLE 1

Changes of the hydroxy proton multiplicity [a] of 2-chloroethanol in CCl_4 with the method of sample preparation, at 21 ± 0.5 °C

Method of sample preparation	Concentration of 2-chloroethanol [d] (M) 0.10 (0.782)	0.08 (0.825)	0.06 (0.828)	0.04 (0.833)	0.02 (0.835)
Volumetric I [b]	t	t	t	t	t
Volumetric II [c]	t	t	s	s	s
In a vacuum line	s	s	s	s	s

[a] s = Singlet, t = triplet. [b] 2-Chloroethanol containing 0.1 wt% of water and CCl_4 freshly distilled were used. The water content was determined by the Karl Fischer titration method. [c] Both alcohol and solvent were freshly distilled and used. [d] The values in parentheses are monomer fractions determined from i.r. spectra.

TABLE 2

Changes of the chemical shift [a] (c.s.) and multiplicity [b] of the hydroxy proton of 2-chloroethanol in CCl_4 with an increase in temperature

Concentration of 2-chloroethanol and method of sample preparation

0.042 (M) (In the vacuum line)		0.060 (M) (Volumetric II) [c]		0.11 (M) (In the vacuum line)	
Temp. (°C)	C.s.	Temp. (°)	C.s.	Temp. (°C)	C.s.
23	171.8(s)	26	171.9(s)	23	195.5(s)
52	165.5(bs)	50	161.8(bs)	53	172.9(s)
78	158.1(t)	100	154.7(t)	68	165.7(bs)
				100	168.6(bs)

[a] Chemical shift values are reported as Hz downfield from internal tetramethylsilane. [b] s = Singlet, bs = broad singlet, t = triplet. [c] See Table 1.

TABLE 3

Changes of the chemical shift [a] (c.s.) and the multiplicity [b] of the hydroxy proton of 2-chloroethanol in CCl_4 with an increase in the amount of water added,[c] at 21 ± 0.5 °C

Concentration of 2-chloroethanol (M)

0.030		0.20		0.22	
Water (μl)	C.s.	Water (μl)	C.s.	Water (μl)	C.s.
0	170.7(s)	0	235.7(s)	0	242.5(s)
4	174.1(bs)	10	237.5(s)	20	249.6(bs)
8	175.3(t)	60	238.6(t)	40	251.3(bs)
				60	253.9(t)

[a] Chemical shift values are reported as Hz downfield from internal tetramethylsilane. [b] s = Singlet, bs = broad singlet, t = triplet. [c] The amount of water is reported as the volume added to 50 ml of each sample solution.

alcohols upon addition of water to the sample solutions, though no change occurs in the OH band of the monomeric alcohol. At the concentrations below 0.008M where no alcohol association occurs, the addition of water does not affect the OH band of the alcohol, indicating that the monomeric alcohol and water are present independently in carbon tetrachloride. The above concentrations are in fact much lower than those used in the n.m.r. experiments. All these measurements show that what is formed in result (4) is not a 1 : 1 complex of water with the monomeric alcohol but a more stable complex of water with the self-associated species of the alcohol.

Results similar to those in (1)—(6) were also obtained for 2-chloroethanol in cyclohexane.

The absence of multiplet structures of alcohol hydroxy protons in carbon tetrachloride has been reported,[2] and the relationship to the impurities in carbon tetrachloride which are not easily removed has been discussed.[3] However, the singlet observed in our result (2) is not due to impurities such as an acid in 2-chloroethanol, but is inherent in the alcohol itself as indicated by result (3). If the singlet observed were due to the proton exchange between the alcohol and impurities, proton exchange should be accelerated with an increase in temperature, and thus the singlet should remain unchanged. The only reasonable explanation for the triplet observed at high temperature is the monomeric alcohol resulting from a dissociation of all self-associated species of the alcohol. This indicates that the alcohol monomer should show a triplet. Results (1)—(3) can be condensed into the experimental observation (I): the associated species of the alcohol is responsible for the singlet observed in almost fully dehydrated sample solutions at room temperature. Furthermore, our results (1) and (4)—(6) can be condensed into the experimental observation (II): a trace of water present in the sample solutions forms hydrogen bonds with the self-associated alcohol species and causes the multiplet structure for the alcohol hydroxy proton. It should be noted from these observations that there are two sources of the triplet, *i.e.* one from the alcohol monomer and the other from the alcohol solutions containing the associated species of the alcohol into which water molecules are incorporated.

The experimental observation (I) seems to be characteristic of 2-chloroethanol which has an additional proton accepting group other than the hydroxy, because the electronegative atom introduced, chlorine, not only increases the acidity of the hydroxy proton of the alcohol,[4] but can also act as a strong proton accepting group in the formation of a hydrogen bond. Thus, the intermolecular hydrogen bond formed in the associated species of the alcohol is strong enough to induce proton exchange within the associated species. Proton exchange, here, refers to a state of hydrogen bonding where the hydroxy protons transfer between the proton accepting and donating groups. It is a well known fact for alcohol solutions that only one resonance peak is observed for the hydroxy proton because of rapid exchange between monomer and associated species. It is reasonable to assume that the rate of proton exchange within the associated species (bonding-site exchange) is faster than that of molecular exchange (monomer to *n*-mer exchange). Consequently, a singlet must be observed for the hydroxy proton as long as the life-time of the alcohol monomer is shorter than the time needed for the spin–spin coupling of the hydroxy proton with CH_2 protons. At the lowest concentration used for our n.m.r. measurements (0.02M), the monomer concentration is still low enough to satisfy the condition of observing a singlet. Thus, our model nicely explains our observation of the singlet in fully dehydrated sample solutions at room temperature.

The experimental observation (II) can be explained in terms of the ability of water to form extensive three-dimensional networks by means of almost tetrahedrally arranged hydrogen bonds.[5] When a trace of water is introduced into the alcohol solutions, water molecules must be incorporated into the associated species of the alcohol, forming intermolecular hydrogen bonds which may be different in nature from those involved in the structure of the associated alcohols.[6] According to Kamlet and Taft,[7] the base strength of water as a hydrogen bond acceptor is much smaller than that of several alkyl chlorides. Therefore, when the hydroxy protons of the self-associated alcohol form hydrogen bonds with the oxygen of water molecules, the oxygen of water is not sufficiently basic to induce the hydroxy proton of the alcohol to exchange as rapidly as in associated R–OH species in which the hydroxy proton can no longer be said to be preferentially bound to RO^-. We believe that all those factors may, in some way, reduce the rapid hydroxy proton exchange in the associated species enough to permit the observation of the hydroxy proton coupling.

We know our explanation conflicts with the data indicating that the hydroxy peak appears as a triplet in the n.m.r. spectra of neat unsubstituted alcohols where associated species are present in high concentrations. However, we must take note of the fact that substituted alcohols such 2-chloroethanol, which have an additional proton accepting group other than hydroxy, have many properties different from those of unsubstituted alcohols such as ethanol. Furthermore, we point out the paper by Kirsch and Coffin [8] which reports only one hydroxy proton signal for several aliphatic alcohols in carbon tetrachloride. They have explained it as the result of rapid molecular exchange of the hydroxy proton between all the hydrogen bonded species in the solution. Slocum and Jennings have attributed the multiplet of the hydroxy proton to an intramolecular hydrogen bond in 2-chloroethanol.[1] This is, however, not likely because they have reported that the triplet structure has been observed even at 66 mole% concentration. Judging from our i.r. measurements, the species predominant at this concentration are not *gauche*-isomers which have intramolecular hydrogen bonds, but *trans*-isomers which form self-associated species. Furthermore, the presence of water is very possible due to the method of preparation of their samples.[9] These facts might make their conclusion doubtful. We think that more extensive studies should be done with fully dehydrated alcohols and their solutions.

[8/770 *Received*, 25*th April*, 1978]

REFERENCES

[1] D. W. Slocum and C. A. Jennings, *Tetrahedron Letters*, 1972, 3543.

[2] M. Saunders and J. B. Hyne, *J. Chem. Phys.*, 1958, **29**, 1319; E. D. Baker and U. Liddel, *J. Mol. Spectroscopy*, 1958, **2**, 1; S. N. Vinogredov and R. H. Ninnell, ' Hydrogen Bonding,' Van Nostrand–Reinhold, New York, 1971, p. 87.

[3] H. Fujiwara and T. Ikenoue, *J.C.S. Faraday I*, 1976, 2375.

[4] J. Cantacuzene, *Bull. Soc. chim. France*, 1962, 754.

[5] D. Eisenberg and W. Kauzmann, 'The Structure and Properties of Water,' Oxford University Press, Oxford, 1969.

[6] A. Coccia, P. L. Indovina, F. Pōdo, and V. Viti, *Chem. Phys.*, 1957, **7**, 30.

[7] M. J. Kamlet and R. W. Taft, *J. Amer. Chem. Soc.*, 1976, **98**, 377.

[8] J. L. Kirsch and D. R. Coffin, *J. Phys. Chem.*, 1976, **80**, 2448.

[9] E. E. Tucker and E. D. Becker, *J. Phys. Chem.*, 1973, **77**, 1783.